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Immobilization of uranium as a function of peat content

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Preface

This research work has been submitted as thesis to fulfill the requirement for Master of Science in Environment and Natural Resource – Specialization in Sustainable Water and Sanitation, Health and Development at the research group of Hydrology and Limnology at department of Environmental Sciences (IMV) at the Norwegian University of Life Sciences (NMBU). This research work was conducted spring 2015 in collaboration with Norwegian Public Road Administration (NPRA) for ''NORWAT'' which is a research and development program, established at NMBU. The batch experiments were performed at IMV laboratory.

The purpose of the project was to document the effect of peat material as adsorbent for uranium and other trace metals under different conditions. I hope this research will help NPRA to assess the concentration of peat as adsorbent for Uranium and other trace metals leaching out from alum shale.

Acknowledgement

All extol and exalt to Allah the Almighty who is the cause of all the comprehension, understanding and astuteness the most Gracious the most Compassionate and Beneficent. All peace to the greatest teacher of humanity and mankind, the Holy prophet Muhammad (peace be upon Him).

No research is conducted without the help of others and I am no exception in recognizing the input of all those people.

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Karl Andreas and Solfid Lohne were the people who did all the chemical analysis (ICP-MS) and provided me results on time.

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The credit of reviewing my thesis and giving me feedbacks goes to **Samai Sanon,** my dear friend and former class fellow at University of Oslo.

I recognize persons from Staten Vegvesen who helped me during my visit to Gran site and provided me samples

I am very much grateful to all above-mentioned people and take great pleasure to acknowledge their input. The acknowledgement goes incomplete without mentioning my family and friends in Norway and back in hometown Pakistan who always supported me in every possible way. Without them I would not be where I am now.

My deepest gratitude in sense of debt goes to my team mates of Friends Cricket Club. They always encouraged and supported me whether it was studies or sports. The time I spent

with them during training sessions and matches was the best. I wish and pray for all the success and happiness in life for them.

Mansoor Ahmad

Abstract

Norwegian Public Road Administration (NPRA) has been constructing a new highway (RV 4) in Hadeland, east Norway since the autumn of 2013. Along this highway, a tunnel is also being constructed near Gran Center. Constructing this tunnel will produce huge masses of rock debris by excavation. The bedrock in Gran is described by presence of alum shale which is rich in uranium. The uranium rich alum shale will be dumped in a pit near to tunnel. By dumping this excavated alum shale, there is a high potential for mobilization of uranium and other trace metals that may contaminate the groundwater. As a precaution, it is suggested that peat should be dumped together with the excavated material due to its capacity to sorb metals. Samples of peat, pit water and alum shale used in this study were collected from the Gran site.

In this study, batch laboratory experiments were designed to investigate the properties of peat as adsorbent for uranium and other trace metals leaching out from the alum shale. The influence of adsorbent dose on adsorption process was studied. The adsorbent dose is defined as product of contact time and initial concentrations of metal ions in aqueous solution. Six doses (100, 20, 10, 4, 2 and 1) of peat were applied to adsorb uranium and other metals from pit water from Gran site and contaminated water which was prepared in laboratory by mixing pit water and alum shale. These two water samples were having different initial concentrations of uranium and other trace metals. Adsorbent and adsorbate solution were shaken with 200 rpm at shaking table at room temperature and samples were taken at interval of 1 and 24 hours and analyzed by Inductively coupled plasma-mass spectrometry (ICP-MS).No pH adjustment was made.

Results revealed that peat is an efficient adsorbent for uranium and some other trace metals leaching out from alum shale like nickel and molybdenum but not for arsenic and sulphur. In this study the most concerned metal was uranium. Adsorption percentage of uranium increased by increasing the adsorbent dose and contact time. Contact time became important factor when adsorbent dose was decreased and initial concentrations of metal ions were increased. Adsorption capacity of adsorbent increased by increasing the initial metal ion concentration and by decreasing the adsorbent dose. 10 g/L of peat proved to be high enough dose to remove worst case contamination concentration in contact time of 1 hour. By decreasing the adsorbent concentration to 4 gram/L, adsorption rate of 90 percent was achieved but it took 24 hours. By decreasing the adsorbent concentration to 2gram/L and 1 gram/L, adsorption percentage decreased. In case of higher initial concentrations of metal ions, higher adsorbent concentration was required and vice versa. Instead of removing arsenic and sulphur from solutions, they leached out from peat and their concentration increased in the solution.

Based on the results it is recommended that at 4 to 10 gram/L of peat can be used for adsorption of uranium and other trace metals (e.g) that may leak out of alum shale.

List of Abbrevations

Bq	Becquerel
Eh	Redox potential
EPA	Environmental Protection Agency
ICP-MS	Inductively coupled plasma-mass spectrometer
Kd	Distribution coefficient(s)
LOD	Limit of Detection
LOQ	Limit of Quantification
mg/g	milligram(s) per gram
mg/L	milligram(s) per liter
ml/g	milliliters per gram
NORM	Naturally-occurring radioactive material
NPRA	Norwegian Public Roads Administration
NMBU	Norwegian University of Life sciences
Norwat	Nordic Road Water
Ppm	Parts Per Million
R2	Correlation Coefficient
RV 4	Riksvei 4 (Highway)
WHO	World Health Organization
µg/g	Microgram(s) per gram

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Chapter 1: Introduction and Background

In the last 10-20 years there has been a substantial growth in traffic in Norway. This has led to significant extensions of the existing road networks and the construction of new roads (Statens Vegvesen, 2011). Norway is one of the countries in the world that has constructed most number of road tunnels (NPRA, 1997). Currently there are more than 1000 road-tunnels in Norway and about 20-30 km new tunnels are being built every year (Vikan and Meland, 2013). There are multiple benefits of having improved transport infrastructure including environmental effects (Daigle, 2010).

NPRA has been constructing a new highway (RV4) in Hadeland east Norway since the autumn of 2013. Along this highway, a tunnel is also being constructed near Gran Center. Constructing this tunnel will produce huge masses of rock debris by excavation. These rock masses are planned to be deposited in a pit near the tunnel. Therefore it is necessary to carry out this study (1) to determine the potential effects of depositing these rock masses on the surrounding natural environment and (2) how to minimize the negative impacts.

This study is important because, The Norwegian pollution Control Act was amended in 2010 (enforced in January 2011) to include a new regulation about radioactive pollution and radioactive waste. According to this new regulation radioactive waste and radioactive discharges must be treated under the same law as hazardous waste and contaminant discharges. This act is applicable to nuclear material and to naturally occurring radioactive material (NORM) as well because the protection of the environment is more important without taking account of source (Liland et al., 2012).

Gran is located north of Oslo in Oppland County. This area is described by the transition of rocks from alum shale and granite containing high level of uranium to sedimentary and igneous mafic rock which contains low level of uranium (Smethurst et al., 2008). Alum shale is a type of black shale. In Norway alum shale is regarded as a rock type which causes environmental threats. Alum shale has great level of sulphide, heavy metals and uranium. The weathering of alum shale generates sulphuric acid that causes rock decomposition and generates acidic runoff with heavy metals and uranium. Radon and Radium are radioactive daughter products of uranium formed when uranium decomposes (Vikan and Meland, 2013).

Elevated concentrations of uranium or its daughter products in the groundwater can result in health problems. Uranium occurs as three isotopes, which are uranium 234, uranium 235, and uranium 238. U 238 is the most abundant isotope of natural uranium, (99.3 percent) by weight. It is also parent element of usually studied isotope of radon Rn 222. Lead (Pb 206) is the final product of uranium after a series of decay until it reaches a stable state (Skeppstrom and Olofsson, 2007). Uranium is more dangerous due to its toxic characteristics as compared to its radioactivity. According to World Health Organization (WHO), uranium is nephrotoxin suggesting it as naturally formed chemical which can cause the kidney problems.

Investigations on humans and laboratory animals showed that exposure to uranium causes kidney problems (Skeppstrom and Olofsson, 2007).

According to (Ansoborlo et al., 2015), World Health Organization guideline values of uranium in drinking water were increased from 15 µg/L in 2004 to 30 µg/L in 2011. In Norway 15 percent of primary drinking water supply is based on groundwater in Norway (Hanne et al., 2010).

The alum shale that is excavated out during the tunnel construction contains sulphide and uranium rich metals. When this material is exposed to oxygen sulphide, will oxidize to sulphate and sulphate will create sulphuric acid in contact with water. These processes and acidity level can cause the mobilization of metals like uranium and other trace metals which can contaminate the groundwater. Thus alum shale excavated from the Gran tunnel may a threat to the environment.

Peat was the first option that was considered to use as sorbent for uranium and other trace metals. The properties of peat like economic viability and its adsorption capacity were the factors taken to take into account. Peat is a material which is containing many organic constituents like lignin, cellulose and humic acid, which make special impression on its capacity to adsorb metals. The diversity of its pore structure and surface area contribute in the process of adsorption by providing vast numbers of adsorption sites (Holmberg, 2006).

According to (Yasemin and Zeki, 2007), adsorption is considered as an effective process to control the pollution caused by the heavy metal ions. The process of adsorption is explain by the growth of substances at the interface of two phases like, liquid-solid, liquid-liquid, gas-solid and gas liquid phase. The ingredients of adsorbent are most important thing to consider for the removal of contaminants from water (Grassi et al., 2012).

It is hypothesized that NORM in generated waste of tunnel construction will be considered as radioactive waste and will be treated as hazardous waste. In the pit mobilization of uranium and other trace elements will take place by exposure of alum shale by the exposure of alum shale to oxygen and moisture because of decrease in pH. This potential mobility of uranium and other trace elements will contaminate the groundwater

In this study, the Batch experiments will be designed to determine the immobilization of uranium and other trace elements as a function of peat content.

1.1 Objective of Study

In this project, following research points will be focused:

1) To estimate the adsorption of uranium as a function of mass of dry peat per liter of water (concentration of peat).
2) Factors affecting the process of adsorption e.g contact time (solution: substrate media), initial concentration of uranium in solution, and concentration of peat.
3) To determine the lowest concentration of peat required to adsorb a specified concentration of uranium.
4) To indicate model parameters for adsorption isotherms of uranium as a function of peat concentration.

Chapter 2: Geochemistry of Uranium

2.1 Radionuclides

Radioactive isotopes or unstable forms of elements are called radionuclides (USGS, 2000). They are described as species of atoms which go through radioactive decay and emit radiation by producing alpha, beta and gamma rays. Nearly 2000 radionuclides are known. These can be naturally occurring or manmade. Naturally occurring radionuclides are ubiquitous and exist as trace elements in soils and rocks. Naturally occurring radionuclides derived from Uranium-238, thorium-232 and uranium-235 are produced from radioactive decay series which is called uranium, thorium and actinium series respectively. Each decay series generates multiple isotopes and follows specific radioactive decay sequence. The actinium series is not a considerable source of radionuclides because U-235 is found in very low concentration in crust. These decay series end when a stable isotope of lead is formed (Focazio et al., 1998).

2.1.1 Occurrence and contamination by Radionuclides in groundwater

Rocks, soil and water contain naturally occurring radioactive elements at a large scale. The existence of radionuclides in groundwater initially depends upon geochemistry of rock and water and local geology of the area. Naturally occurring radioactive elements like uranium-238 and thorium-232 undergo radioactive decay and produce radioactive daughter products such as uranium (U), radium (Ra) and radon (Rn). These daughter products can undergo radioactive decay and have different chemical properties. These radionuclides have no color, taste and odor when dissolved in water. Recent studies have shown that occurrence of radionuclides has become environmental concern and can pose potential health problems in drinking water (USGS, 2000).

2.2 Black shale

Black shale is fine grained clastic sedimentary rock with dark color. According to lithology it is defined as a big class of sedimentary rocks consisting of clay and silt size mineral grains containing enough organic matter, iron sulphide or manganese oxide which gives the rock gray to black color (Swanson, 1961). Black shales of different geological ages are found in all continents of the world. Especially large deposits of black shales exist in Brazil, China, Australia, USA and Russia (Falk et al., 2006).

2.3 Alum shale

Alum shale is a type of black shale (Falk et al., 2006). It was given name because it was utilized to make alum salt, a hydrated potassium aluminum sulphate three hundred years ago in Sweden (Walker, 1994). It was also used as raw material to produce red paint, uranium, oil and gas, sulphur and nitrogen (Falk et al., 2006).

2.3.1 Composition of Alum shale

The alum shale is composed of different types of silicate and sulphides minerals, calcites, bituminious limestone and organic substances. Alum shale is generated from sediment material in ocean under anaerobic and comparably stable circumstances with the great amount of inorganic and organic material is available. The organic material is not completely oxidized under these conditions, which cause reduction of sulphates ($SO_4{}^{2-}$) to hydrogen sulphides (H_2S). These sulphide ions (S^{2-}) can precipitate heavy metals in the environment into sulphide minerals like pyrire (FeS_2). Heavy metals like lead, zinc, copper and cadmium can also precipitate in the sediments in form of solid sulphides in the sediments (Jeng, 1992 cited in Falk et al., 2006).

2.3.2 Weathering of alum shale

The weathering of alum shale can take place when air and moisture is available. In the process of weathering, first step is oxidation of sulphide minerals that generates sulphuric acid and free metal cations and second step is destabilization of silicate minerals and kerogen by sulphuric acid, finally releasing elements (Jeng, 1991, 1992 cited in Falk et al., 2006).

2.3.3 Alum shales in Oslo Rift

A stratigraphic sequence of sedimentary rocks occurs from Eocambrian to Ordovician age in the north part of Oslo rift. Alum shales are sedimentary rocks and were deposited in time interval between Late- Middle Cambrian to Early Ordovician age in Oslo Rift (Gautneb & Sæther, 2009). The alum shales are distinguished by geochemical impression which consists of organic carbon, vanadium and uranium. Bjørlykke (1974) reported that, alum shale contains organic carbon content of 10 percent and sulphur of 12 percent in Oslo rift (Walker, 1994).

Rosenquist (1948), Siggerud (1956), Skjeseth (1958), reported that alum shale in Oslo region was deposited during a period of 40-50 million years. The thickness of alum shale is 40-50 m, and contains uranium level of 50-100 ppm, while in layers of thickness up to 10cm, the maximum uranium level was found up to 170ppm (Lindahl, 1983).

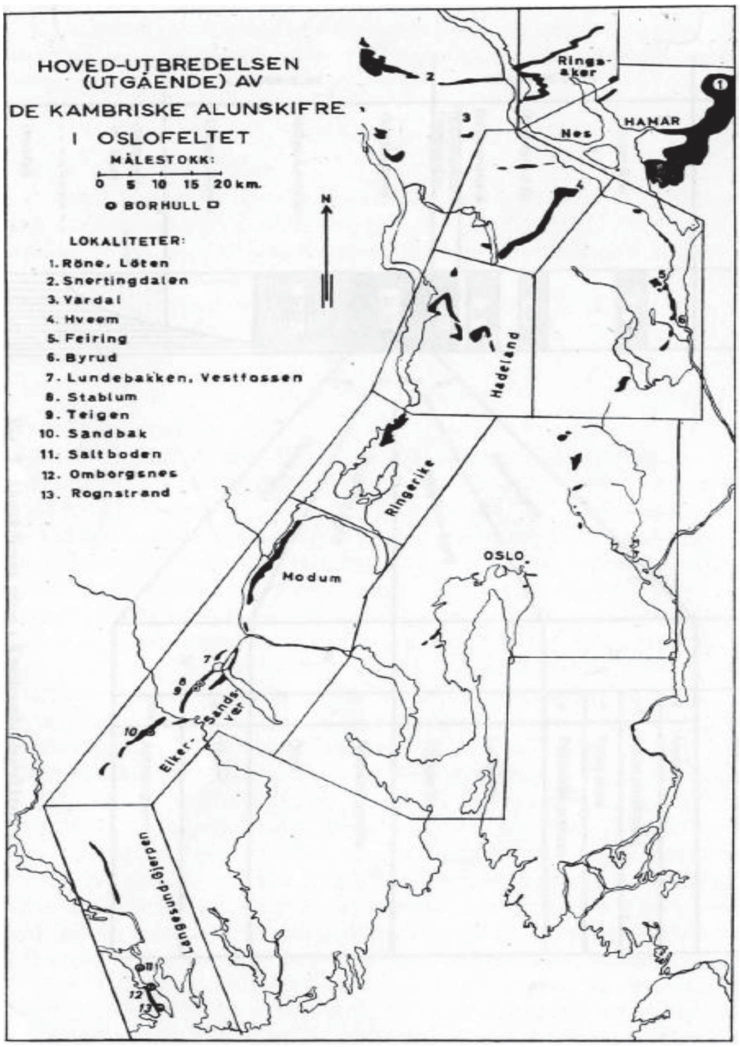


Figure 2.1: The geographical distribution of rocks in the Alum Shale Formation in the Oslo Rift, The black areas show location of outcrops of alum shales, modified from (Skjeseth 1958 in Walker, 1994).

2.4 Introduction of uranium

Uranium is an element which was discovered by Martin Heinrich Klaproth who was a German chemist (1743-1817) in 1789, and he named it after the Planet Uranus. Its typical natural abundance is 2-4 ppm in the crust (Keith et al., 2007). Grey, (1993) reported that after 50 years in 1841, E.M. Péligot discovered that the uranit found by Klaproth was uranium dioxide, UO_2 but not metallic uranium. By thermally reducing anhydrous uranium tetrachloride, UCl_4, true elemental uranium was attained in the presence of potassium (Craft et al., 2004). The periodic table keeps uranium in actinide series and it can occur in any of six oxidation states (0, +2, +3, +4, +5, and + 6). The +4 is stable and associated with fluorides, phosphates and hydroxides and +6 is most stable state when it occurs as octaoxide U_3O_8. The +4 and +6 are most important for commercial efforts and human exposure (Keith et al., 2007).

Uranium is silvery, ductile and one of the densest metal and having an atomic number of 92. It is the heaviest naturally occurring metal on earth and exists in oxidized form in nature because it is easily oxidized in air (Craft et al., 2004) Uranium is frequent as arsenic and more abundant than cadmium, mercury and antimony. It exists in multiple minerals also in lignite, phosphate fertilizers and phosphate rock. Its exists as trace element in drinking water and many foods due to its occurrence in rocks, soil, air, plants and surface and groundwater (Bleise et al., 2003).

The radioactive nature of uranium was discovered by Antonie Henry Becquerel in 1896. (Keith et al., 2007). Naturally occurring uranium exists as three isotopes uranium 234, uranium 235, uranium 238 (Bleise et al., 2003). Isotopes of an element contain same number of electrons and protons but different number of neutrons but however they behave in a similar way chemically (Dingman, 2002). Uranium 235 and Uranium 238 have their own decay series, while uranium 234 is the midway outcome of uranium 238 decay series. Wilkening (1990) reported that uranium 238 is most abundantly occurring isotope (99.23 %) by weight. When uranium 238 goes to decay series, it produces most considered isotope of radon Rn 222 and Pb 206 as final product before reaching to stable state. Figures 2.2 and 2.3 are showing the decay series of uranium 235, uranium 238, and uranium 234 in which intermediate daughter products are produced along with the emitting of radiation in the form of alpha (α) and beta (β) particles (Skeppstrom and Olofsson, 2007).

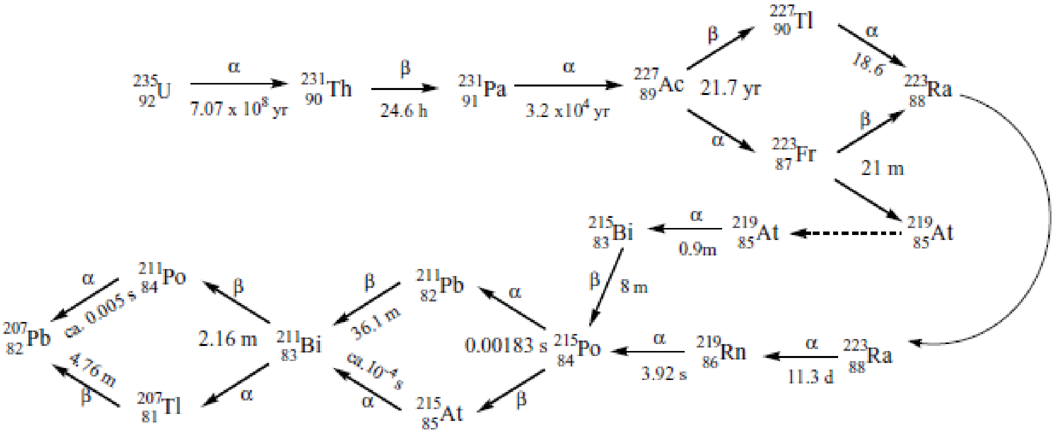


Figure 2.2: Decay series for the naturally occurring uranium isotope U235 (adapted from Clark et al., 1997 in Craft et al., 2004).

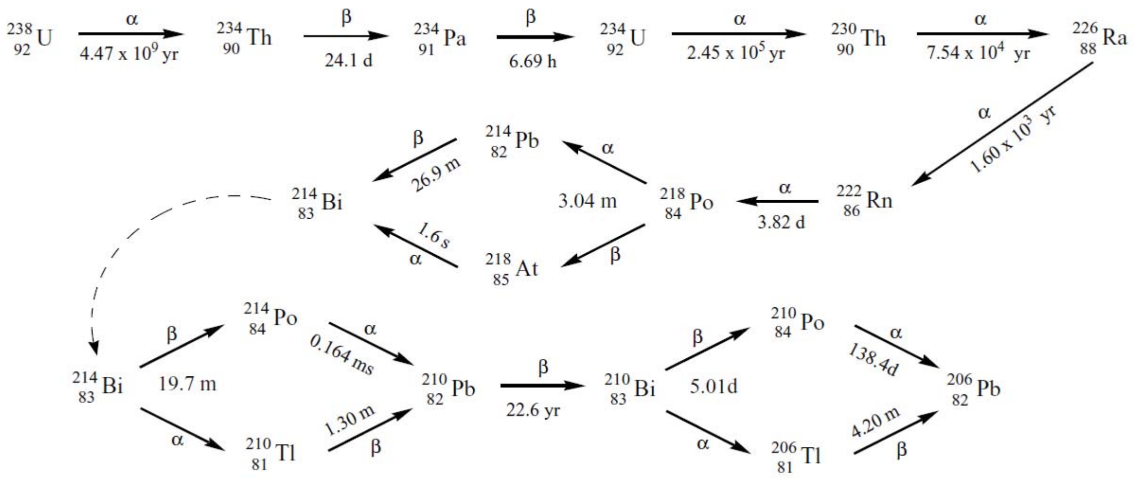


Figure 2.3: Decay series for the naturally occurring uranium isotope U 238 and U234 (adapted from Clark et al., 1997 in Craft et al., 2004).

2.4.1 Uranium in soils and Rocks

Uranium occurs naturally in environment and commonly exists in plants, rocks, soil and in water. It is found in earth at 3 parts per million (ppm) approximately (CSEM, 2009). The concentration of uranium and its daughter products can vary at a big scale even in same area between and within the rocks. Specific type of rocks contains high level of uranium like granites, carbonates and black shale such as alum shale. Alum shale is Cambrian black shale which is uranium enriched found in Norway, Sweden and an Island of Denmark called as Bornholm (Åkerblom et al., 2000).

2.5 Geochemistry Of uranium

Uranium is found in the aqueous environment in the oxidation states of +3, +4, +5, and +6. Under naturally found reducing conditions dissolved Uranium +3 oxidized to Uranium +4. The Uranium +5 $(UO_2)^+$ easily changes to Uranium +4 and Uranium +6 $(UO_2)^{2+}$. At the end the most commonly founded oxidation states of uranium found in environment are Uranium +4 and Uranium +6. The Uranium +6 occurs under oxidizing to slightly reducing conditions while Uranium +4 is relatively immobile and is stable under reducing environment (Krupka and Serne, 2002).

Uranium +6 is soluble and highly mobile under oxidizing conditions and under nearly neutral conditions it forms soluble complexes initially with phosphates and carbonates, and at lower pH it forms complexes with fluorides and sulphates (Porcelli and Swarzenski., 2003). Under reducing conditions uranium is found as Uranium +4 and is less soluble as compared to Uranium +6 and under expected pH sparingly soluble minerals are formed like uraninite (UO_2) (Krupka and Serne, 2002).

In the presence of oxygen elemental uranium U is oxidized to Uranium +4, Uranium +4 is described as UO_2 in following reaction.

$U + O_2 \rightarrow UO_2$ Eq 1.1

According to environmental conditions further oxidation takes place to form Uranium +6, Uranium +6 is described as UO_2^{2+}.

$UO_2 + 2\,H^+ + \frac{1}{2}\,O_2 \rightarrow UO_2^{\,2+} + H_2O$ Eq 1.2

Uranium can be oxidized by water to release hydrogen in the absence of oxygen.

$U + 2H_2O \rightarrow UO_2 + 2H_2$ Eq 1.3
$U + 3H_2O \rightarrow UO_2^{\,2+} + 3H_2$ Eq 1.4

At higher oxidation states Uranium +6, the cations will react with water, a reaction called as hydrolysis. Uranium +6 in the aqueous solution thus present as the uranyl $(UO_2)^{2+}$ (Bourdon et al., 2003). Both species of uranium, Uranium +4 and Uranium +6 hydrolyze easily but Uranium +4 is most easily hydrolyzed because of its ionic charge (EPA, 1999).

Figure 2.4 is showing the dominant hydrolytic and complexed species of Uranium +4 and uranium +6 as a function of Eh and pH. Species of Uranium +6 dominates over entire pH when conditions are oxidizing and lightly reducing. Under pH values lower than 5, the hydrolysis of Uranium +6 is not notable. At pH less than 5 the dominant species are $UO_2^{2+,}$ and at pH between 5 and 9 dominant species are $UO_2\,(OH)_2$ (aq) and at pH between 9 to 14 $UO_2\,(OH)_3^-$ are dominant species of Uranium +6. Uranium +4 is stable under reducing conditions and when pH becomes greater than 2, neutral species like U(OH)4 (aq) dominates the hydrolysis of Uranium +4 (Krupka and Serne, 2002).

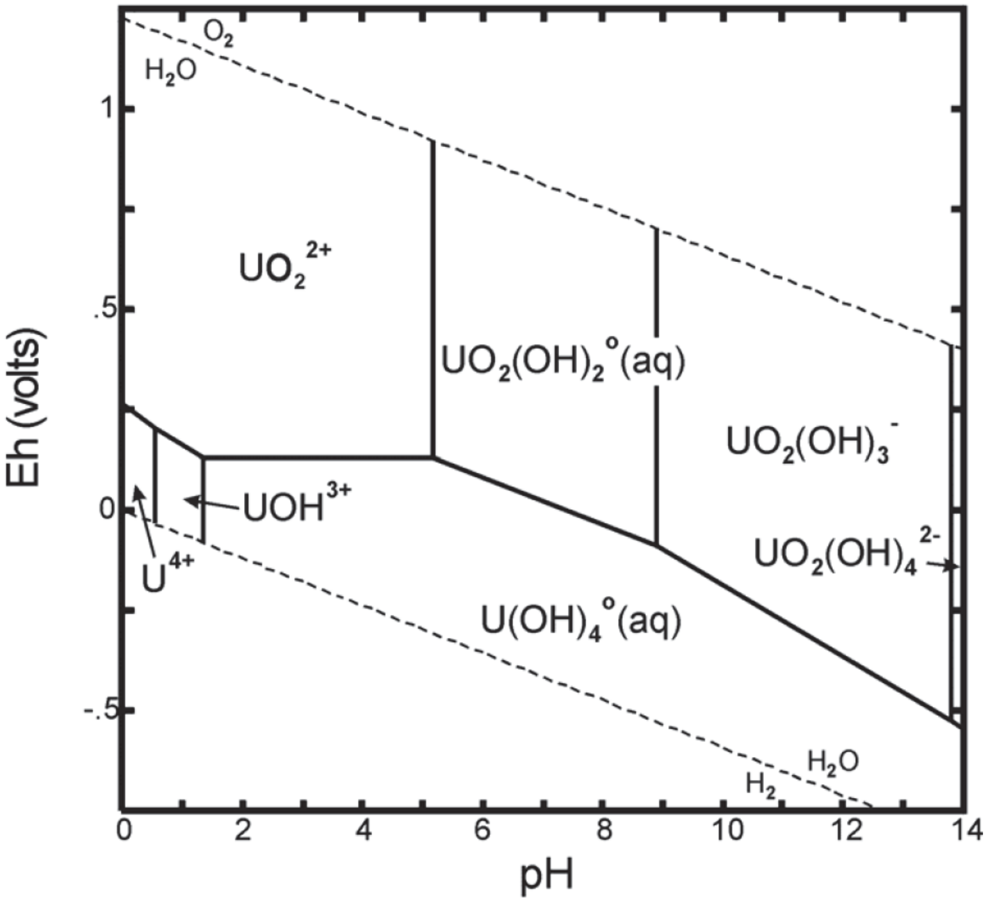


Figure 2.4: Eh-pH Diagram showing the dominant aqueous complexes of uranium [Diagram was calculated at 25 ºC and a concentration of 10^{-7} mol/L total dissolved uranium in the presence of dissolved chloride, nitrate, carbonate, and sulfate.] (Krupka and Serne, 2002).

2.6 Solubility of uranium

Murphy and Shock, (1999) reported that some factors such as oxidation reduction potential, pH and dissolved carbonate control the solubility of uranium in aqueous solution (Giammar, 2001). The solubility of uraninite is shown by shaded area in (Figure. 2.7) and described by large Eh-pH region. The Eh-pH area of uraninite will become large and oversaturates to slightly higher oxidizing conditions and at lower pH when concentration of dissolved uranium increases. Carbonate complexes are dominating at pH over 3. $UO_2CO_3{}^0$ dominates until pH 5.5, while from 5.5 to 8 $UO_2\,(CO_3)^{2-}$ dominates, and from pH over 8 $UO_2\,(CO_3)_3$ dominates (Krupka and Serne, 2002).

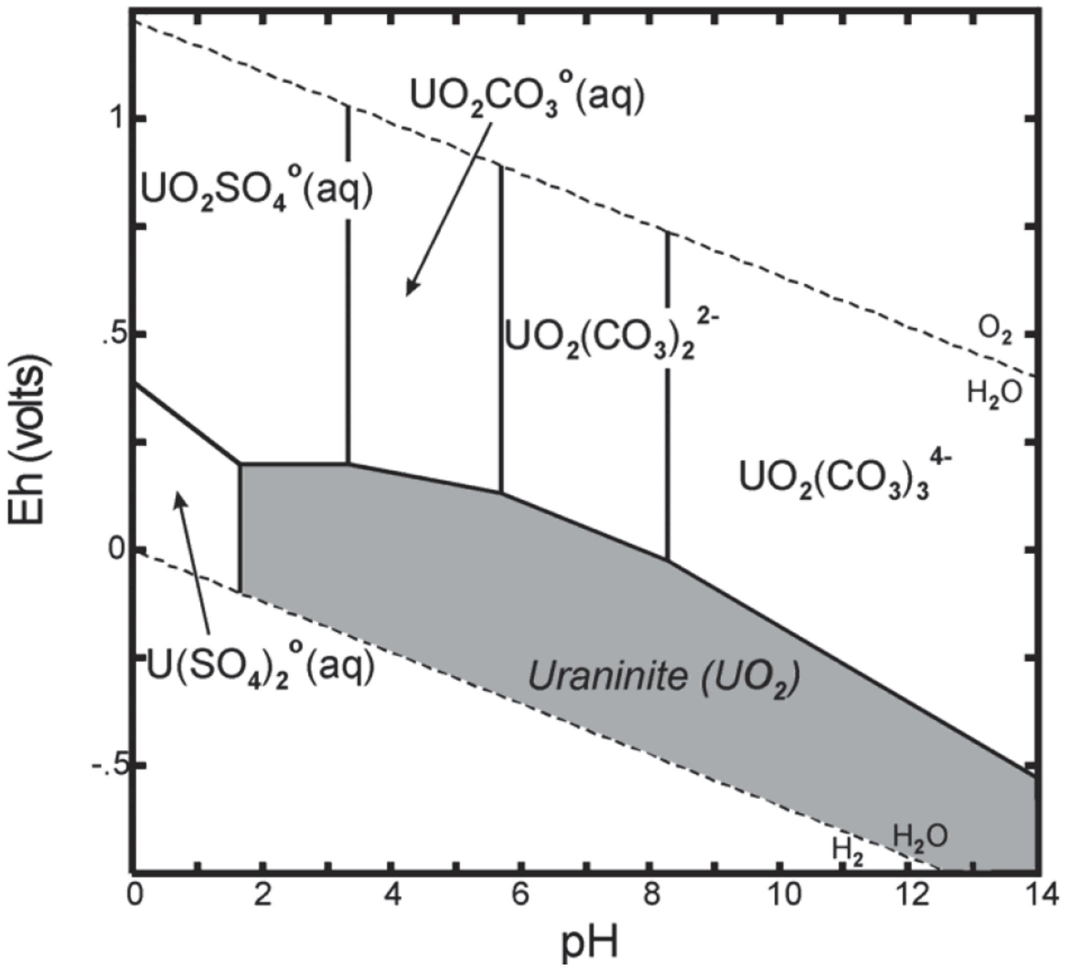


Figure 2.5: Eh-pH Diagram Showing Dominant Aqueous Species of Uranium and Eh-pH Region (Shaded Area) Where the Solubility of Uraninite has been exceeded (Krupka and Serne, 2002).

2.7 Dissolution /Precipitation / co-precipitation

In groundwater these three processes dissolution, precipitation and co-precipitation have larger effect on concentration of U (IV) as compared to U (VI). Most of the times in the oxygenated groundwater away from uranium source these processes do not control the concentrations of U (VI). These processes become very important in reducing environment or near to uranium source and depending on the conditions of environment many (co)precipitates are formed. In deep aquifers reducing conditions are found and that could be the reason to precipitate U (IV) (Frondal, 1907).

2.8 Sorption and Desorption

The sorption of uranium has been reported by quite a few authors. (Ames et al., 1982; Chisholm-Brause et al., 1994) studied sorption of uranium onto clays, (Hsi and Langmuir, 1985; Waite et al., 1994) studied on oxides, while (Borovec et al., 1979, Shanbhag and Choppin, 1981) studied onto organics. They concluded that adsorption and cation exchange are the main processes in controlling dissolved uranyl concentrations in solutions having low ionic strength and low U (VI) concentration. In the higher ionic strength solutions uranyl ion will be displaced from exchange site by other ions such as Ca^{2+}, Mg^{2+}, K^{+} due to which uranyl ion is found in mobile state. In higher ionic strength solution, carbonate ions make soluble complexes with uranyl ion that causes to increase the concentration of uranium in solution (EPA, 1999).

2.9 Factors affecting the sorption of uranium

(Prikryle et al., 2001) reported that sorption is an important process to remove the uranium concentration from groundwater. Sorption of uranium depends upon properties of aqueous solution and sorbing materials. Aqueous solution properties includes pH, Eh, ionic strength, concentration of uranium, and presence of complexing ligands and properties of sorbing material includes composition, surface area, and density of surface sites. But these factors make difficult to predict the retardation of uranium (EPA, 1999).

2.10 Sources of Uranium in groundwater

The distribution of uranium to groundwater takes place through dissolution and erosion of rock and soil naturally. The mobilization of uranium in water is controlled by concentration of uranium in soil, pH, oxidation-reduction potential, presence and nature of sorbents and properties of complexing agents. In high alkaline and oxygenated water, uranium occurs in solution as carbonate complex. Where the acidity of water is high, high concentrations of dissolved organic matter, and low concentration of inorganic ions there uranium occurs as the soluble organic complex. Groundwater happens to contain higher levels of uranium as compared to surface water, because of higher surface area and contact time with soil and rock particles through which water flows (Keith et al., 2007).

The use of uranium containing phosphate fertilizers, nuclear industry emissions and waste from uranium mill tailings can also be a source of uranium to environment. But the main source of uranium in drinking water is natural deposits (WHO, 2012).

2.11 World Health Organization Guidelines for Uranium in Drinking water

Uranium is considered as more toxic due to its chemical properties rather than its radioactivity. Therefore chemical toxicity was the main factor to be considered by World Health Organization (WHO) to design all health based drinking water guidelines for uranium. World Health Organization (WHO) announced a 2 µg/L drinking water guideline for uranium provisionally in 1998 in second edition of Guidelines for drinking water quality. The tolerable daily intake (TDI) was used to derive the chemical toxicity of uranium because there was no satisfactory chronic research on uranium health effects at that time. In the third edition of Guidelines for drinking water Quality in 2004, WHO increased the guideline value for uranium from 2 µg/L to 15 µg/L. It was also based on the tolerable daily intake (TDI). There was no reference provided by (WHO) to increase these values. In 2011, this provisional guideline value was further increased to 30 µg/L by (WHO) in the fourth edition of Guidelines for drinking water Quality. This value is currently being used (WHO, 2012).

2.12 Environmental Concerns of Uranium

In contrast to some heavy metals, uranium has no important part in the normal biochemical reactions of plants, animal and man (Ansoborlo et al., 2006). Uranium is having a complex process of decay that results in emitting of different types of radiation and also produces multiple radioactive daughter products (SDWC, 1983). In the decay series of uranium 238, isotopes like Uranium 234, Radium 226, and Radon 222 are formed that can be potential health effect due to their occurrence in drinking water (Cothern and Robers, 1990).

Uranium and radium exists as solids while radon occurs in form of gas in environment naturally. The time taken by a substance to drop half of its radioactivity is called as half-life. The half-life of radon is about four days (EFS, 2007). Radon-222 is the most common isotope of radon (ATSDR, 2012). Radium-226 has half-life of 1600 years and uranium 238 is having a half-life of 4.5 billion years.

2.13 Toxicology of Uranium and daughter products

Uranium is natural component of soil, so it is found in food, water and air. Ingestion of food and water and inhalation are the main sources of human exposure to uranium (Keith et al., 2007). Ingestion is the main source to enter in human body (SDWC, 1983). The mechanism of accumulation, transportation and transferring into body determines the toxicity of uranium (Stadler et al., 2012). Once uranium is absorbed to blood, its solubility and oxidation state control its distribution and elimination. Uranium enters in body as tetravalent and transformed to hexavalent as a uranyl ion. In body it exists as uranyl ion complex $(UO2)^{+2}$. Uranyl ion is complexed with bicarbonate or plasma proteins in body fluids (ASTDR, 2013, Keith et al., 2007). Uranium can also bind itself with transferrin which is iron transport protein and to red blood cells haemoglobin (Ansoborlo et al., 2006).

Uranium in blood (99%) is cleared in 24 hours. 67 % in blood is filtered through kidney and excreted through urine, and reaming is distributed to tissues preferably to bone, liver and kidney. The weight of uranium in human body is 90 µg, 66% in skeleton, 16% liver, 8% kidney and 10 % in other tissues (ASTDR, 2013).

The primary effect that is caused by uranium due to its chemical toxicity is Nephritis (Inflammation of one or both kidneys). There is not sufficient data available in reference to uranium carcinogenicity and chronic health effects of uranium in experimental animals and humans (WHO, 2012).

Radium is radioactive metal and found in very low concentration in soil, water, rocks and plants. It can enter in body through breathing and swallowing with water and food and with drinking water if water source is rich in radium. Nearly 80 percent of swallowed radium leaves body through feces, while rest of 20 percent enters in blood stream and taken to other parts of body. Harmful effects like anemia, fractured teeth, bone cancer and death can happen by exposure to higher level of radium for a long period of time (ATSDR, 1990).

Radon exists in those drinking water supplies whose source is groundwater because radon is insoluble gas and in surface water supplies it quickly degasses. Through water supplies radon can enter in the house and sets itself free when water is consumed for cooking, washing dishes, washing clothes and bathing. Inhalation is the major exposure route for radon by above mechanisms, while ingestion is a minor route (Cothern and Rebers, 1990). In Norway about each year 14 percent of lung cancer cases are caused by the long term exposure to radon and its progenies. The occurrence of alum shale in an area is enough to consider it as high radon hazard area because alum shale is rich in uranium. The radon hazard exists in area around Brandbu-Jaren-Gran due to occurrence of alum shale near the surface of ground (Smethurst et al., 2008).

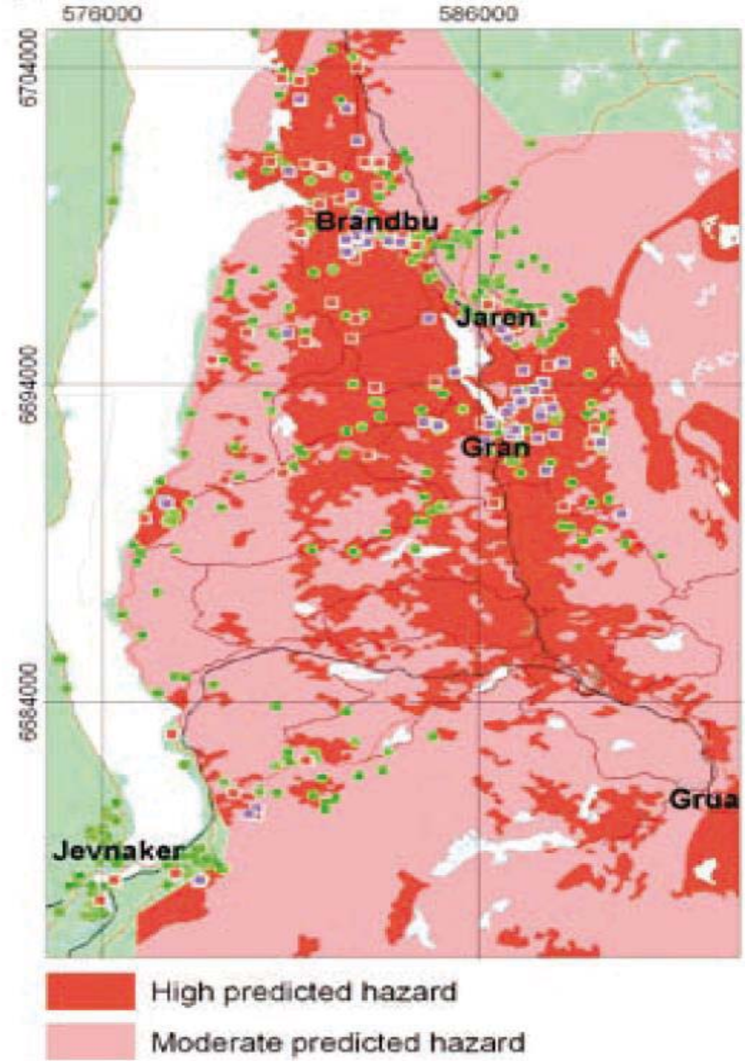


Figure 2.6: Prediction of radon hazard in Gran area (Smethurst et al., 2008).

Chapter 3: Peat and Adsorption Process

In this chapter mechanism of sorption by peat e.g. adsorption processes, properties of peat, role of humic substances, and the factor affecting process of sorption of uranium will be presented.

3.1 Reactivity and Mobility of Pollutants in groundwater

The occurrence of trace elements in the groundwater is controlled by some factors such as sources and nature of trace elements, speciation, reactivity and processes of mobility and transport (Tanji and Valoppi, 1989). Naturally occurring geochemical processes such as dissolution/precipitation, sorption/desorption and redox reactions play an important role in the mobilization of uranium in soil and groundwater (Bachmaf and Merkel, 2011). Figure 3.1 is showing some biotic and abiotic processes which can affect the mobility and transport of trace elements. From these processes sorption is very important in mobilization and transport of trace elements (Tanji and Valoppi, 1989). Abiotic processes involve physical factors like wind and water while biotic processes involve living organisms and populations (Hakonson et al., 1992).

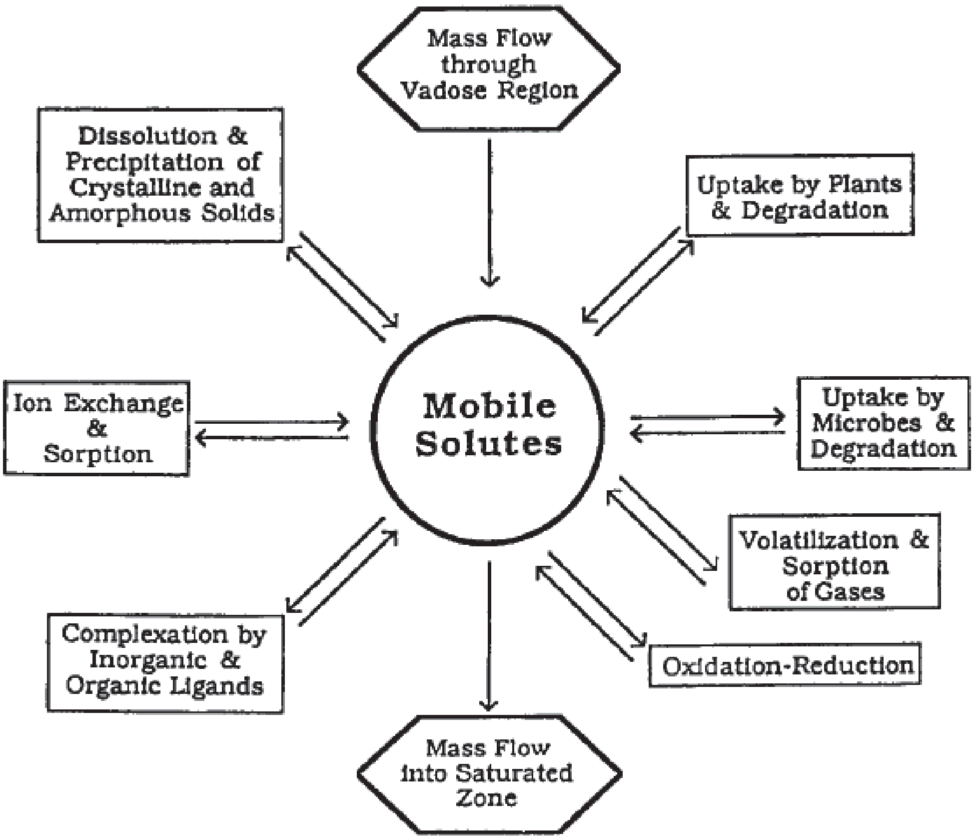


Figure 3.1: Possible biotic and abiotic processes affecting the reactivity and mobility of pollutant (Tanji and Valoppi, 1989).

3.1.1 Sorption

Sorption can be explained as the interaction between solid and a contaminant (Piwoni and Keelay, 1990). It is general term use to indicate three different processes that includes adsorption, absorption and ion exchange (Figure 3.2). The term adsorption suggests to attachment of chemical to solid surface, absorption involves penetration of chemical into solid while in ion exchange one chemical replaces to another at the surface of solid (Appelo and Postma, 2005).

According to Sposito (1984), sometimes it is not easy to isolate sorption from those reactions that include solid surfaces like precipitation and dissolution. The presence of pre-occurrence of solid surface is a characteristic of sorption. Increased concentrations of heavy metals in water supplies presents a severe problem around the world. Sorption controls the transport of pollutant in soils and aquifer and considered as very important topic by Hydrologists (Appelo and Postma, 2005).

Different types of material present in soils and aquifers such as organic matter, clay minerals and metal oxy- hydroxides which are capable to sorb the chemicals. In the process of sorption, a pollutent e.g heavy metal ions are binded to surfaces of oxides or organic matter that have variable charge. These variable charged solid surfaces sorb ions without delivering other ions in equal quantity in solution. The charge on the solid surface can be negative or positive depends on the composition of solution and pH, however these variable charge solids regulate the mobility of negatively charged heavy metals as well as positively charged heavy metals. Oxides and hydroxides surfaces achieve a charge that depends on pH because they sorb protons and others ions from solution. A potential difference is created between the solution and surface due to surface charge which influences the approach of ions towards the surface (Appelo and Postma, 2005).

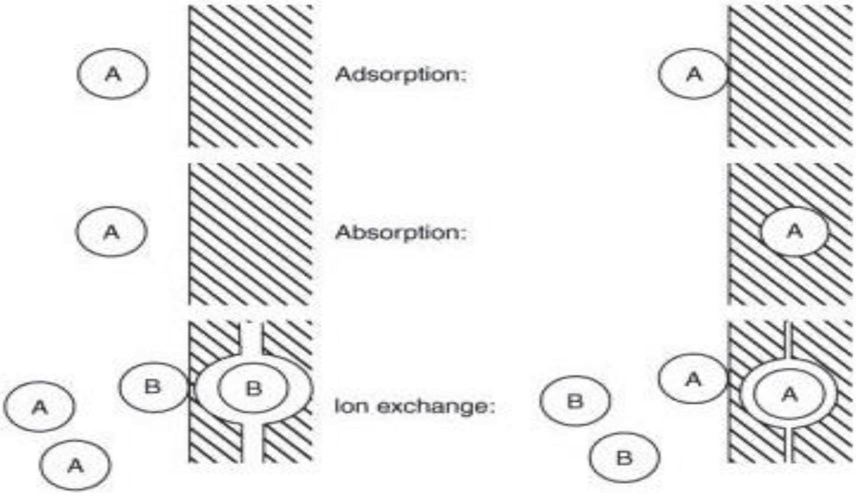


Figure 3.2: Pictorial demonstration of three sorption processes (Appelo and Postma, 2005).

3.2 Mechanisms of adsorption

A mass transfer process in which substances accumulate at the interface of two phases is called adsorption. These phases can include liquid-solid, gas-solid, gas-liquid and liquid-liquid. The adsorbing material is called as adsorbent and substance which is being adsorbed is called as adsorbate. The specifications of adsorbents and adsorbate are according to their ingredients. The ingredients of adsorbents are important and liable for removing specific contaminants from water (Grassi et al., 2012).

The process of adsorption can be physical or chemical. The force present between adsorbed molecules and solid substances is the main factor that classifies adsorption. When the forces acting between adsorbed molecules and solid surface are physical, then this process is called physical adsorption or physisorption. The attraction forces called van der Waals forces. These forces are quite weak and process of physical adsorption is reversible. If the attraction forces between adsorbed substances and solid surface are caused by chemical bonding, then this process is called chemical adsorption or chemisorption. The substances which are adsorbed by chemical adsorption are not easy to desorb due to stronger forces (Grassi et al., 2012) and bond strength. Physical adsorption can be favored by appropriate temperature and pressure conditions and can occur on all surfaces while chemical adsorption happen only between specific adsorbent and adsorptive species in case if chemically active surface is clear of formly adsorbed molecules which means that chemical adsorption, only happen if adsorptive directly attaches to solid surface while in physical adsorption adsorbed molecules can make multiple layers (Webb, 2003). Both process physical adsorption and chemical adsorption can happen simultaneously or alternatively. (Grassi et al., 2012).Molecules can be adsorbed physically on already chemically adsorbed layer of molecules (Webb, 2003).

Concentrations of the solutes on the solid surface are involved during the removal of ions from aqueous solution. The solutes are adsorbed and de-adsorbed continuously at the same until equilibrium state is reached. This is called adsorption equilibrium. At this point the concentration of solute does not change in solution or at solid surface. The entire system is responsible for the position of adsorption equilibrium and it is based on solute, solvent, adsorbent, temperature and pH (Faust and Aly, 1987 cited in Holmberg, 2006).

3.3 Factors affecting adsorption process

Including the chemical and physical characteristic of adsorbent and adsorbate, there are some parameters that can be considered during the process of adsorption:

(1) Adsorbent dose,
(2) initial concentration of metal ions,
(3) contact time,
(4) temperature and
(5) pH.

3.3.1 Effect of Temperature

Adsorption capacity of adsorbent can be affected by temperature depending on the type of adsorbent used. Depending on the exothermic or endothermic nature of process, adsorption equilibrium can be changed by temperature (Abas et al., 2013).

3.3.2 Effect of pH

pH value of the solution affects the surface charge of the adsorbent, species of adsorbate and the degree of ionization. Therefore pH-value of the solution is also an important factor controlling the adsorption process of metals. Metal sorption can be increased in certain pH range and by increase in pH, adsorption can be reduced (Abas et al., 2013).

3.3.3 Effect of adsorbent dose

Adsorbent dose also influences the adsorption process. The adsorption rate increases, when adsorbent dose is increased. But after one point adsorption rate can decrease when adsorbent dose is further increased because of presence of more occupied active sites when concentration gradient of adsorbate does not increase (Abas et al., 2013).

3.3.4 Effect of contact time

The interactions of functional groups between surface of adsorbent and solution can also affect the process of adsorption. When equilibrium time is achieved between solution and adsorbent, then adsorption is considered to be complete. To achieve equilibrium, specific time is required that ensures the completion of adsorption (Abas et al., 2013).

3.3.5 Effect of initial concentrations of metal

Metal removal efficiency can also be changed by the effect of initial concentration of metal ions. This happens because of availability of specific surface functional groups and their ability to bind the metal ions. Mass transfer resistance of metal between solid phase and aqueous phase can be overcome by driving force provided by initial concentrations of solution. Studies have shown that longer contact time is required when initial concentrations of metals ions are high (Brown et al., 2000)

3.4 Peat

The use of peat or peat moss to remove heavy metals from water is a subject of debate in recent years (Zhang and Banks, 2010) Peat moss is extensively occurring natural material that originates from partial decomposition of vegetation (Omar et al., 2006). According to Spedding, 1988, peat is considered as first step in the making process of coal. This process begins with inhibited decay of different species of plant and trees in water saturation environment like swamps, marshes and bog (Brown et al., 2000). The conditions are poor by oxygen level and vegetation material accumulates at higher concentration as compared to its decay by micro-organisms (Couillard, 1993). As a result semi decayed vegetative matter builds up gradually at different stages of decomposition, this material is considered as peat (Delicato, 1996). This is taken as biochemical step of metamorphosis which happens near the surface of earth in the depth of few meters of earth and peat exists constantly with a lot of moisture content in depth of 2 to 5 meters. This process is very long and can take 10,000 years to finish. Different factors like type of vegetation, climate of region, water acidity and intensity of metamorphosis determine the exact composition of peat. When peat is buried under the surface of earth and pressure and temperature rise for 40 million years, then peat is converted into lignite and lignite into coal (Brown et al., 2000).

Peat is a complex substance whose main constituents are cellulose, lignin, fulvic and humic acids (Ho and McKay, 1998). Cellulose and lignin are the material which makes up the cell wall of plant. Cellulose has simple structure which makes it accessible to attacked by micro-organisms and it is the material of cell wall which is removed first. Lignin is the material which is more resistance to decay as compared to other call wall constituents (Delicato, 1996).

These compounds contain polar functional groups like alcohols, carboxylic acid, ketones, aldehydes, phenolic hydroxides and ethers (Couillard, 1993). Figure 3.3 is showing the structure of lignin. These polar functional groups play a role in chemical bonding and also give rise to polar characteristics to peat due to which specific adsorption potential is high for metals and polar organic molecules. Based on these characteristic, peat has been examined to remove dissolved metals from contaminated water (Lalancette, 1974 cited in Brown et al., 2000). According to Couillard (1992), peat is a highly porous material shown by microscopic studies. The porosity of partially decomposed peat is found to be very high (nearly 95 %) and also large surface area of $200m^2/g$ (Couillard, 1993, Babel and Kurniawan, 2002).

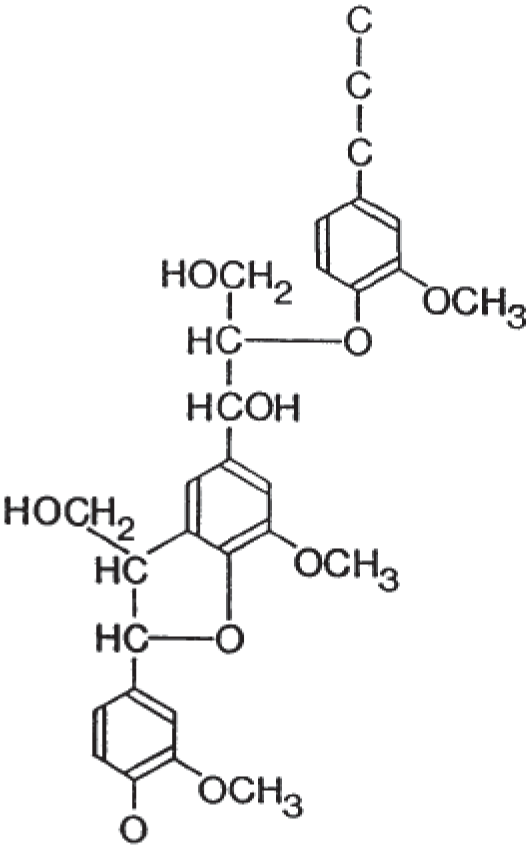


Figure 3.3: Structure of lignin (Couillard, 1993).

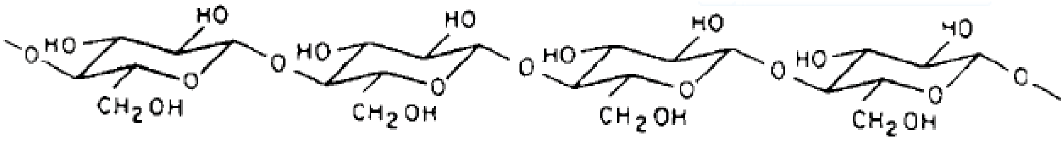


Figure 3.4: Structure of Cellulose (Delicato, 1996).

3.5 Adsorption processes on peat

As an adsorbent, peat is a cheap and effective material to remove pollutants (Sun and Yang, 2003, Bulgariu et al., 2009, Ringqvist et al, 2002). Peat contains (60-80 %) contents of organic matter which make peat distinguish to use as adsorbent (Melo et al., 2014). Metal adsorption capacity of organic matter is quite high and cation exchange capacity (CEC) of soil is deter minded by organic content of soil (Ringqvist and Oborn, 2001).

The mechanism of reaction by which ions are sorbed by peat has been a matter of huge controversy. Different studies on the sorption behavior of peat have been carried out which have shown different results (Brown et al., 2000). Only existence of ion exchange was reported by some studies like Aho and Tummavuori (1984) and Bunzl et al, (1976), while Coleman et al., (1956) suggested both mechanisms of complexation and ion exchange can happen (Chen et al., 1990). The correlation of these studies is difficult due to different factors such as preparation of peat, type of peat and methodology, which was used during those studies. The processes which can be considered in sorption of metals onto peat include surface adsorption, chemisorption, complexation, ion exchange and adsorption-complexation (Brown et al., 2000). The values for complexation and ion exchange and adsorption capacity depend on different factors like type of peat, concentration of peat, ionic strength and pH (Bailey et al,. 1999) while concentration of metal in solution and complex forming substances can also affect the metal adsorption (Ringqvist et al, 2002).

3.6 The Role of Humic substances in adsorption

Humic substances are the category of organic substances that are yellow to blackish in color and carry high molecular weight. They are biogenic, naturally occurring and heterogeneous. They are sub-divided into humic acid, fluvic acid and humin (Sparks 2003).There are sub divided on the basis of solubility in different alkaline acid conditions. Humin is the substance which is not soluble in alkali and acidic conditions. Humic acid is soluble in alkali solutions, but once solution is acidified it pricipitates and fulvic acids remains in solution when humic acid is precipitated by acidification. There are different hypothesis about the formation of humic substances. It is poorly understood and a complex process. The general perception is that they are formed from vegetative matter through decomposition and transformation in soil (Delicato, 1996).The structures of humic acids are tough to explain, because they vary in their composition according to soil (Dupay and Douay, 2001). Humic substances have ability to interact with metal ions to make metal organic complexes of different capabilities and strengths. The presence of functional groups containing high levels of oxygen such as carboxyl (COOH), hydroxyl (OH), and carbonyl(C=0) which make them able to bind with metals (Piccolo and Stevenson, 1982).

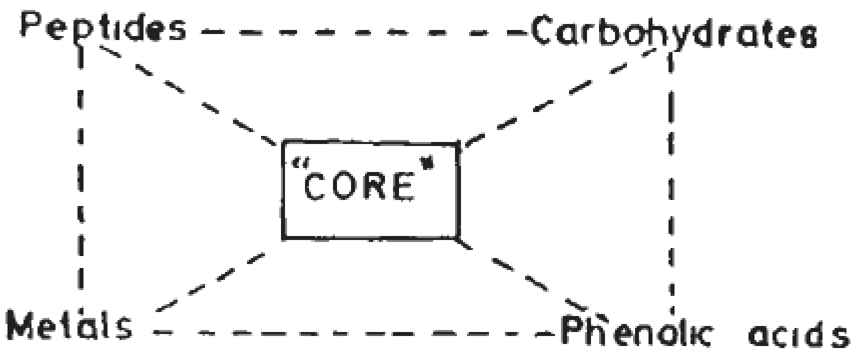


Figure 3.5: Schematic structure of Humic acid proposed by Haworth (Delicato, 1996).

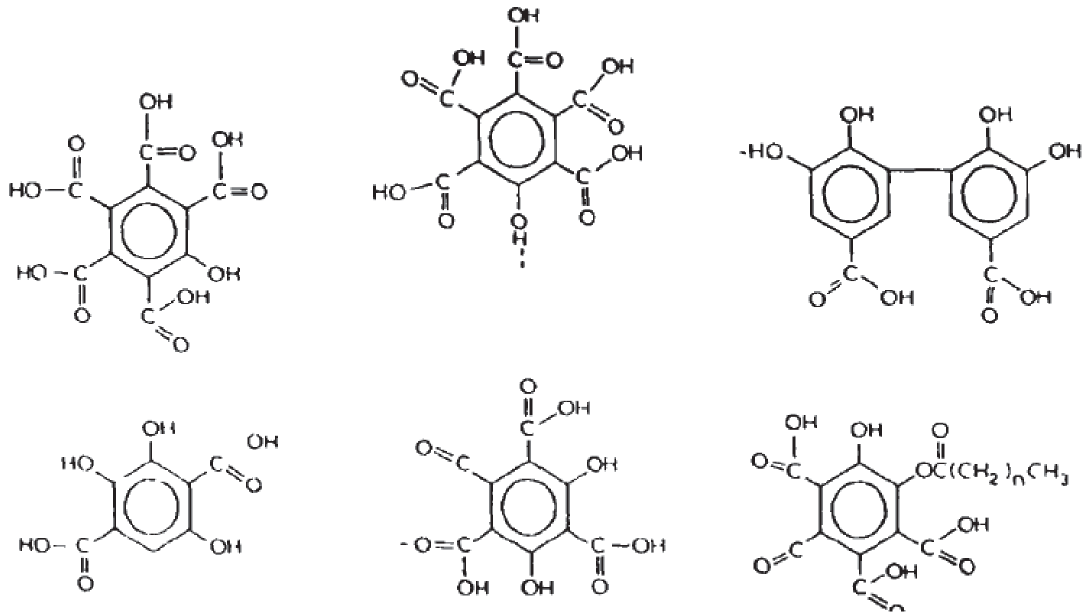
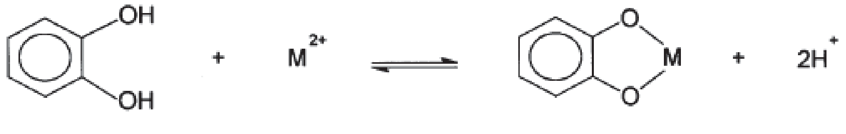
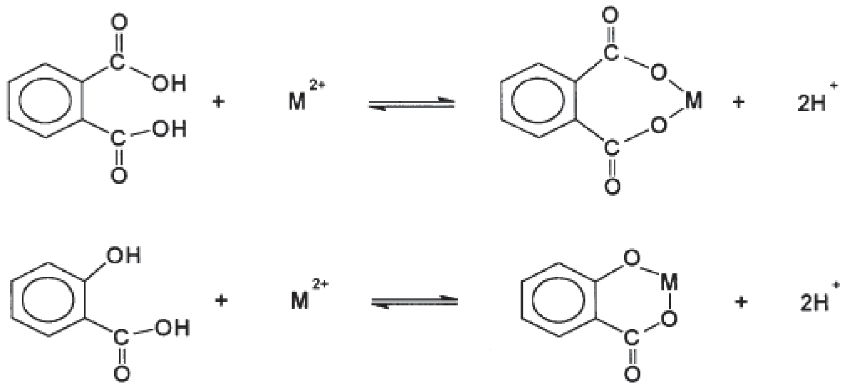


Figure 3.6: Structure of Fulvic acid proposed by Schnitzer (Delicato, 1996).

An assumption is that metal complexation can be affected by the size of these humic molecules, but precise study is still lacking on metal binding to humic substances. The chemical composition of humic substances suggests that concentration of different functional groups changes among the humic substances of different areas. Natural organic matter is considered as important sorbent and that's why a better idea about metal ion binding to humic substances is of great attention (Christl et al., 2001). According to Stevenson and Fitch (1981), a huge debate exists in a reference to importance of every group and about the nature of linkages whether they are ionic or covalent. In accordance to one point of view humic substances are rounded, cross linked polymers which are not capable of forming structures which have characteristics of chelate complexes, but they can easily retain metal ions in exchangeable forms(Figure 3.6 and 3.7). Other school of thought says that there are two main types of chelate linkage; one involves two COOH groups to make a ring like phthalate (Reaction 2) and other involves phenolic OH and COOH to form a ring like salicylate (Reaction 3) (Piccolo and Stevenson, 1982). Reaction 3 and 4 are showing the mechanism of interaction between ketone carbonyls and divalent metals (Holmberg, 2006).



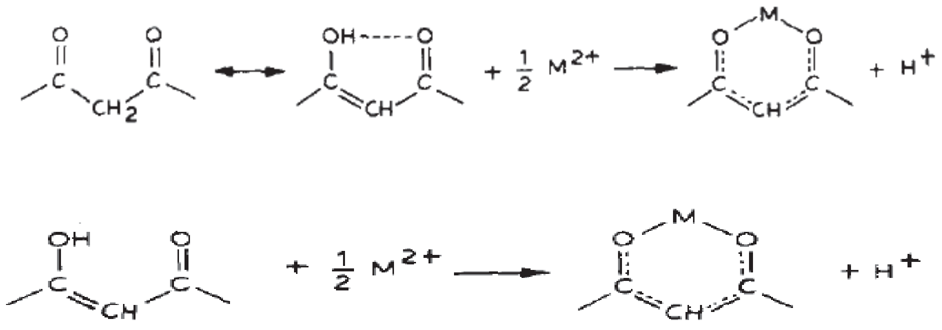
E.q 3.1



E.q 3.2

E.q 3.3

Figure 3.7: Mechanism between humic acid and metals (Dupay and Douay, 2001).



E.q 3.4

E.q 3.5

Figure 3.8: Mechanism between humic acid and metals (Piccolo and Stevenson, 1982).

3.7 Surface Complexation

Some studies like Ho et al, (1995), and Gosset et al (1986), concluded that complexation is also an important process to remove metals ions by peat (Brown et al., 2000). A stable molecular entity is created when surface functional groups react with molecule or an ion exist in soil solution that is called as surface complex and this reaction is known as surface complexation. Surface complexes can be of two types, inner-sphere and out-sphere. The surface complex will be outer-sphere if a water molecule exists between bound metal ion and surface functional group and if water molecule is not present between bound metal ion and surface functional, then this is called inner sphere complex (Sparks, 2003). In case of peat, the functional groups like phenolic, carboxylic and carbonyl bind with metal ions (Holmberg, 2006). The difference in opinion comes in formation of complexation whether inner sphere complexes or outer sphere complexes are formed and peat used as adsorbent. One opinion is that chelation occurs and inner surface complexes are formed while according to other point of view the formation of outer-sphere takes place, and ions are bounded electrostatically (Brown et al., 2000).

Many studies agree with this opinion metals react with humic acid to form chelate that involves neighboring carboyxl COOH and phenolic OH groups, or perhaps two adjacent COOH groups (Brown et al., 2000). The surface complex is affected by the factors like pH, ionic strength, type of sorbent, time and surface loading (Sparks, 2003).

Outer-sphere complexation is faster than inner-sphere complexation and also reversible. This happens only on that surface which is appositively charged to adsorbate. Because of electrostatic interactions takes part in binding in Outer-sphere complexes, that’s why these are weak as compared to inner-sphere complexes where ionic or covalent binding takes place. Ionic strength of aqueous phase can affect adsorption by outer-sphere complexes. While on the other hand inner-sphere complexation is irreversible and ionic strength of aqueous phase does not affect adsorption at a great extent by these mechanisms. Surface charge does not matter in adsorption by inner-sphere complexation (Sparks, 2003).

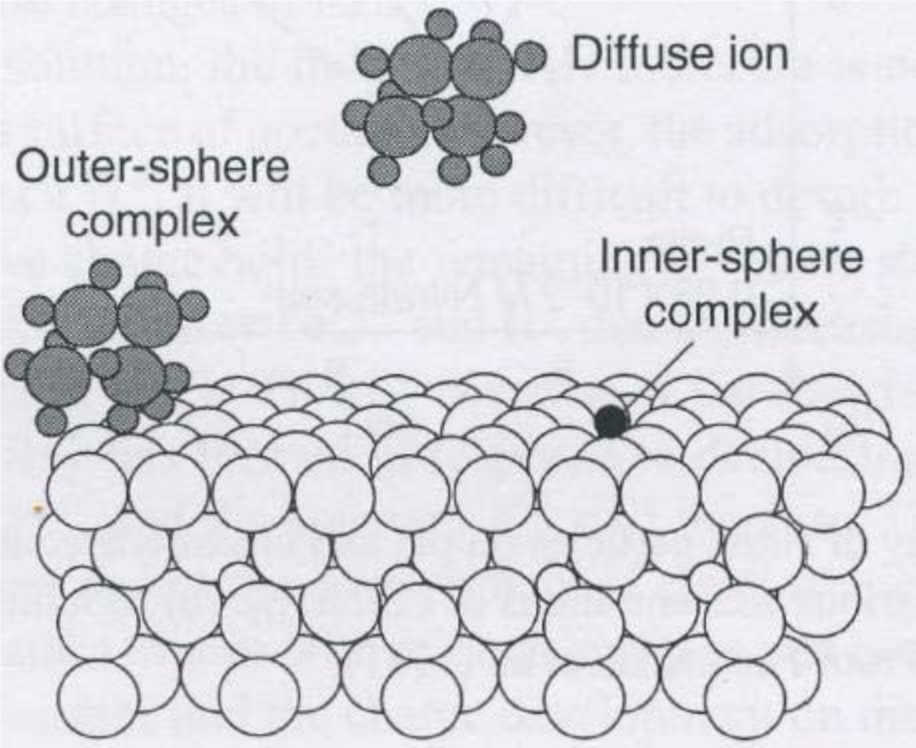


Figure 3.9: Charge surface showing inner-and outer sphere bonding and ions in diffuse double layer (Appelo and Postma, 2005).

The other mechanism in which metal ions are bound with peat is surface adsorption. This process happens at surface where negatively charged surface attracts positively charged ions without any exchange of any electrons and ions. Availability of more surface area can increase the rate of adsorption. Chemisorption is also found to be involved in binding process may be by exchanging electrons but not by exchanging ions (Brown et al., 2000).

3.8 Ion exchange

Ion exchange is regarded as most dominant process in metal uptake in case of peat. Ion exchange happens at acidic sites that originates when humification occurs. The reaction of metals takes places with phenolic and carboxylic acid groups of humic and fulvic acids to let off protons or if the pH is high enough metals react with their anion sites to displace an actual metal (Christ et al., 1996).

Chapter 4 Study Area

The new highway (R4) between Jaren and Gran is about 9km in total length including a 1.7km tunnel section outside Gran center (see yellow lines in Figure 4.1). Excavating this tunnel produces large amount of surplus alum shale rock materials that is planned to be deposited in a pit located Bråten.

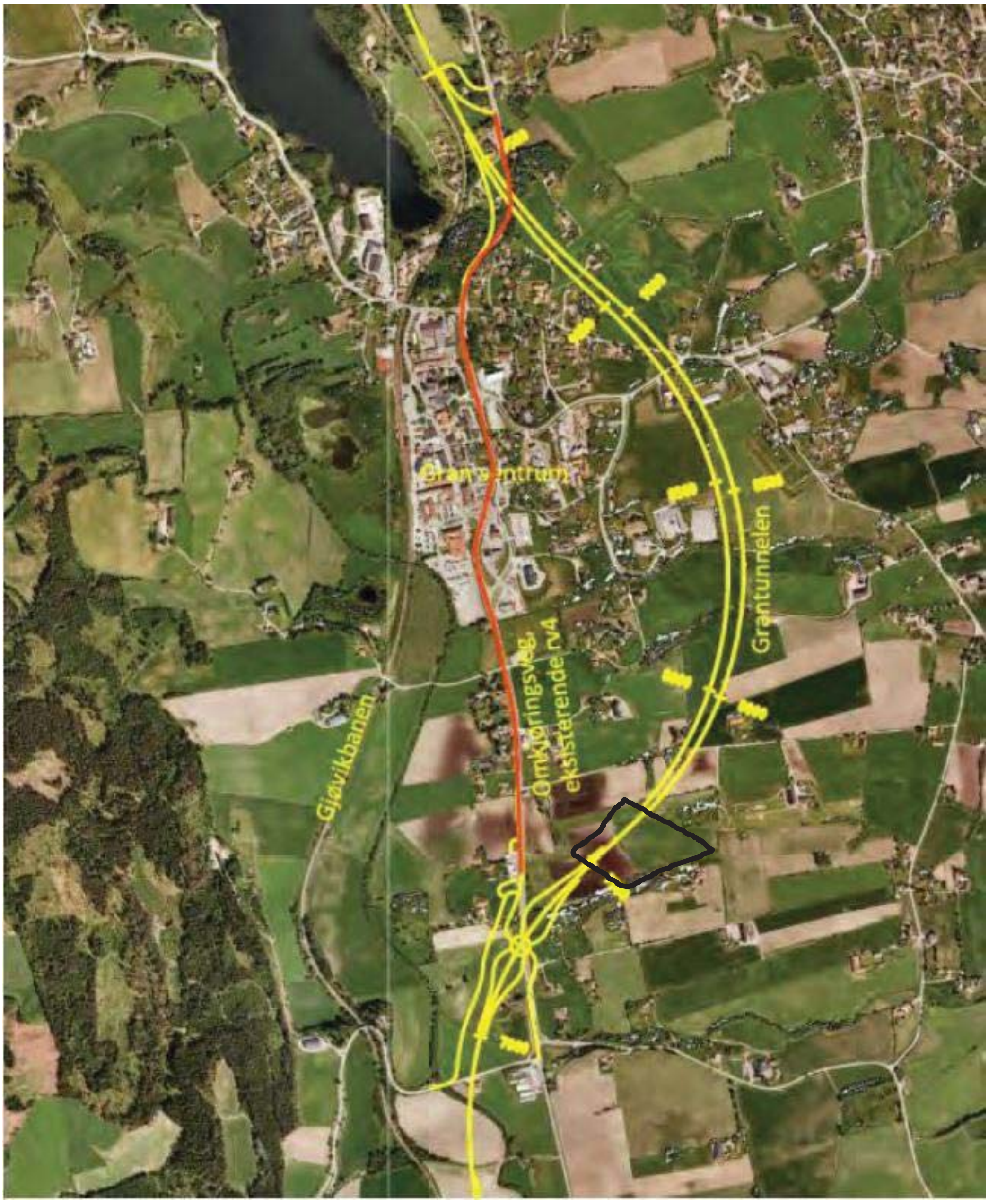


Figure 4.1: Current location of highway Rv4 is shown by red line and yellow line showing the proposed road section. Black line indicates the proposed pit section.

4.1. Geology of study area

Gran is located north of Oslo in Oppland County. (Figure 4.2) explains the bedrock geology around Gran area. This area is described by the transition of rocks from alum shale and granite containing high level of uranium to sedimentary and igneous mafic rock which contains low level of uranium. Superficial deposits of impermeable marine clay and glaciofluvial sand and clay with high permeability are also present. The high radon hazard in area around Brandbu-Jaren-Gran is due to the alum shale that is present near to surface of ground. The presence of superficial deposits and alum shale contains high level of uranium are the main cause of radon in this area (Smethurst et al., 2008).

4.2 Deposit area

The deposit area is located near to tunnel, where excavated material will be dumped. Alum shale is uranium rich rock and can be mobilize. As a precaution peat can be dumped along with rock material which can adsorb uranium and other trace metal leaching out from alum shale.

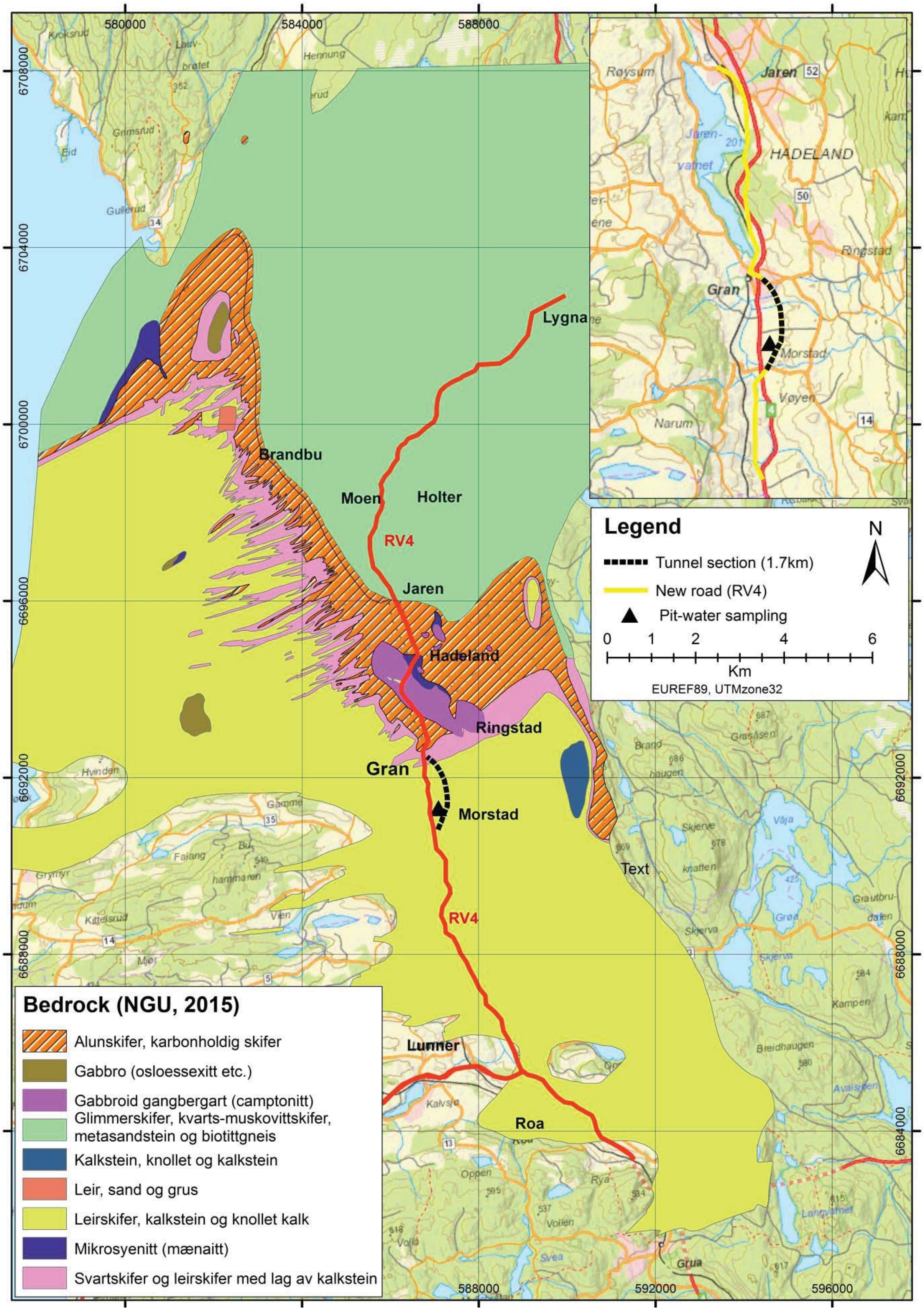


Figure 4.2: Geology of the Gran area.

Chapter 5: Material and Methods

5.1 Collection of samples

A field trip was arranged to Gran tunnel site by Nils Otto Kitterød at 17th December 2014 to visit the study area and also to collect samples. Samples of alum shale, peat and pit water were collected. Pit water was store in fridge, while alum shale and peat were stored in store at NMBU to use later.

Figure 5.1: Collection of water samples at Gran site.

5.2 Crushing of alum shale samples

The samples of alum shale collected from Gran site were of bigger sizes. They were crushed by using stone cracker at NMBU. The measured level of uranium by x-rays diffraction in alum shale was 150 ppm.

Figure 5.2: Size of alum shale sample before and after crushing.

5.3 Preparation of peat

Peat was dried for 13 days at temperature of 37 degree and then sieved at level of 2mm.

Figure 5.3: Drying of peat.

Figure 5.4: Size of peat before and after sieving.

5.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma-mass spectrometry (ICP-MS) is an influential technique to analyze the concentration of trace elements in environmental samples (Bazilio and Weinrich, 2012). It is form of mass spectrometry, which is very sensitive and can determine the concentration of various metals and non-metals at level down to part per trillion, while some elements can be measured at part per quadrillion level. This technique is superior in high speed, precision and sensitivity as compared to other methods (Batsala et al., 2012).

An ICP-MS couples a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The atoms of elements present in sample are converted to ions by ICP source. Mass spectrometer separates and detects these ions (Wolf, 2005)

The sample is imported into ICP plasma as an aerosol by aspirating a liquid into a nebulizer. Once the sample goes into ICP torch, it is desolvated and aerosol elements are transformed to gaseous atoms. At the end of plasma theses gaseous atoms are changed into ions. These ions are brought into mass spectrometer by interface cones, separated by their mass-to-charge ratio and detected by suitable detector (Wolf, 2005). Water samples which contain particulates are filtered and acidified to provide stability and comparability with calibration standards before ICP-MS analysis (wolf, 2005).

5.5 Limit of detection and quantification

Blanks were included in analysis to find out the limit of detection (LOD) and limit of quantification (LOQ). LOD is lowest concentration of an analyte that can be measured or reliably shown to present under defined conditions or that point where analysis becomes feasible. LOQ is that concentration at which quantitative results can be shown with high confidence (Armbruster, 1994). These both values are measured by following equations.

LOD = 3x standard deviation (concentration in blanks)
LOQ = 10x standard quantification (concentration in blanks)

5.6 Preparation of worst case contaminated water

The first step was the preparation of worst-case contaminated water by uranium leaching from alum shale. This was achieved by getting the possibly higher dissolved values of uranium in water. A batch experiment was designed for this purpose. The crushed alum shale were putted into plastic container of 1.5 liter capacity and filled with pit water up to its capacity. The measured pH of pit water was 7.55. This plastic container was closed tightly and fixed on shaking table for 24 hours with the frequency of 200 rotations per minute. After shaking maximum possible contaminated water was separated from shaked mixture. This contaminated water was centrifuged for 10 minutes with speed of 10000 rpm and after which this contaminated water was filtered with 0.45 um filter. The measured pH of contaminated water was 7.94. Then this contaminated water was sent for ICP-MS along with pit water.

The ICP-MS analysis shows that concentration of uranium in pit was 0.18mg/L, which was increased to 2mg/L in contaminated water. Uranium was the most concerned from all the elements leeched out from alum shale, that’s why, uranium will be discussed in more detail.

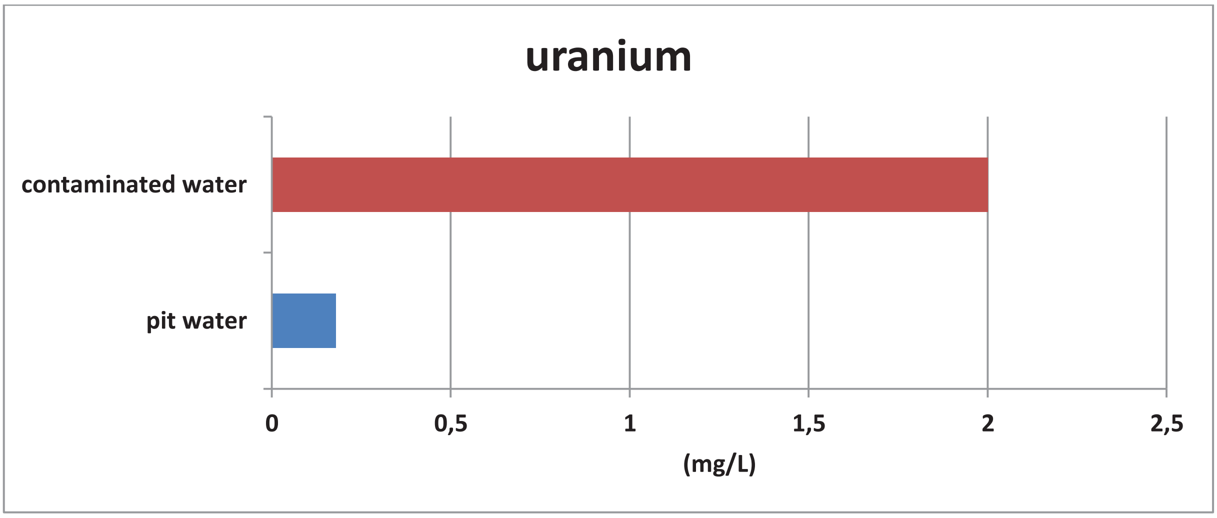


Figure 5.5: Concentration of uranium in pit water and contaminated water.

After the first three ratios which were (1-10, 1-50, and 1-100) the contaminated water was finished. Due to this same procedure was repeated to prepare contaminated water again for (1-250, 1-500, and 1-1000). The concentration of uranium was increased from 2mg/L to 2.2 mg/L. The results are shown in graph.

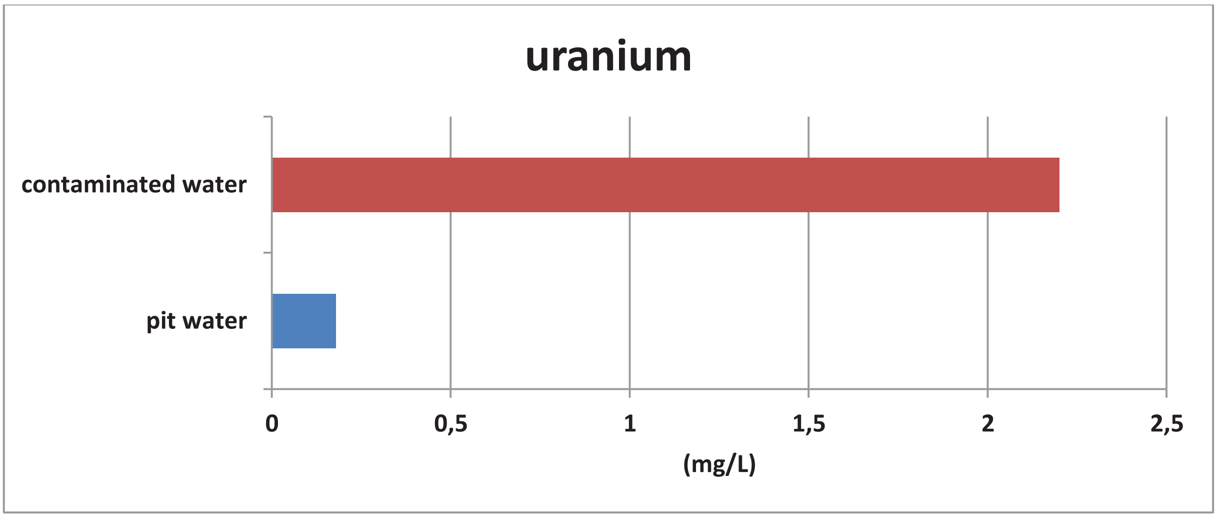


Figure 5.6: Concentration of uranium in pit water and contaminated water (2nd time).

5.7 Blank samples

Blank samples (clean water) were prepared using the same procedure as for other batch experiments to determine the limit of detection (LOD) and limit of quantification (LOQ) of elements. 3 parallels of each of blank samples were run to increase the precision and accuracy in results. LOD is lowest concentration of an analyte that can be measured or reliably shown to present under defined conditions or that point where analysis becomes feasible. LOQ is that concentration at which quantitative results can be shown with high confidence (Armbruster, 1994). These both values are measured by following equations.

LOD = 3x standard deviation (concentration in (clean water), blanks)
LOQ = 10x standard quantification (concentration in (clean water), blanks)

Table 5.1: Limit of detection and limit of quantification of different elements

	U (µg/L)	Ni (µg/L)	Mo (mg/L)	As (µg/L)	S (mg/L)
LOD	0,05	0,2	0,005	0,02	0,05
LOQ	0,15	0,72	0,015	0,05	0,18

5.8 Control Samples

3 types of control samples were run to control background concentrations. Control samples are given in following table.

Table: 5.2: Control samples and their shaking time

No	Sample Name	Shaking time	Parallels
Control 1	Clean water	24	3
Control 2	Contaminated water	24	3
Control 3	Clean water+ peat	24	3

5.8.1 Control sample 1

Clean water sample was prepared using the same procedure and material and analyzed to determine the background level of uranium and other elements to see if some contaminated happened. The results show that concentrations of all elements are under the limit of detection and no contamination took place.

Table 5.3: Results from control sample 1.

Elements	U (µg/L)	Ni (µg/L)	Mo (mg/L)	As (µg/L)	S (mg/L)
Concentrartions	<LOD	<LOD	<LOD	<LOD	<LOD

5.8.2 Control sample 2:

Contaminated water sample was prepared and analyzed to see if some concentrations of different elements are lost due to sorption with the walls of container. The concentration of 15 mL of contaminated water was used. The results are presented in table 5.4.

Table 5.4: Results from control sample 2.

Name of Element	**Original concentration (mg/L)**	**Concentration After 24 hours (mg/L)**
Uranium	2	1,85
Nickle	1,3	1,2
Molybdenum	27	25
Arsenic	0,0085	0,0079
Sulphur	286	274

The graph of uranium is shown in figure 5.7, while rest of graphs are shown in Appendix A.

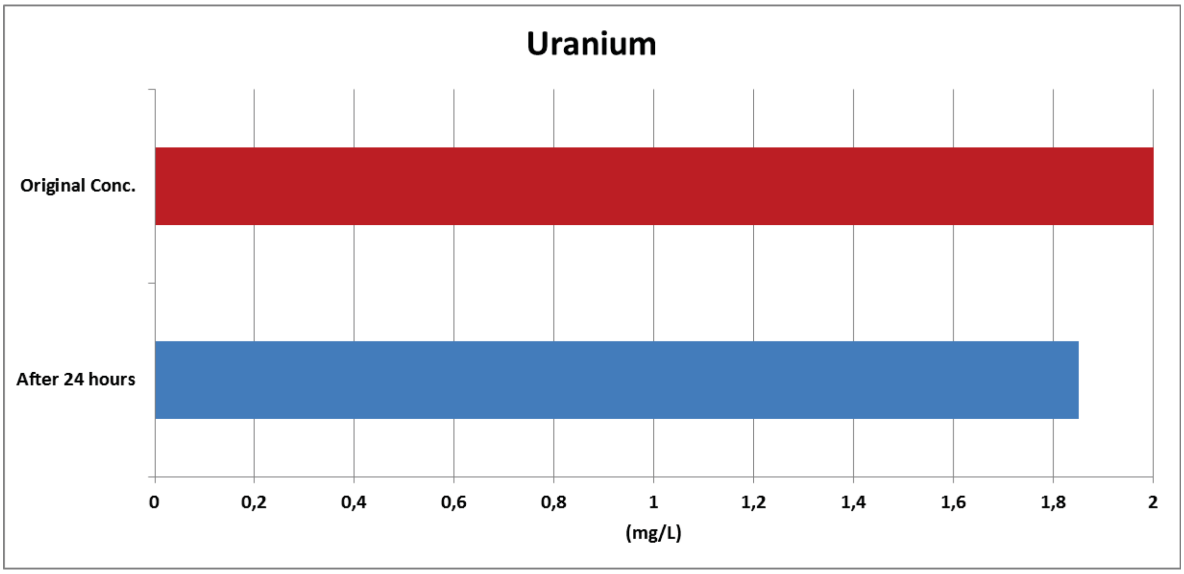


Figure 5.7: Sorption of uranium to walls of container.

5.8.3 Control sample 3

Peat + clean water samples were prepared using the same procedure and analyzed to see if some concentration of elements is leaching from peat to water. 1: 100 ratios were used. 0.15g of peat and 0.15mL of water was used. Results are given in table below.

Table 5.5: Results from control samples 3

Elements	U (µg/L)	Ni (µg/L)	Mo (mg/L)	As (µg/L)	S (mg/L)
Concentrartions	<LOD	1,4	<LOD	2,1	3,4

5.9 Batch Experiments

6 series of batch experiments were designed to see the adsorption behavior of uranium and some other metals and to investigate the adsorption properties of peat. 6 different soil/solution ratios including (1-10, 1-50, 1-100, 1-250, 1-500 and 1-1000) were used to investigate the effect of adsorbent dosage, effect of time and effect of initial concentration of metals in solutions on adsorption. Two types of aqueous solutions (Pit water and contaminated water) were used with different initial concentrations of different metals. Peat was used as soil. Soil and solution were mixed in 50mL centrifuge tubes and shaked on shaking table with 200 rpm for 1 and 24 hours. After shaking all samples were centrifuged at speed of 10000 rpm for 10 minutes. At the end they were filtered with 0.45um size filter paper and sent for ICP-MS analysis. 3 parallels of each sample was prepared, run and analyzed using same procedure to minimize the chances of error and to increase the accuracy in results. In results their mean value was used. All the experiments were performed at room temperature.

Figure 5.8: Shaking of sample at shaking table.

Figure 5.9: Centrifuge timing and speed.

5.9.1 Soil/Solution Ratio 1-10

In the soil/solution ratio (1-10) 2 g of peat and 20 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.6.

Table 5.6: Sample parameters with soil/solution ratio 1-10.

Sample Name	Shaking time (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.9.2 Soil/Solution Ratio 1-50

In the soil/solution ratio (1-50) 0.30 g of peat and 15 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.7.

Table 5.7: Sample parameters with soil/solution ratio 1-50.

Sample Name	Shaking time (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.9.3 Soil/Solution Ratio 1-100

In the soil/solution ratio (1-100) 0.15 g of peat and 15 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.8.

Table 5.8: Sample parameters with soil/solution ratio 1-100.

Sample Name	Shaking time (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.9.4 Soil/Solution Ratio 1-250

In the soil/solution ratio (1-250) 0.14 g of peat and 35 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.9.

Table 5.9: Sample parameters with soil/solution ratio 1-250.

Sample Name	Shaking time (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.9.5 Soil/Solution Ratio 1-500

In the soil/solution ratio (1-500) 0.07 g of peat and 35 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.10.

Table 5.10: Sample parameters with soil/solution ratio 1-500.

Sample Name	Shaking (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.9.6 Soil/Solution Ratio 1-1000

In the soil/solution ratio (1-1000) 0.035 g of peat and 35 mL of solutions of two types including contaminated and pit water were used. Shaking time and parallels are given below in table 5.11.

Table 5.11: Sample parameters with soil/solution ratio 1-1000.

Sample Name	Shaking time (hours)	Parallels
Pit water + peat	1	3
Pit water + peat	24	3
Contaminated water +peat	1	3
Contaminated water +peat	24	3

5.10 pH values

pH values of samples are presented in table. Every value is a mean of 3 values because three duplicates were run for every sample. However the effect of pH on adsorption was not studied.

Table 5.12: pH vales for pit water samples.

Ratio	**Sample Name**	**Shaking time**	**pH**
1:10	Pit water	1	6.33
1:10	Pit water	24	6.30
1:50	Pit water	1	7.01
1:50	Pit water	24	6.81
1:100	Pit water	1	7.12
1:100	Pit water	24	7.07
1:250	Pit water	1	7.28
1:250	Pit water	24	7.33
1:500	Pit water	1	7.45
1:500	Pit water	24	7.79

1:1000	Pit water	1	7.62
1:1000	Pit water	24	7.64

Table 5.13: pH values for contaminated water samples.

Ratio	Sample Name	Shaking time	pH
1:10	Contaminated Water	1	6.43
1:10	Contaminated Water	24	6.33
1:50	Contaminated Water	1	6.72
1:50	Contaminated Water	24	6.53
1:100	Contaminated Water	1	6.94
1:100	Contaminated Water	24	6.62
1:250	Contaminated Water	1	7.40
1:250	Contaminated Water	24	7.27
1:500	Contaminated Water	1	7.56
1:500	Contaminated Water	24	7.61
1:1000	Contaminated Water	1	7.76
1:1000	Contaminated Water	24	7.70

5.11 Quality of ICP-MS analysis

To increase in precision in samples 3 parallels of each sample were prepared in same manner and analyzed by ICP-MS. Mean, standard deviation and coefficient of variation was calculated from the ICP-MS analysis results of samples. Coefficient of variation is calculated by dividing the standard deviation by mean. The value of coefficient of variation less than 30 percent shows fair precision in data (Brown, 1998). The difference in concentration of elements in parallels can be caused by contamination in samples during preparation, due to material used and due to differences in collected samples. Coefficient of variation is increasing from one to 24 % which shows that samples have good precision. Only in one co efficient of variation is increasing to 66 %, which may be due to contamination in sample preparation.

Table 5.14: Mean, standard deviation and co-efficient of variation in pit water samples.

Ratio	Shaking time	Mean (mg/L)	Standard deviation (mg/L)	Co-efficient of variation (%)
1-10	1	0,00021	0,00014	66
1-10	24	0,000096	0,000017	17
1-50	1	0,0024	0,00008	3
1-50	24	0,00045	0,000042	9
1-100	1	0,013	0,0009	6
1-100	24	0,0018	0,00044	24
1-250	1	0,031	0,0055	17
1-250	24	0,0080	0,00037	4
1-500	1	0,076	0,0066	8
1-500	24	0,026	0,0045	17
1-1000	1	0,10	0,0075	7
1-1000	24	0,05	0,001	1

Table 5.15: Mean, standard deviation and co-efficient of variation in contaminated water samples.

Ratio	Shaking time	Mean (mg/L)	Standard deviation (mg/L)	Co-efficient of variation (%)
1-10	1	0,0002	0,10	10
1-10	24	0,00006	0,088	8,8
1-50	1	0,00105	0,026	2,7
1-50	24	0,00023	0,082	8,2
1-100	1	0,0061	0,021	2,1
1-100	24	0,00045	0,031	3,1
1-250	1	0,057	0,050	5,0
1-250	24	0,03	0,14	14
1-500	1	0	0	0
1-500	24	0,051	0,059	5,9
1-1000	1	0	0	0
1-1000	24	0,057	0,034	3,4

Chapter 6: Results and Discussions

All the samples were analyzed by ICP-MS. As already mention that all the samples were prepared in duplicates of three by using the same procedure to increase the accuracy and precision in results. The final results were the average values of those duplicates.

The adsorption of different elements including uranium, molybdenum nickel, Sulphur, and arsenic were studied on peat as adsorbent under different factors such as dosage of adsorbent, contact time of adsorbent and solution and initial concentration of metals ions in aqueous solution. In this chapter results are presented.

6.1 Removal of Uranium

6.1.1Removal of uranium under effect of adsorbent dosage

Generally removal efficiency increases as the dose of adsorbent increases. This is due to availability of more surface area (Anber, 2011). Table 6.1 provides the different parameters like mass of adsorbent, volume of aqueous solution, initial concentration of uranium in pit water, and concentrations remained non-adsorbed in aqueous solutions after 1 and 24 hours.

Table 6.1: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in pit water.

Sample Name	Parameters	Ratio	Initial concentrations (mg/L)	Concentration after 1 hour (mg/L)	Concentration after 24 hours (mg/L)
Peat +Pit water	M = 2g, V = 20mL	1-10	0,18	0,00022	0,000096
Peat +Pit water	M = 0.30g, V = 15mL	1-50	0,18	0,0024	0,00045
Peat +Pit water	M = 0.15g, V = 15mL	1-100	0,18	0,013	0,0018
Peat +Pit water	M = 0.14g, V = 35mL	1-250	0,18	0,031	0,0080
Peat +Pit water	M = 0.07g, V = 35mL	1-500	0,18	0,077	0,026
Peat +Pit water	M = 0.035g, V = 35mL	1-1000	0,18	0,1	0,055

The influence of adsorbent dosage on the adsorption of uranium was investigated. By increasing the adsorbent dosage, the uranium adsorption percentage also increased. This happens because of increase in surface area of adsorbent material which provides more adsorption sites.

Adsorption percentage

Adsorption percentage can be calculated by equation 6.1.

Adsorption percentage (%) = C_o-C_f/C_0 *100 Eq 6.1

$C_{o\,=}$ Initial concentration of solute (mg/L)

$C_{f\,=}$ Final concentration of solute (mg/L)

From the soil/solution ratios that have been used, the mass of adsorbent in terms of (gram/L) has been calculated and presented in table 6.2 with adsorbent percentages.

Table 6.2: Adsorption percentages of uranium in 1 hour and 24 hours in pit water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat +Pit water	100	99,8	99,9
Peat +Pit water	20	98,6	99,7
Peat +Pit water	10	92,7	99
Peat +Pit water	4	82,7	95,5
Peat +Pit water	2	57,2	85,5
Peat +Pit water	1	44,4	69,4

The adsorption percentage of uranium in pit water at different doses of peat from 1 gram/L to 100 gram/L is shown in table 6.2. Adsorption percentage has been influenced by variation in mass of peat. In time of one hour, adsorption percentage increased from 44.4 to 99.8 when mass of adsorbent increased from 1 gram/L to 100 gram/L. By looking at 24 hours of time, adsorption percentage increased from 69.4 to 99.9 when mass of adsorbent was increased from 1 gram/L to 100 gram/L. Increasing the mass of peat up to 10mg/L, 99 percent of adsorption was achieved. It means that when mass of peat was increased, there are many empty adsorption sites are available for adsorption. The graph is shown in figure 6.1.

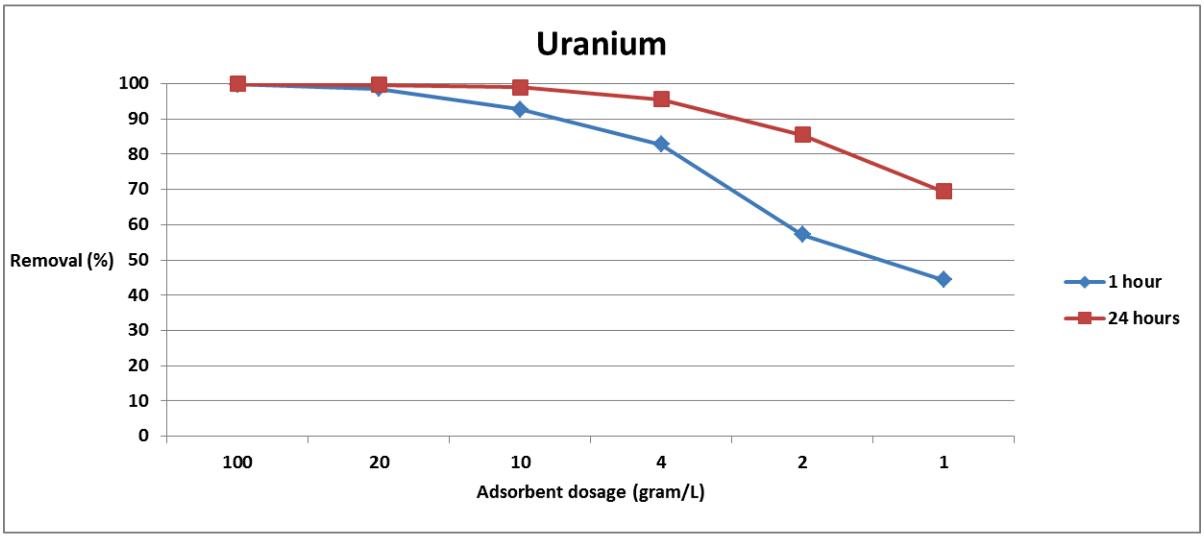


Figure 6.1: Adsorption percentages of uranium in 1 hour and 24 hours in pit water different adsorbent dosages.

Table 6.3 provides the different parameters like mass of adsorbent, volume of aqueous solution, initial concentration of uranium in contaminated water, and concentration remained after 1 and 24 hours in solution.

Table 6.3: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in contaminated water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat + Cont. water	M = 2g, V = 20mL	1-10	2	0,002	0,0007
Peat + Cont. water	M = 0.30g, V = 15mL	1-50	2	0,038	0,0028
Peat + Cont. water	M = 0.15g, V = 15mL	1-100	2	0,288	0,014
Peat + Cont. water	M = 0.14g, V = 35mL	1-250	2,2	1,13	0,2
Peat + Cont. water	M = 0.07g, V = 35mL	1-500	2,2	1,6	0,85
Peat + Cont. water	M = 0.035g, V = 35mL	1-1000	2,2	1,9	1,6

Table 6.4: Adsorption percentages of uranium in 1 hour and 24 hours in contaminated water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat +contaminated water	100	99,9	99,9
Peat +contaminated water	20	98,1	99,8
Peat +contaminated water	10	85,6	99,3
Peat +contaminated water	4	50	90,9

Peat +contaminated water	2	27,2	61,3
Peat +contaminated water	1	13,6	27,2

The adsorption percentage of uranium in contaminated water at different doses of peat from 1 gram/L to 100 gram/L is shown in table 6.4. Adsorption percentage has been influenced by variation in mass of peat. In time of one hour, adsorption percentage increased from 13.6 to 99.9 when mass of adsorbent increased from 1 gram/L to 100 gram/L. By looking at 24 hours of time, adsorption percentage increased from 27.2 to 99.9 when mass of adsorbent was increased from 1 gram/L to 100 gram/L. Increasing the mass of peat up to 10mg/L, 99.3 percent of adsorption was achieved. The graph is shown in figure 6.2.

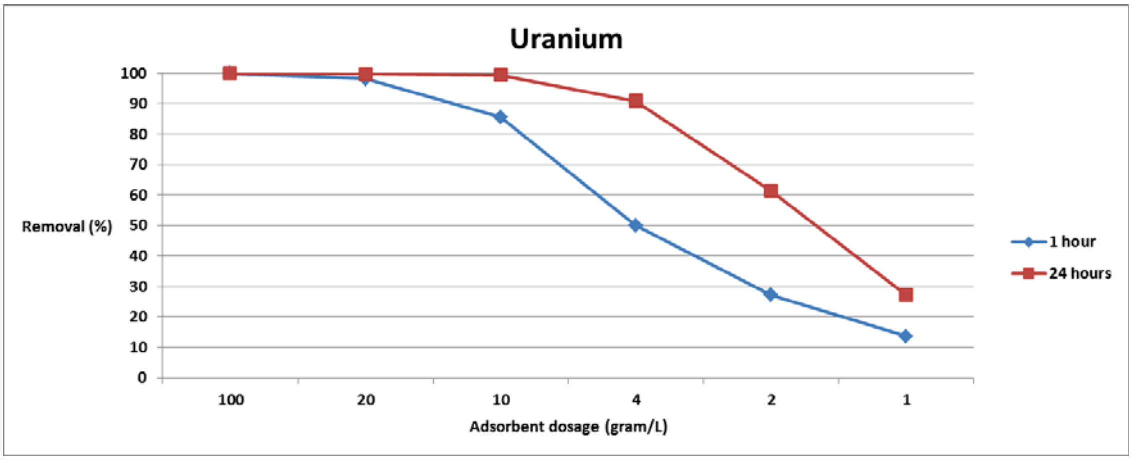


Figure 6.2: Adsorption percentages of uranium in 1 hour and 24 hours in contaminated water different adsorbent dosages.

6.1.2 Removal of Uranium under the Effect of Contact time

The longer contact time will be. The more complete adsorption process will be. That’s why it is very important to give required time for adsorption process to be complete (Anber 2011). The effect of contact time on the adsorption of uranium ions was investigated from 1 hour to 24 hours. The effect of time on the adsorption percentage of uranium in pit water was not significant when mass of adsorbent was high. It is becoming observable as the mass of adsorbent is going low. In case where I gram/L of peat was used, the adsorption percentage increased from 44.4 to 69.4 from one hour to 24 hours and when 2 gram/L of peat was used, the adsorption percentage increased from 57.2 to 85.5 from one hour to 24 hours. After that when mass of peat was increased the difference between adsorption percentage after 1 hour and 24 hours became quite low. The values are given in table 6.2 and graph is shown in figure 6.1.

The effect of time on the adsorption percentage of uranium in contaminated water was more significant than pit water. As the concentration of peat is going lower, the time is becoming factor of importance. At higher concentration of peat, most of uranium ions are getting adsorbed in first hour for example, when concentration of peat is 100 gram/L and 20 gram/L nearly 100 percent and 98.1 percent of uranium was adsorbed respectively. The adsorption percentages are increasing from 27.2 to 61.3, 50 to 90.9 and 85.6 to 99.3 from one hour to 24 hours when 2 gram/L, 4 gram/L and 10 gram/L of peat was applied. The values are given in table 6.2 and the graph is shown in figure 6.2

6.1.3 Removal of Uranium under initial concentration

When initial concentration increases, adsorption sites become fewer (Anber 2011).

The influence of initial uranium ions in aqueous solution was investigated. For this purpose adsorption capacity of adsorbent was calculated by following equation and presented in tables according to different soil to solution ratios.

$q_e = (C_o - C_f)\ V/M$ Eq 6.2

$q_=$ Adsorption capacity

C_o = initial concentration of solute (mg/L)

C_e = Final concentration of solute (mg/L)

V = Volume of solution (L)

M = adsorbent dose (g)

6.1.4 Solid/ liquid partition coefficients, Kd

Mobility and distribution of elements can be estimated by solid/liquid partition coefficients or distribution coefficients. Distribution coefficient is the ratio of concentration of an element at solid phase to concentration of an element in contacting liquid

Equilibrium time was considered to be 24 hours. Kd was calculated by using the following equation and presented in tables

$$K_d = \frac{V_w\ (C_0 - C_i)}{M_{sed}\ C_i}$$

Eq. 6.3

C_o = initial concentration of solute (mg/L)

C_i = Final concentration of solute (mg/L)

V = Volume of solution (L)

M_{sed} = adsorbent dose (g)

Table 6.5: Adsorption capacity in 1 hour and 24 hours in contaminated water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Adsorption capacity after 24 hours (mg/g)**	**Kd L/g**
Peat + Pit water	100	0,18	0,00179	0,00179	18,74
Peat + Pit water	20	0,18	0,00888	0,00897	19,95
Peat + Pit water	10	0,18	0,0167	0,01782	9,9
Peat + Pit water	4	0,18	0,03722	0,043	5,3
Peat + Pit water	2	0,18	0,0515	0,077	2,9
Peat + Pit water	1	0,18	0,08	0,125	0,37

Table 6.6: Adsorption capacity of uranium in 1 hour and 24 hours in contaminated water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Adsorption capacity after 24 hours (mg/g)**	**Kd L/g**
Peat + Cont. water	100	2	0,01998	0,0199	28,56
Peat + Cont. water	20	2	0,0981	0,0998	35,6
Peat + Cont. water	10	2	0,171	0,1986	14,1
Peat + Cont. water	4	2,2	0,275	0,500	2,5
Peat + Cont. water	2	2,2	0,300	0,675	0,79
Peat + Cont. water	1	2,2	0,3	0,6	0,37

Tables 6.5 and 6.6 show that adsorption capacity (q) increases with increasing the initial concentrations of uranium metal ions in solution. When 100 gram/L of peat was applied in pit water where initial concentration of uranium metal ions 0.18mg/L, the adsorption capacity after 24 hours was 0.00179mg/g, while in case of contaminated where initial concentration of uranium metal ions was 2mg/L, the adsorption capacity after 24 hours was 0.0199 mg/g. When 1 gram/L of peat was applied, the adsorption capacity in case of pit after 24 hours was 0.125 mg/g and in contaminated water, the adsorption capacity was 24 hours was 0.6 mg/g. This makes clear that adsorption capacity of peat was higher where initial concentration of uranium ions was high. The graph is shown in figure 6.3.

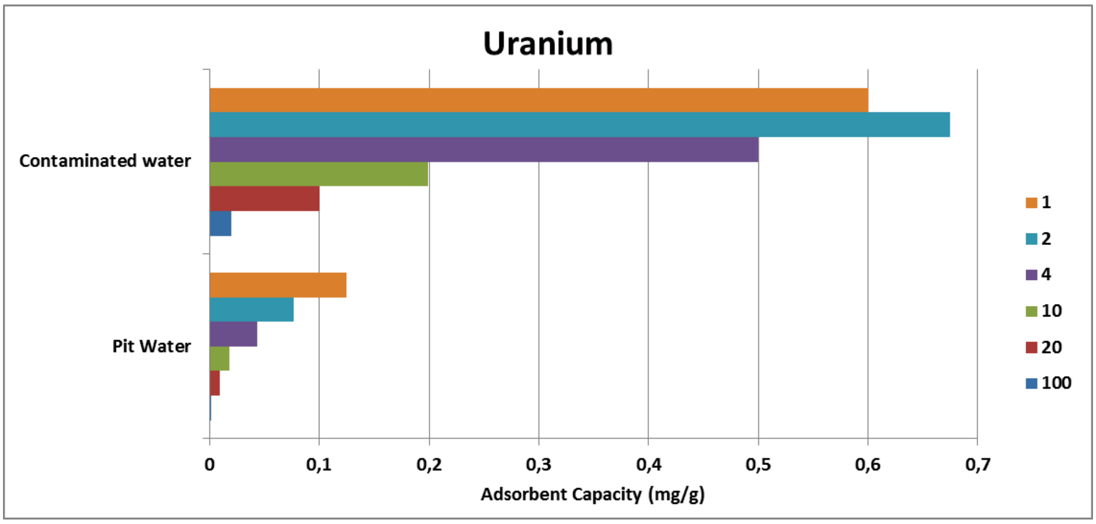


Figure 6.3: Comparisons of adsorption capacities of peat in pit water and contaminated water.

6.2 Removal of Molybdenum

6.2.1 Removal of Molybdenum under the effect of adsorbent dosage

Table 6.7 provides the different parameters like mass of adsorbent, volume of aqueous solution, initial concentration of molybdenum in pit water, and concentration remained after 1 and 24 hours in solution.

Table 6.7: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in pit water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat +Pit water	M = 2g, V = 20mL	1-10	0,53	0,0094	0,0025
Peat +Pit water	M = 0.30g, V = 15mL	1-50	0,53	0,077	0,036
Peat +Pit water	M = 0.15g, V = 15mL	1-100	0,53	0,13	0,081
Peat +Pit water	M = 0.14g, V = 35mL	1-250	0,53	0,15	0,14
Peat +Pit water	M = 0.07g, V = 35mL	1-500	0,53	0,18	0,18
Peat +Pit water	M = 0.035g, V = 35mL	1-1000	0,53	0,2	0,2

Table 6.8: Adsorption percentage of molybdenum in 1 hour and 24 hours in pit water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat +Pit water	100	98,2	99,5
Peat +Pit water	20	85,4	93,2
Peat +Pit water	10	75,4	84,7
Peat +Pit water	4	71,6	73,5
Peat +Pit water	2	66	66
Peat +Pit water	1	62,2	62,2

The adsorption percentage of molybdenum in pit water at different doses of peat from 1 gram/L to 100 gram/L is shown in table 6.8. Adsorption percentage has been influenced by variation in mass of peat. In time of one hour, adsorption percentage increased from 62.2 to 98.2 when mass of adsorbent was increased from 1 gram/L to 100 gram/L. By looking at 24 hours of time, adsorption percentage increased from 62.2 to 99.5 when mass of adsorbent was increased from 1 gram/L to 100. The graph is shown in figure 6.4.

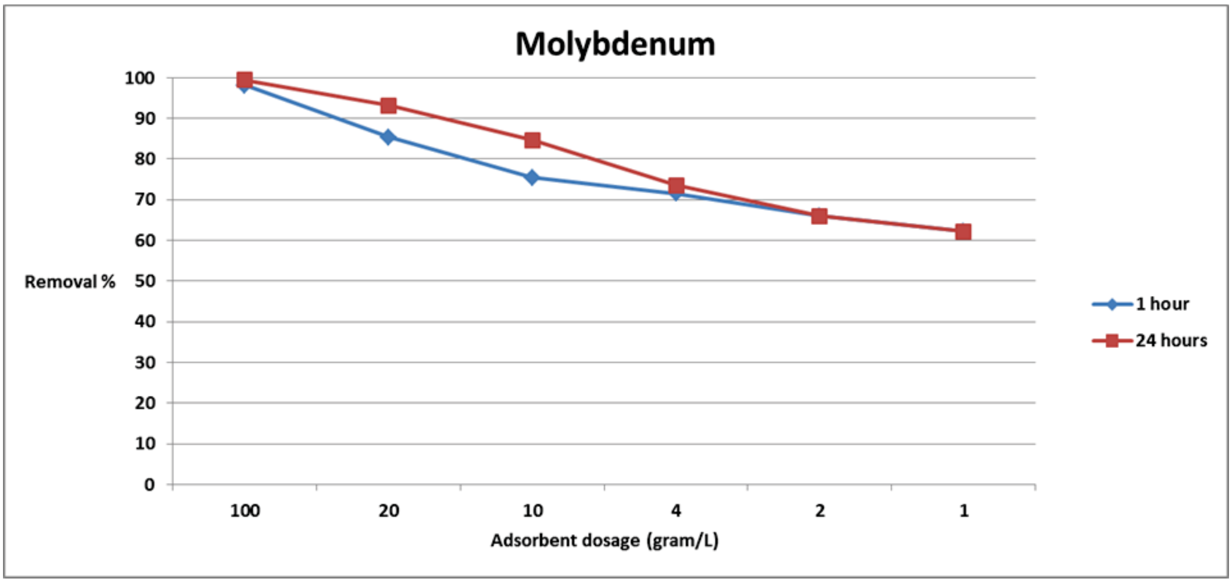


Figure 6.4: Adsorption percentages of molybdenum in 1 hour and 24 hours in pit water different adsorbent dosages.

Table 6.9: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in contaminated water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat + Cont. water	M = 2g, V = 20mL	1-10	26	1,2	0,62
Peat + Cont. water	M = 0.30g, V = 15mL	1-50	26	14	11
Peat + Cont. water	M = 0.15g, V = 15mL	1-100	26	19	17
Peat + Cont. water	M = 0.14g, V = 35mL	1-250	21	18	20
Peat + Cont. water	M = 0.07g, V = 35mL	1-500	21	19	21
Peat + Cont. water	M = 0.035g, V = 35mL	1-1000	21	20	21

Table 6.10: Adsorption percentages of molybdenum in 1 hour and 24 hours in contaminated water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat + contaminated water	100	95,3	97,6
Peat + contaminated water	20	46	57,6
Peat + contaminated water	10	26,9	23
Peat + contaminated water	4	11,5	3,8
Peat + contaminated water	2	7,6	0
Peat + contaminated water	1	3,8	0

The adsorption percentage of molybdenum in contaminated water at different doses of peat from 1 gram/L to 100 gram/L is shown in table 6.10. Adsorption percentage has been influenced significantly by variation in mass of peat. In time of one hour, adsorption percentage increased from 3.8 to 95.3 when mass of adsorbent increased from 1 gram/L to 100 gram/L. By looking at 24 hours of time, adsorption percentage increased from 0 to 97.9 when mass of adsorbent was increased from 1 gram/L to 100 gram/L. When mass of peat were 1 gram/L and 2 gram /L, there was no adsorption of molybdenum was noticed. This is due to less surface area and competition for adsorption with other metal. But as the surface area is increasing adsorption rate is also increasing and it is reaching to 97.6 when 100 gram/L of peat was used. This increase in adsorption rate with increase in surface area tells the importance of mass of adsorbent. The graph is shown in figure 6.5.

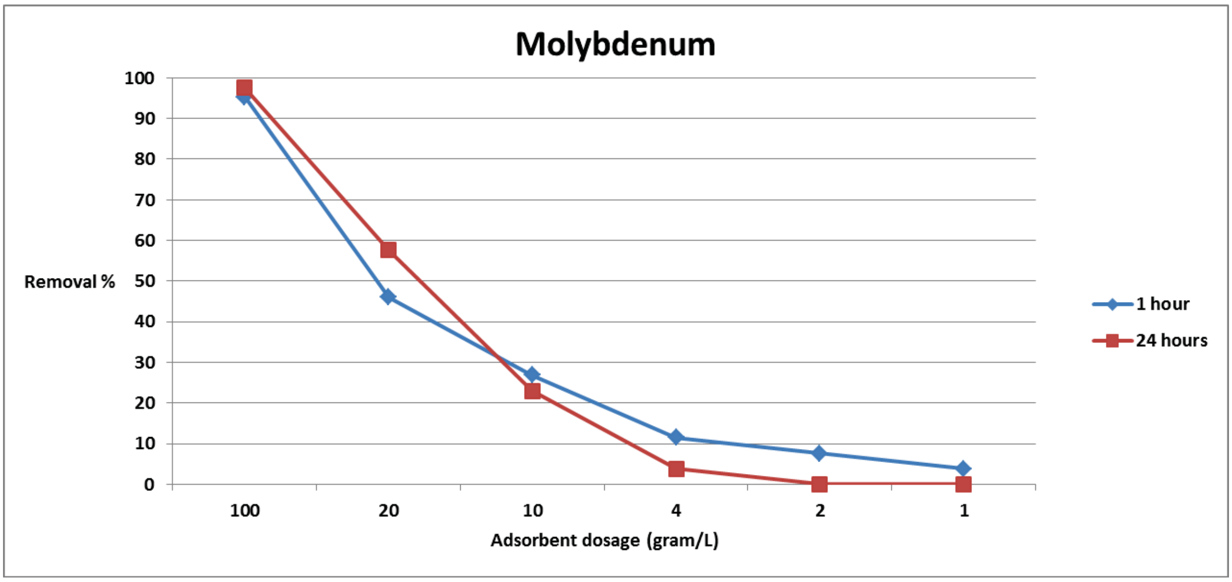


Figure 6.5: Adsorption percentages of molybdenum in 1 hour and 24 hours in contaminated water different adsorbent dosages.

6.2.2 Removal of Molybdenum under the effect of contact time

The effect of contact time on the adsorption of molybdenum ions was investigated from 1 hour to 24 hours and values are given in table 6.8. The effect of time on the adsorption percentage of molybdenum in pit water was not significant when mass of adsorbent was very high and very low. When mass of peat 1 gram/L, the adsorption percentage only increased from 98.2 to 99.5. Here time is not making big difference because most of ions have been adsorbed in first hour. When mass of peat reduced to 20 gram/L and 10 gram/L, time became important and adsorption percentage increased from 85.4 to 93.2 and 74.4 to 84.7 from one hour to 24 hours respectively. But when peat reduced to 2 gram/L and 1 gram/L, adsorption percentage remained constant and it did not increased. The graph is shown in figure 6.5.

The effect of time on the adsorption percentage of molybdenum in contaminated water was only of importance when concentration of peat 100 gram/L and 20 gram/L because adsorption percentage is increasing from 95.3 to 97.6 and 46 to 57.6 from one hour to 24 hours respectively. After that increasing the time, adsorption percentage is decreasing and desorption is happening. This may due to less surface area and competition for adsorption with other metals. The graph is shown in figure 6.9

6.2.3 Removal of Molybdenum under effect of initial concentration

The adsorption capacity (qe) also increased by increasing the initial concentrations of molybdenum in aqueous solution. The initial concentration of molybdenum in contaminated water is more than pit water. So the adsorption capacity was higher as well. Table 6.11 showing the adsorption capacity peat in pit water, table 6.12 showing adsorption capacity of peat in contaminated water and graph 6.10 showing the comparison of adsorption capacities in pit water and contaminated water.

Table 6.11: Adsorption capacity in 1 hour and 24 hours in pit water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Adsorption capacity after 24 hours (mg/g)**
Peat + Pit water	100	0,53	0,005206	0,005275
Peat + Pit water	20	0,53	0,02265	0,0247
Peat + Pit water	10	0,53	0,04	0,0449
Peat + Pit water	4	0,53	0,095	0,0975
Peat + Pit water	2	0,53	0,175	0,175
Peat + Pit water	1	0,53	0,33	0,33

Table 6.12: Adsorption capacity in 1 hour and 24 hours in contaminated water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Concentration after 24 hours (mg/g)**
Peat + Cont. water	100	26	0,248	0,2538
Peat + Cont. water	20	26	0,6	0,75
Peat + Cont. water	10	26	0,7	0,9
Peat + Cont. water	4	21	0,75	0,25
Peat + Cont. water	2	21	1	0
Peat + Cont. water	1	21	1	0

When 100 gram/L of peat was applied in pit water where initial concentration of molybdenum metal ions 0.53mg/L, the adsorption capacity after 24 hours was 0.005275mg/g, while in case of contaminated where initial concentration of uranium metal ions was 26mg/L, the adsorption capacity after 24 hours was 0.2538 mg/g. When 1 gram/L of peat was applied, the adsorption capacity in case of pit after 1 hour was 0,33mg/g and in contaminated water, the adsorption capacity was 24 hours was 1 mg/g. This makes clear that adsorption capacity of peat was higher where initial concentration of molybdenum ions was high. The graph is shown in figure 6.6**.**

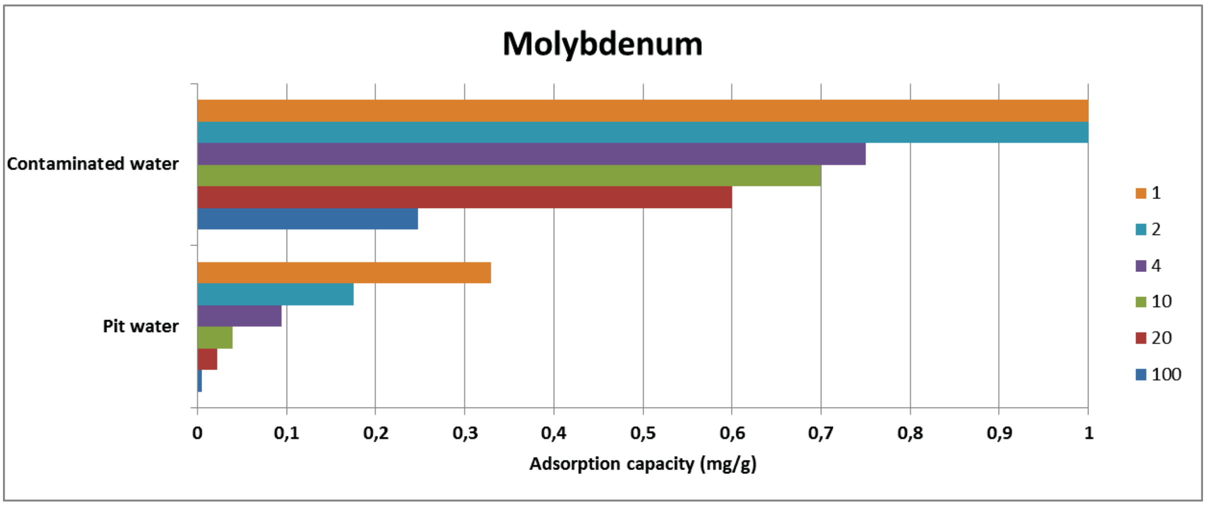


Figure 6.6: Comparisons of adsorption capacity of peat in pit water and contaminated water after 1 hour.

6.3 Removal of Nickel

6.3.1 Removal of Nickel under the effect of adsorbent dosage.

Table 6.13 provides the different parameters like mass of adsorbent, volume of aqueous solution, initial concentration of nickel in pit water, and concentration remained after 1 and 24 hours in solution.

Table 6.13: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in pit water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat +Pit water	M = 2g, V = 20mL	1-10	0,027	0,0018	0,0013
Peat +Pit water	M = 0.30g, V = 15mL	1-50	0,027	0,0012	0,0015
Peat +Pit water	M = 0.15g, V = 15mL	1-100	0,027	0,00104	0,00098
Peat +Pit water	M = 0.14g, V = 35mL	1-250	0,027	< 0,0013	< 0,0013
Peat +Pit water	M = 0.07g, V = 35mL	1-500	0,027	0,0019	< 0,0013
Peat +Pit water	M = 0.035g, V = 35mL	1-1000	0,027	0,0024	< 0,0013

Table 6.14: Adsorption percentages of nickel in 1 hour and 24 hours in pit water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat +Pit water	100	93,3	93,3
Peat +Pit water	20	95,5	94,4
Peat +Pit water	10	96,1	96,3
Peat +Pit water	4	95,5	95,5
Peat +Pit water	2	92,2	95,5
Peat +Pit water	1	91,1	95,5

The adsorption percentage of nickel in pit water increased by increasing the adsorbent dosage up to 10 gram/L. At this dose of adsorbent, the adsorption percentage is 96.1, after that it does not increase by increasing the adsorbent dose. This may be due to overlapping of adsorption sites due to overcrowding of adsorbent particles. Overall 1 gram/L of peat is looking effective to remove big concentration of nickel in solution. The graph is shown in figure 6.7.

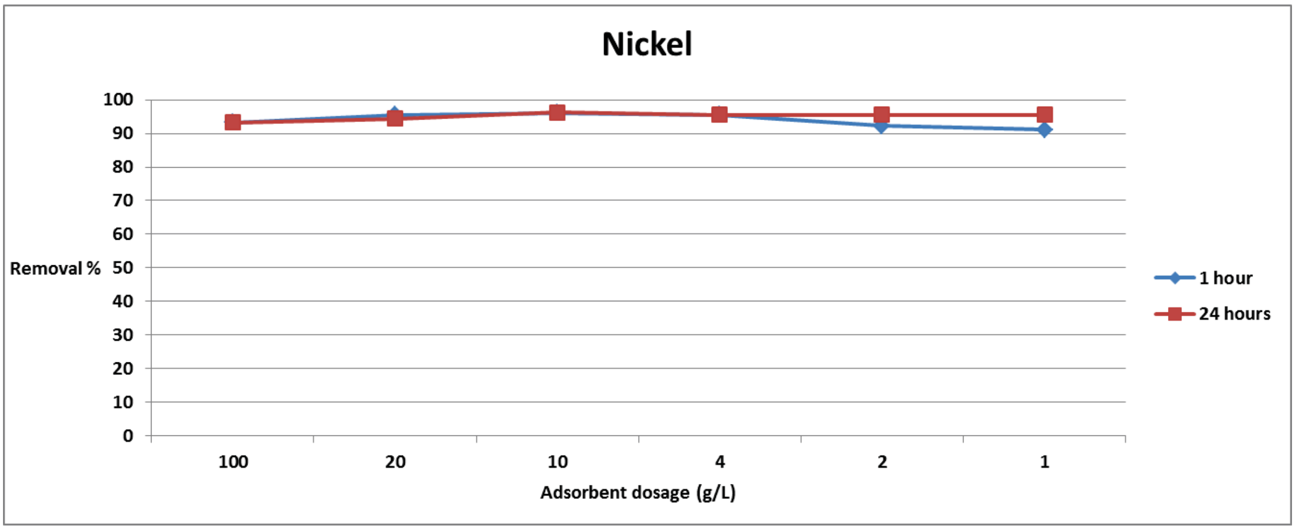


Figure 6.7: Adsorption percentages of nickel in 1 hour and 24 hours in pit water different adsorbent dosages.

Table 6.15: Initial parameters and non-adsorbed concentrations after 1 and 24 hours in pit water.

Sample Name	**Parameters**	**Ratio**	**Initial Concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat + Cont. water	M = 2g, V = 20mL	1-10	1,3	0,008	0,0056
Peat + Cont. water	M = 0.30g, V = 15mL	1-50	1,3	0,024	0,011
Peat + Cont. water	M = 0.15g, V = 15mL	1-100	1,3	0,044	0,016
Peat + Cont. water	M = 0.14g, V = 35mL	1-250	1,1	0,087	0,04
Peat + Cont. water	M = 0.07g, V = 35mL	1-500	1,1	0,17	0,08
Peat + Cont. water	M = 0.035g, V = 35mL	1-1000	1,1	0,32	0,13

Table 6.16: Adsorption percentages of nickel in 1 hour and 24 hours in contaminated water at different adsorbent dosages.

Sample Name	**Adsorbent dosage (g/L)**	**Adsorption percentage in 1 hour**	**Adsorption percentage in 24 hours**
Peat + contaminated water	100	99,3	99,5
Peat + contaminated water	20	98,1	99,1
Peat + contaminated water	10	96,6	98,7
Peat + contaminated water	4	92	96,3
Peat + contaminated water	2	84,5	92,7
Peat + contaminated water	1	70,9	88,1

The adsorption percentage of nickel in contaminated water at different doses of peat from 1 gram/L to 100 gram/L is shown in table 6.12. Adsorption percentage has been influenced significantly by variation in mass of peat. In time of one hour, adsorption percentage increased from 70.9 to 99.3 when mass of adsorbent increased from 1 gram/L to 100 gram/L. By looking at 24 hours of time, adsorption percentage increased from 88.1 to 99.5 when mass of adsorbent was increased from 1 gram/L to 100 gram/L. The graph is shown in figure 6.8.

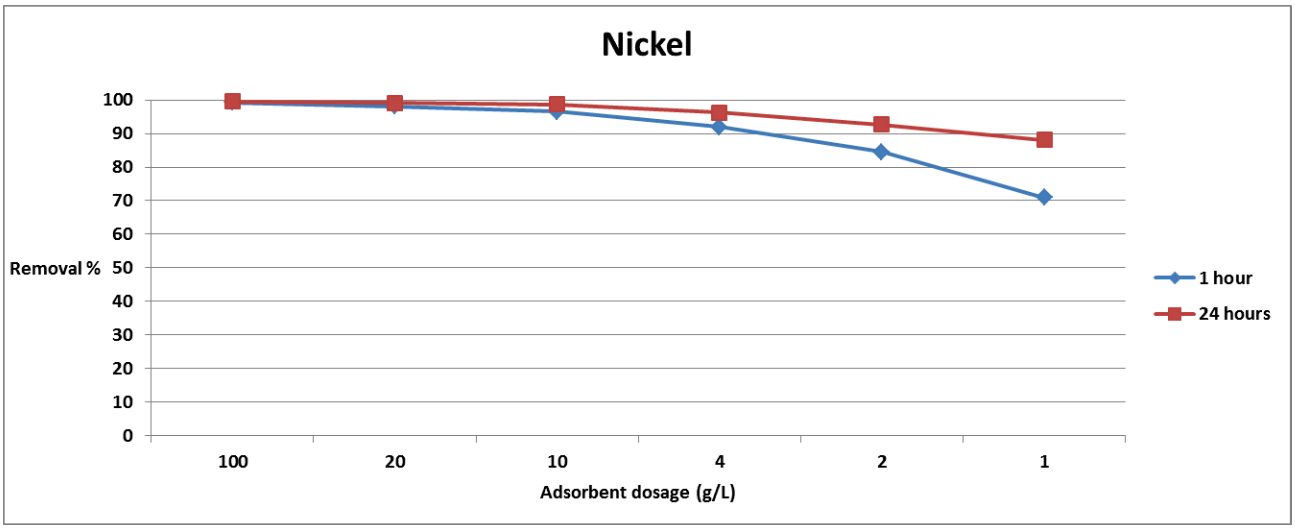


Figure 6.8: Adsorption percentages of nickel in 1 hour and 24 hours in pit water different adsorbent dosages.

6.3.2 Removal of Nickel under the effect of time

The effect of contact time on the adsorption of nickel ions was investigated from 1 hour to 24 hours and values are given in table 6.14. The effect of time on the adsorption percentage of nickel in pit water was not significant because adsorption percentage was very high in first hour. When 100 gram/L of adsorbent was used, adsorption percentage was 93.3 and it remained constant by increasing time to 24 hours. When 1 gram/L of peat was used adsorption percentage increased from 91.1 to 95.5 from first hour to 24 hours. The graph is shown in Figure 6.13.

The effect of time on the adsorption percentage of nickel in contaminated water was not very significant. As the concentration of peat is going lower, the time is becoming factor of importance. At higher concentration of peat, most of nickel ions are getting adsorbed in first hour for example, when concentration of peat is 100 gram/L and 20 gram/L 99.3 percent and 98.1 percent of nickel was adsorbed respectively. The adsorption percentages are increasing from 92 to 96.3, 84.5 to 92.7 and 70.9 to 88.1 from one hour to 24 hours when 10 gram/L, 2 gram/L and 1 gram/L of peat was applied. The graph is shown in figure 6.14.

6.3.3 Removal of Nickel under the effect of Initial concentration

By increasing the initial nickel ion concentration, the adsorption capacity also increased. The values are presented in tables 6.17 and 6.18 and graph is presented in figure 6.15.

Table 6.17: Adsorption capacity in 1 hour and 24 hours in pit water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Adsorption capacity after 24 hours (mg/g)**
Peat + Cont. water	100	0,027	0,000252	0,000257
Peat + Cont. water	20	0,027	0,00129	0,001275
Peat + Cont. water	10	0,027	0,002596	0,002602
Peat + Cont. water	4	0,027	0,00645	0,00645
Peat + Cont. water	2	0,027	0,01255	0,0129
Peat + Cont. water	1	0,027	0,0246	0,0258

Table 6.18: Adsorption capacity in 1 hour and 24 hours in pit water at different soil/solution ratios.

Sample Name	**Adsorbent dosage (g/L)**	**Initial concentrations (mg/L)**	**Adsorption capacity after 1 hour (mg/g)**	**Concentration after 24 hours (mg/g)**
Peat + Cont. water	100	1,3	0,01292	0,012944
Peat + Cont. water	20	1,3	0,0638	0,06445
Peat + Cont. water	10	1,3	0,1256	0,1284
Peat + Cont. water	4	1,1	0,25325	0,265
Peat + Cont. water	2	1,1	0,465	0,51
Peat + Cont. water	1	1,1	0,78	0,97

When 100 gram/L of peat was applied in pit water where initial concentration of nickel metal ions 0.027mg/L, the adsorption capacity after 24 hours was 0,000257mg/g, while in case of contaminated where initial concentration of nickel metal ions was 26mg/L, the adsorption capacity after 24 hours was 0.012944 mg/g. When 1 gram/L of peat was applied, the adsorption capacity in case of pit after 1 hour was 0.0246 mg/g and in contaminated water, the adsorption capacity was 24 hours was 0,78 mg/g. This makes clear that adsorption capacity of peat was higher where initial concentration of molybdenum ions was high. The graph is shown in figure 6.9**.**

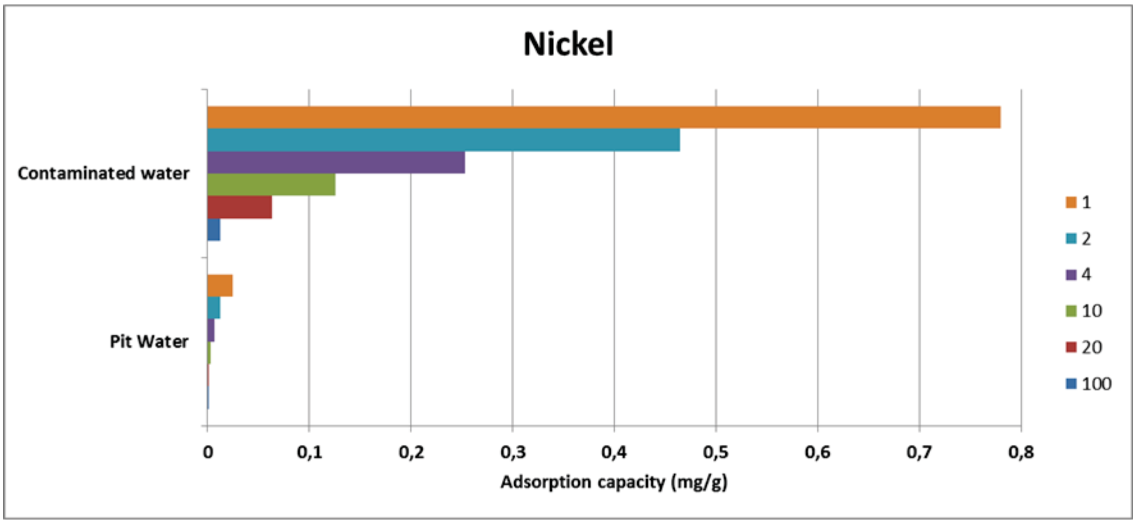


Figure 6.9: Comparisons of adsorption capacity of peat in pit water and contaminated water after 1 hour.

6.4 Removal of Sulphur

Sulphur was not adsorbed by peat not in pit water and neither in contaminated water. Increasing the adsorbent, increasing the contact time did not make any adsorption of Sulphur. Instead of adsorption, some concentrations of sulphur leached out from peat due to which concentration of sulphur in solution. Tables 6.19 and 6.20 showing the initial and final concentrations of sulphur in solutions

Table 6.19: Initial and final concentration of sulphur in pit water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat +Pit water	M = 2g, V = 20mL	1-10	0,14	0,18	0,15
Peat +Pit water	M = 0.30g, V = 15mL	1-50	0,14	0,16	0,15
Peat +Pit water	M = 0.15g, V = 15mL	1-100	0,14	0,15	0,14
Peat +Pit water	M = 0.14g, V = 35mL	1-250	0,14	0,14	0,15
Peat +Pit water	M = 0.07g, V = 35mL	1-500	0,14	0,14	0,15
Peat +Pit water	M = 0.035g, V = 35mL	1-1000	0,14	0,14	0,15

Table 6.20: Initial and final concentration of sulphur in contaminated water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (mg/L)**	**Concentration after 1 hour (mg/L)**	**Concentration after 24 hours (mg/L)**
Peat + Cont. water	M = 2g, V = 20mL	1-10	0,29	0,31	0,3
Peat + Cont. water	M = 0.30g, V = 15mL	1-50	0,29	0,29	0,28
Peat + Cont. water	M = 0.15g, V = 15mL	1-100	0,28	0,28	0,28
Peat + Cont. water	M = 0.14g, V = 35mL	1-250	0,37	0,37	0,41
Peat + Cont. water	M = 0.07g, V = 35mL	1-500	0,37	0,38	0,4
Peat + Cont. water	M = 0.035g, V = 35mL	1-1000	0,37	0,37	0,37

6.5 Removal of Arsenic

Arsenic was not removed by peat as well. Like sulphur Arsenic also leached out from peat and concentrations of arsenic increased in solution. Higher concentration of peat leached higher concentrations of arsenic.

Table 6.21: Initial and final concentration of arsenic in pit water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (µg/L)**	**Concentration after 1 hour (µg/L)**	**Concentration after 24 hours (µg/L)**
Peat +Pit water	M = 2g, V = 20mL	1-10	0,86	4,9	5,1
Peat +Pit water	M = 0.30g, V = 15mL	1-50	0,86	1,7	2,8
Peat +Pit water	M = 0.15g, V = 15mL	1-100	0,86	1,2	1,8
Peat +Pit water	M = 0.14g, V = 35mL	1-250	0,86	0,83	1,1
Peat +Pit water	M = 0.07g, V = 35mL	1-500	0,86	0,66	0,83
Peat +Pit water	M = 0.035g, V = 35mL	1-1000	0,86	0,66	0,68

Table 6.22: Initial and final concentration of arsenic in contaminated water.

Sample Name	**Parameters**	**Ratio**	**Initial concentrations (µg/L)**	**Concentration after 1 hour (µg/L)**	**Concentration after 24 hours (µg/L)**
Peat + Cont. water	M = 2g, V = 20mL	1-10	8,5	9,4	9,9
Peat + Cont. water	M = 0.30g, V = 15mL	1-50	8,5	8,4	6,7
Peat + Cont. water	M = 0.15g, V = 15mL	1-100	8,5	8,2	6,6
Peat + Cont. water	M = 0.14g, V = 35mL	1-250	7,2	6,8	7,3
Peat + Cont. water	M = 0.07g, V = 35mL	1-500	7,2	7	7,4
Peat + Cont. water	M = 0.035g, V = 35mL	1-1000	7,2	6,9	7

6.6 Discussions

To design the adsorption system, adsorption isotherms or equilibrium data are the basic needs. When adsorbent material reaches to its capacity and rate of adsorption becomes equal to rate to desorption, equilibrium is achieved. Adsorption isotherm helps to calculate the theoretical adsorption capacity of an adsorbent. Langumuir and Freundlich are the two basic types of adsorption isotherms. Adsorption isotherms show that how adsorbate molecules (metal ions in aqueous solution) is shared between adsorbents solid and solution at equilibrium concentration (Anber, 2011)

Experimental results were studied by using Langmuir and Frendulich isotherms.

6.6.1. Langmuir adsorption isotherm

Langmuir adsorption isotherm explains that adsorbate molecules adsorbed as mono layer on the outer surface of adsorbent after which adsorption process stops. Therefore Langmuir confirms the distribution of metal ions at equilibrium between liquid phase and solid (Anber, 2011).

$$q_e = Q^0 bC_e/(1 + bC_e) \qquad \text{E.q 6.4}$$

The linear form of equation can be written as

$$C_e/q_e = 1/bQ^0 + C_e/Q^0 \qquad \text{E.q 6.5}$$

24 hours’ time was taken as equilibrium time, because 24 hours’ time is sufficient to achieve equilibrium time generally (OECD, 2011)

Ce = the equilibrium concentration in solution (mg/L)

qe = concentration adsorbed for unit mass of adsorbent (mg/g)

Q^o = maximum monolayer coverage (mg/g)

b = Langmuir constant, it tells about energy of adsorption.

Q^0 and b is determined from slope and intercept of the straight line results in figure

Slope = $1/Q^o$

Intercept = $1/b^* Q^o$

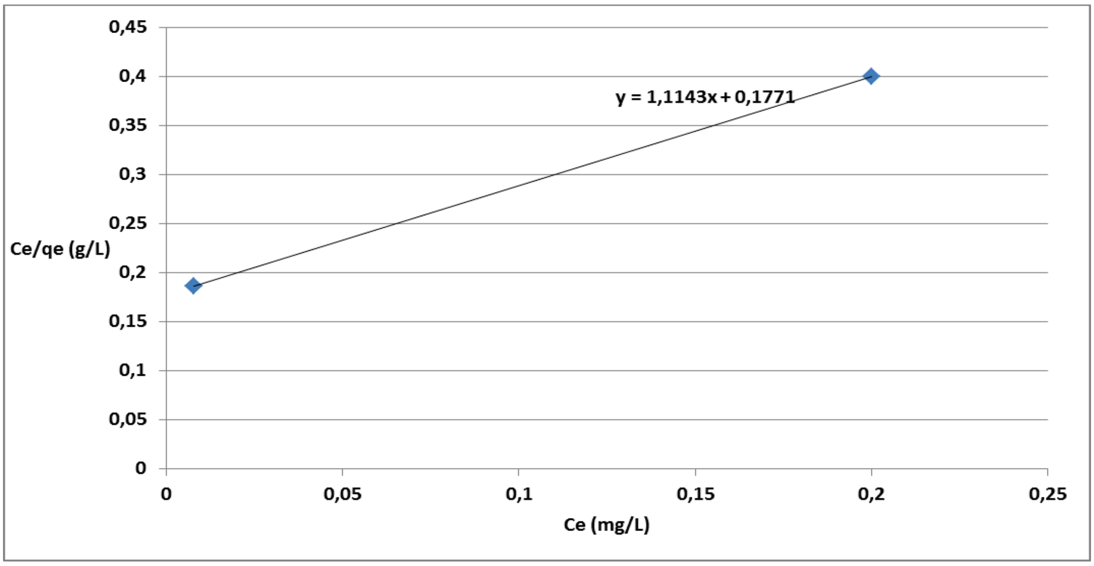


Figure 6.10: Langmuir adsorption isotherm at adsorbent dose of 4g/L.

Table 6.23: Value of qmax and b

b	**Q^o (mg/g)**	**R2**
6.27	0.90	1

The plot of Ce/qe versus Ce at 4mg/L o peat was found to be linear. This indicates the applicability to Langmuir model to data. Normally the fitting of data to adsorption model of Langmuir isotherm is tested by the statistical significance of the correlation coefficient (R2) for Ce/qe versus Ce, which is found to be 1. Langmuir isotherm fits well with data this may be homogenous distribution of active sites on the peat. Results are presented in table 6.23.

The isotherm shape effect is explained by dimensionless separation factor R_L by determining that if adsorption system is favorable or unfavorable.

$$R_L = 1/(1+bC_i)$$ E.q 6.6

0 < RL <1 states that, adsorption reaction is favorable (Mahmoud, 2013).

R_L was found between 0.06 to 0.46 which states that adsorption process on peat is favorable.

6.6.2 Freundulich Adsorption isotherms

Freundulich adsorption isotherm explains the adsorption characteristics for the surfaces which are heterogeneous. It tells that initial adsorption is followed by condensation effect that results from adsorbate interaction (Anber, 2011). The equation of Freundlich is used on large scale for isothermal adsorption. In this special case heterogeneous surface energies where the energy term (b) in Langmuir equation changes with surface coverage (qe) because of change in heat of adsorption (Jian 2001 cited in (Yasemin and Zeki, 2007).

$$q_e = K_f (C_e)^{1/n} \quad n > 1$$

E.q 6.7

Equation 6.6 can be re written as

$$ln\ q_e = ln\ K_f + (1/n) ln\ C_e$$

E.q 6.8

qe = concentration adsorbed for unit mass of adsorbent (mg/g)

K_f = Freundlich constant which is related to adsorption capacity (mg/g).

n = adsorption intensity

Kf and n can be determined from straight line that results in graph.

Where, the slope = (1/n)

Intercept = ln k_F

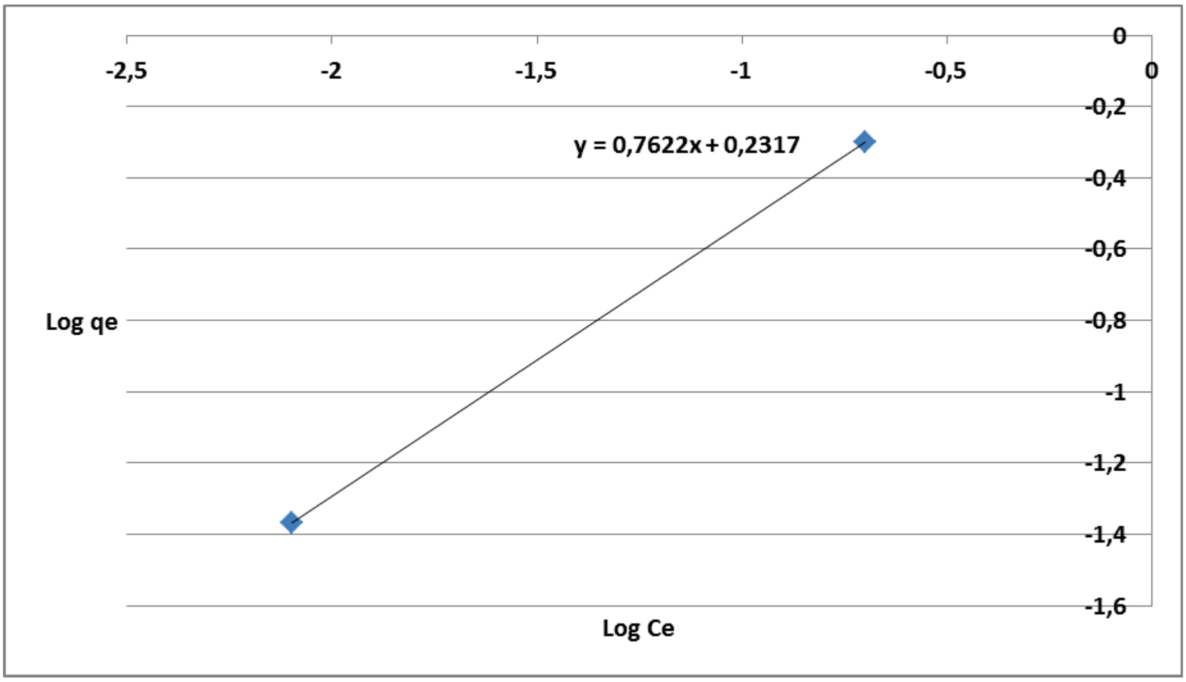


Figure 6.11: Freundlich adsorption isotherm at adsorbent dose of 4g/L.

Table 6.24: Values of Kf and n

n	Kf	R2
1.31	5.78	1

n gives the indication that how favorable is the adsorption process. It describes the degree of nonlinearity between adsorption and solution concentration. The values of n between 1- to 10 describe the good adsorption (Desta, 2013).

If n = 1, then adsorption is linear

n > 1, then adsorption is chemical process

n < 1 then adsorption is physical process

The plot of logCe versus logqe at 4mg/L o peat was found to be linear. This indicates the applicability to Langmuir model to data. Adsorption capacity is indicated by the intercept of line while adsorption intensity is indicated by the slope. In this case correlation coefficient R^2 is also found to be 1. The results are presented in table 6.24.

In both cases, the obtained plots were linear that explains the applicability of these of these models to data set. To see the most fitted model values of correlation coefficient (R^2) are compared. But In our data set in both cases the value of R^2 was found 1. This may be due to low concentration of metal ions and high enough capacity of solid to make both isotherm equations linear. Isotherm validity for both models can be checked by increasing the concentration range of metal ions, and then one of the isotherms may better with data.

6.7 General Discussions

It is evident from results that peat is found to be good adsorbent for uranium and other trace metal leaching out from alum shale like molybdenum and nickel under certain conditions. Initial concentration of metal ions in solution, contact time and, adsorbent dose were found important factor affecting adsorption percentage and adsorption capacity of peat.

Actually this study was not designed to find the equilibrium time. Equilibrium time is when there is no change in concentration of solution on solid surface or in bulk solution. For high adsorbent doses of peat like 100 gram/L and 20 gram/L, it looks that equilibrium time was achieved in 1 hour because 99 percent uranium removal rate was achieved in first hour. After that by decreasing adsorbent dose, different adsorption rates were achieved in first hour and increased by increasing contact time.

100g/L and 20 g/L of peat were found too high as adsorbent to remove desired concentrations of uranium, molybdenum and nickel in this study. By using the 100 g/L of peat as adsorbent, 99 percent of uranium was adsorbed in first hour. By decreasing the concentration of peat 20 g/L, there was not much difference in case of uranium, 98 percent adsorption rate was noticed in first hour.

Time factor became important when 10 g/L of peat was used. 85 and 92 were the adsorption rate in pit water and contaminated water respectively in hour and it increased to 99 in 24 hours. But 4g/L of peat was also found to be very good concentration and it removed more than 90 percent of uranium in 24 hours. By lowering to 2 gram/L and 1 gram/L shows that adsorption rate decreased certainly because of decrease in adsorption sites and competition with other metals.

In case of nickel, even 1 gram/L of peat was enough to remove 95 percent from pit water and 88 percent from contaminated at 24 hours. By increasing the adsorbent doses, adsorption rate increased. Contact time was not important in removal of nickel as most of the nickel as it was important in case of uranium at low adsorbent doses. By increasing the initial concentration of nickel ions, adsorption capacity of peat for nickel also increased.

In case of molybdenum, higher concentration of adsorbent was required when initial concentration of molybdenum was higher. When concentration of adsorbent was reduced, adsorption rate of molybdenum decreased. This is due to competition with other metals for adsorption. But adsorption capacity of peat was higher when adsorbent doses were low. When concentration of adsorbent reduced to 2 g/L and 1 g/L, adsorption rate was very low and desorption happened after 1 hour. It’s due to that very less surface area is available for adsorption and competition is also there with other metals.

Chapter 7: Conclusion and Recommendations

7.1 Conclusion

The use of peat for removal of heavy metals from contaminated water is achieving great attention because of its lower prices, effectiveness, and simplicity and it is abundant and easily available (Brown et al., 2000). The process of metal binding by peat is not still clear (Omar et al., 2006). Different results have been reported by different authors. But the different material used, metals studied and methodology have made it difficult to compare their results. However surface adsorption, ion-exchange, chemisorption, complexation and adsorption complexation are considered main processes for metal removal by peat. Sorption capacity depends upon the composition of water treated. The occurrence of different metals in solution can cause competition for adsorption sites present on surface of adsorbent (Brown et al., 2000).

Batch experiments showed that peat proved as very good adsorbent for uranium, molybdenum and nickel but not for sulphur and arsenic. Peat has efficient adsorption capacity and can be used to remove uranium, molybdenum and nickel from water. 99 percent removal rate of these metals was achieved by using peat as adsorbent. Thus peat can be used as cost-effective and efficient adsorbent for metal ions.

The adsorption rate was influenced by adsorbent dosage, contact time and initial metal concentration in solution. Uranium, nickel and molybdenum were adsorbed rapidly when higher doses of adsorbent were used irrespective to initial concentrations of metal ions in solution. Contact time became important when initial concentrations of metal ions were increased and adsorbent dose was decreased. At higher adsorbent dose, adsorption percent increased rapidly and became slow down with time. At higher concentration of adsorbent dose, contact time was less important as compared to lower concentration of adsorbent dose.

Uranium was our most concerned metal. Pit water concentration of uranium, 0.18mg/L and worst case contaminated water concentration of uranium 2 mg/L and 2.2 mg/L were removed by 99 percent by using 10 g/L peat as adsorbent and providing enough time of contact of 24 hours. In both cases adsorption rate was different; it was 92 percent in pit water and 85 percent in contaminated water. This shows that by increasing the initial concentration of metal ions, more time is required for removal but adsorption capacity of adsorbent also increases. At peat concentration of 4mg/L, its adsorption capacity in pit water was 0.0178 mg/g while in contaminated water it increases to 0.198 mg/g. By increasing peat concentration to 20g/L and 100 g/L more than 98 percent removal rate was achieved in first hour.

The drawback of using peat is the leaching of sulphur and arsenic in water.

7.2 Comparison with other studies

The removal of uranium has been reported by some other authors. (Omar et al., 2006) concluded that under optimized condition, the removal rate of uranium onto peat moss can be very efficient and can go up to 99 percent. (Bordelet et al., 2013) achieved 90 percent of removal rate of under optimized conditions. (Humelnicu et al., 2010) reported that adsorption rate of uranium by peat increases by increasing contact time, peat dosage, and initial uranium metal ions in solution.

7.3 Recommendations for NPRA

100 g/L and 20 g/L looked very high dose to remove the desired concentrations because with 10g/L 99 % removal efficiency was achieved. So it seems that 10 g/L of peat looks good enough to remove concentrations of uranium in pit water and in worst-case contaminated water by alum shale. By lowering dose to 4 g/L, still 90 percent removal rate was achieved in 24 hours in both cases. So the peat doses of between 4 to 10 gram/L can be used to remove uranium leaching out from uranium in worst case. Peat dose lower than 2 g/L and 1 g/L are too low to remove desired concentration of uranium.

7.4 Recommendations for further studies

Although this study reveals satisfactory results about the removal of uranium and other metals leaching out from uranium, this study can be enhanced with more dedication in terms of time and funds.

There were some gaps in this study, which can be filled up with further studies. During this study, only two time intervals were decided for sampling due to laboratory working schedule. As shown by results, with higher adsorbent dosages, nearly 99 percent of adsorption rate was achieved in first hour which shows that increasing time to 24 hours was of no use with higher adsorbent dosages. In further studies higher initial uranium concentrations can be used and testing time intervals can be reduced to 1h, 2h 3h, 4h, 8h, 12h and 24h to find out the exact equilibrium time and to have better idea about effect of contact time.

There was no specific information available about the constituents of peat that was used. Constituent of peat can be determined to know its exact composition to have better idea on adsorption.

8. Refrences

Abas, S. N. A., Ismail, M. H. S., Kamal, M. L., Izhar, S., 2013. Adsorption process of heavy metals by low-cost adsorbent: A review, World Applied Sciences Journal 28 (11): 1518-1530.

Ames, L. L, McGarrah, J. E., Walker, B. A., Salter, P. F., 1982. Sorption of uranium and cesium by Hanford basalts and associated secondary smectite. Rockwell international Corp., Richland, WA (USA). Rockwell Handford opearations.

Ansoborlo, E, Lebaron-jacobs, L.O., 2015. Uranium in drinking- water: A unique case of guideline value increases and discrepancies between chemical and radiochemical guidelines. Environment international 77, 1-4.

Appelo, C.A.J., and Postma, D., 2005. Geochemistry, groundwater and pollution, 2nd edition.

ASDR, Agency for toxic substances and disease registry, Toxicological profile for radium., 1990. U.S public health service in collaboration with U.S. environmental protection agency.

ASDR, Agency for toxic substances and disease registry, Toxicological profile for radon., 2012. U.S. Department of health and human services. Public Health service.

Babel, S., Kurniawan, T. A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials B97. 219–243.

Bailey, S. E., Olin, T. J., Bricka, M., Adrian, D. D., 1999. A review of potentially low-cost sorbents for heavy metals. Wat. Res. Vol 33, No, 11, pp. 2469-2479.

Batsala, M., Baburao, C., Sakala, B., Nama, S., Domatoti, S., 2012. Inductively coupled plasma mass spectrometry (ICP-MS). International journal of research in pharmacy and chemistry.

Bachmaf, S., Merkel, B, J., 2011 Sorption of uranium (VI) at the clay mineral-water interface. Environ Earth Sci, 63.925-934. DOI 10.1007/s 12665-010-0761-6.

Bazilio, A., Weinrich J., 2012. Inductively coupled plasma-mass spectrometry (ICP-MS).

Bleise, A., Danesi, P. R., Burkart. W., 2003. Properties, use and health effects of depleted uranium (DU): a general review. Journal of Environmental Radioactivity 64, 93-112.

Borovec, Z., Kribek, B., Tolar, V., 1979. Sorption of uranyl by humic acids. Chemical geology, 27, 39-46.

Bordelet, G., Beaucaire, C., Phrommavanh, V., Descostes, M., 2013. Sorption properties of peat for U(VI) and ^{226} Ra in U mining areas. Procedia earth and planetary sciences 7, 85-88.

Bourdon, B., Henderson G.M., Lundstron C.C., Turner S.P., 2003. Reviews in mineralogy and geochemistry. Volume 52. Uranium-series geochemistry.

Brown, P. A., Gill, S. A., Allen, S. J., 2000. Metal removal from wastewater using peat. Wat. Res. Vol. 34, No. 16, pp. 3907-3916,

Bulgariu, L., Ratoi, M., Bulgariu, D., Macoveanu, M., 2009. Adsorption potential of mercury (II) from aqueous solutions onto Romanian peat moss. Juurnal of environmental science and health, Part A: toxic / Hazardous substances and environmental engineering, 44:7, 700-706.

Chen, X.H, Gosset, T., Thevenot, D. R., 1990. Batch copper ion binding and exchange properties of peat. Water Res. Vol.24, No 12, pp. 1463-1771.

Christl, I., Milne, C. J., Kinniburgh, D. G., Kretzschmar, R., 2001. Relating ion bibding by fulvic and humic acids to chemical composition and molecular size. 2 metal binding. Environ.Sci. Technol, 35, 2512-2517.

Chisholm-Brause, C., Conradson, S, D,, Buscher, C. T., Eller, P. G., Morris, D. E ., 1994. Speciation of uranyl sorbed at multiple binding sites on montmorillonite. Geochimica et cosmochimica acta Vol, 58, No, 17, pp 3623-3623.

Craft, E, S, Abu-Qare, A, W., Flaherty, M, M., Garofolo, M, C,, Rincavage, H. L., Abou-Donia, M. B., 2004. Depleted and natural uranium: Chemistry and toxicological effects. Journal of Toxicology and Environmental Health, Part B, 7:297–317.

Couillard, D., 1994. The use of peat in wastewater treatment, Review. Wat. Res. Vol.28, No, 6, pp.1261-1274.

Cothern, C. R., Rebers, P.A., 1990. Radon, Radium and Uranium in drinking water.

Daigle, P., 2010. A summary of the environmental impacts of roads, management responses, and research gaps: A literature review. BC Journal of Ecosystems and Management. BC journal of ecosystems and management.

Delicato, B. A.,1996. Physical-chemical properties and sorption characteristics of peat. A phd thesis.

Desta, M.B., 2013. Batch sorption experiments: Langmuir and freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (Eragrostis tef) agricultural waste. Journal of thermodynamics, article ID 375830.

Dingman, S.L., 2002. Physical hydrology. Second edition.

Dupay, N., Douay, F., 2001. Infrared and chemometrics study of the interaction between heavy metals and organic matter in soils. Spectrochimica Acta part A 57, 1037-1047

Environmental protection agency., 1999. Understanding variation in partition coefficient , Kd, values. Volume II, Review of geochemistry and available kd values for cadmium, cesium, chromium, Lead, Plutonium, Radon, Strontium, Tritium (^{3}H), and Uranium.

Environmental fact sheet., 2007. New Hampshire department of Environmental services. Accessed at 21-03-2015. Available at : http://des.nh.gov/organization/commissioner/pip/factsheets/ard/documents/ard-ehp-22.pdf.

Falk, H., Lavergren, U., Bergback, B., 2006. Metal mobility in alum shale from Oland, Sweden. Journal of geochemical exploration 90, 157-165.

Focazio, M. J, Szabo, Z,, Kraemer, T, F., Mullin, A. H., Barringer, T. H., Depaul, V, T., 1998. USGS, Occurrence of selected radionuclides in ground water used for drinking water in the United States: A reconnaissance survey. Prepared in cooperation with the U.S. environmental protection agency.

Frondel C., 1907. Systematic mineralogy of uranium and thorium. Washington, U.S. Govt. Print.off., 1958.

Giammar, D., 2001. Geochemistry of uranium at mineral-water interfaces: rates of sorption-desorption and dissolution-precipitation reactions. A phd Thesis. Accessed 15-04-2015. Available at: http://thesis.library.caltech.edu/1903/1/Giammar-Thesis.pdf.

Gosset, T., Trancart, J.L, Thevonot, D. R., 1986. Batch metal removal by peat, Kinetics and thermodynamics.

Grassi, M., Kaykioglu, G,, Belgiorno, V,, Lofrano, G., 2012. Chapter2, Removal of emerging contaminants from water and waste water by adsorption process. G. Lofrano (ed.), Emerging compounds removal from wastewater. SpringBriefs in Green Chemistry for Sustainability, DOI: 10.1007/978-94-007-3916-1_2.

Hanne, M. L. K., Fiksdal, L., 2010. Waterborne disease in Norway; emphasizing outbreaks in groundwater systems. Water science & technology.

Hakonson, T. E., Lane, L. J., Springer, E.P., 1992. Biotic and abiotic processes. Deserts as dumps ? The disposal of hazardous materials in arid ecosystems. Charles C. Reith and Bruce M. Thomson (eds.), Chapter 4,pp.101-146.

Ho, Y. S, Wase, D. A. J., Forster, C. F., 1995. Batch nickle removal from aqueous solution by sphagnum moss peat. Wat. Res. Vol. 29, No.5, pp.1327-1332.

Håvard, G., Ola, M. S., 2009. A compilation of previously published geochemical data on the lower Cambro-Silirian sedimentary sequence, including the alum shales in the Oslo region. Geological survey of Norway.

His, C.K. D., Langmuir, D., 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. Geochimica et cosmochimica acta Vol, 49. Pp, 1931-1941.

Ho, Y. S., Mckay, G., 1998. Sorption of dye from aqueous solution by peat. Chemical engineering journel 70, 115-124.

Holmberg, J. P., 2006. Competitive adsorption and displacement behavior of heavy metals on peat. A master thesis in applied environmental measurement techniques. Chalmers university of Technology.

Humelnicu, D., Bulgariu, L., Macoveanu, M., 2010. On the retention of uranyl and thorium ions from radioactive solution on peat moss. Journal of hazardous materials 174, 782-787.

Keith, L. S, Faroon, O. M, Fowler, B, A., 2007 Uranium.

Krupka, K. M., Serne, R. J., 2002. Geochemical factors affecting the behaviour of antimony, cobalt, europium, technetium, and uranium in vadose zone. Prepared for CH2M HILL Hanford group, Inc., and the U.S. department of energy.

Kollerud, P., Blaasaas, K., Ganerød, G., Daviknes, H, K., Aune, E., Claussen, B., 2014. Using geographic information systems for radon exposure assessment in dwellings in the Oslo region, Norway.

Liland, A., Strand. P., Amundsen, I., Natvig. H., Nilsen. M., Lystad. R., Frogg. K. E., 2012. Advances in NORM management in Norway and the application of ICRP'S 2007 recommendations.

Lindahl. I., 1983. Classification of uranium mineralization in Norway. Geological survey of Norway.

Melo, C. D. A., Oliveira, L. K. D., Goveia, D., Fraceto, L. F., Rosa, A. H., 2014. Enrichment of tropical peat with micronutrients for agricultural applications: evaluation of adsorption and desorption processes. J. Braz. Chem. Soc., Vol, 25, No.1,36-49.

Mahmoud, M.A., 2013. Removal of uranium (VI) from aqueous solution using low cost and eco-friendly adsorbent. J chem eng process technol 4: 169.doi 10.4172/2157-7048.1000169.

Norwegian Public Roads Administration., 1997. Studies on Norwegian road tunnels, an analysis on traffic accidents and car fires in road tunnels. Road transport and safety department, Transport analysis division.

OECD guideline for the testing of chemicals. 2000. Adsorption-Desorption using a batch equilibrium method.

Omar, H. A, Aziz. M., Shakir, K., 2007. Adsorption of U(VI) from dilute aqueous solutions onto peat moss. Radiochim. Acta 95, 17–24, DOI 10.1524/ract.2007.95.1.17.

Porcelli, D., Swarzenski, P. W., 2003. The behavior of U- and Th-series nuclides in groundwater. Reviews in mineralogy and geochemistry.

Prikryl, J. D., Jain. A., Turner, D, R., Pabalan, R. T., 2001. Uranium ^{VI} sorption behaviour on silicate mineral mixtures. Journal of contaminant hydrology 47, 241-253.

Piwoni, M, D., Keeley, J. W., 1990. Groundwater issue. Basic concepts of contaminant sorption at hazardous waste sites. United States environmental protection agency. Office of research and development.

Piccolo, A., Stevenson, F. J., 1982. Infrared spectra of Cu^{2+}, Pb^{2+} andCa^{2+} complexes of soil humic substances. Geoderma, 27, 195-208.

Ringqvist, L., Holmgren, A., Oborn, I., 2002. Poorly humified peat as an adsorbent for metals in wastewater. Water Research 36, 2394–2404.

Ringqvist, L., Oborn,l., 2002. Copper and zinc adsorption onto poorly humified sphagnum and carex peat. Water Research 36, 2233-2242.

Safe Drinking water committee. 1983. Drinking water and health: Volume 5. Board on toxicology and Environmental Health Hazards. Commission on life Sciences. National Research Council.

Statens vegvesen, Norwat-Nordic Road Water. Road and Water pollution., 2011. A review and identification of research gaps, Environment assessment section. Report No 46.

Shanbhag, P.M., Choppin, G.R., 1981. Binding of uranyl by humic acid. J.inorg.nucl.Chem. Vol.43,43, No 12,pp 3369-3372.

Smethurst, M, A., Sundal, A. V., Strand, T., Bingen, B., 2008. Testing the performance of a recent radon-hazard evaluation in the municipality of Gran, eastern Norway. Geological survey of Norway (NGU).

Skeppstrom, K., Olofsson, B., 2007. Uranium and radon in groundwater. An overview of the problem. European Water 17/18: 51-62, 2007.

Swanson, V. E., 1961. Geology and geochemistry of uranium in marine black shales, a review. Uranium in carbonaceous rocks. Geological survey professional paper 356-C.
Sun, Q., Yang, L., 2002. The adsorption of basic dyes from aqueous solution on modified peat-resin particle. Water Research 37, 1535-1544.

Sparks, D. L. (1995). Environmental Soil Chemistry. San Diego, California, Academic Press, Inc.

Stadler E, Blanc A, Haldimann M, Dudler V., 2012. Occurance of uranium in Swiss drinking water. Chemosphere 86, 672-679.

Tanji, K,, Valoppi, L., 1989., groundwater contamination by trace elements. Agriculture, Ecosystems and environment, 26, 229-274. Elsvier Science publishers B.V., Amsterdam.

USGS., 2000. Naturally occurring radionuclides in the ground water of southeastern Pennsylvania.

Vikan, H., Meland, S., 2013. Purification practices of water runoff from construction of Norwegian tunnels – status and research gaps. S. Rauch et al. (eds.), urban environment, DOI 10.1007/978-94-007-7756-9_42.

Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A., Xu, N., 1994. Uranium (VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochimica et cosmochimica acta, vol. 58, No, 24, pp 5465-5478,

Walker, P., 1994. Airborne radon hazard mapping- løten, Hedmark County, Norway. Jounrnal of Geochemical exploration 90, 157-165.

Webb, P. A., 2003. Introduction to chemical adsorption analytical techniques and their applications to catalysis. MIC Technical publications.

Wolf, R. E., 2005. Research Chemist, USGS/Central Region/Crustal Imaging & Characterization Team. Accessed at 20-05-2015. Available at : **http://crustal.usgs.gov/laboratories/icpms/intro.html**.

World Health Oraganization ., 2012. Uranium in drinking water. Background document for development of WHO guidelines for drinking-water quality.

Yasemin, B., Zeki T., 2007. Removal of heavy metals from aqueous solution by sawdust adsorption. Journal of environmental sciences 19, 160-166.

Åkerblom, G., Mjones, L., Annanmaki, M., Strand. T., Ulbak, K., 2000. Naturally occurring radioactivity in the Nordic Countries- Recommendations. The radiation protection authorities in Denmark, Finland, Iceland, Norway and Sweden.

Appendices

Apendix A

Results from Control sample 2

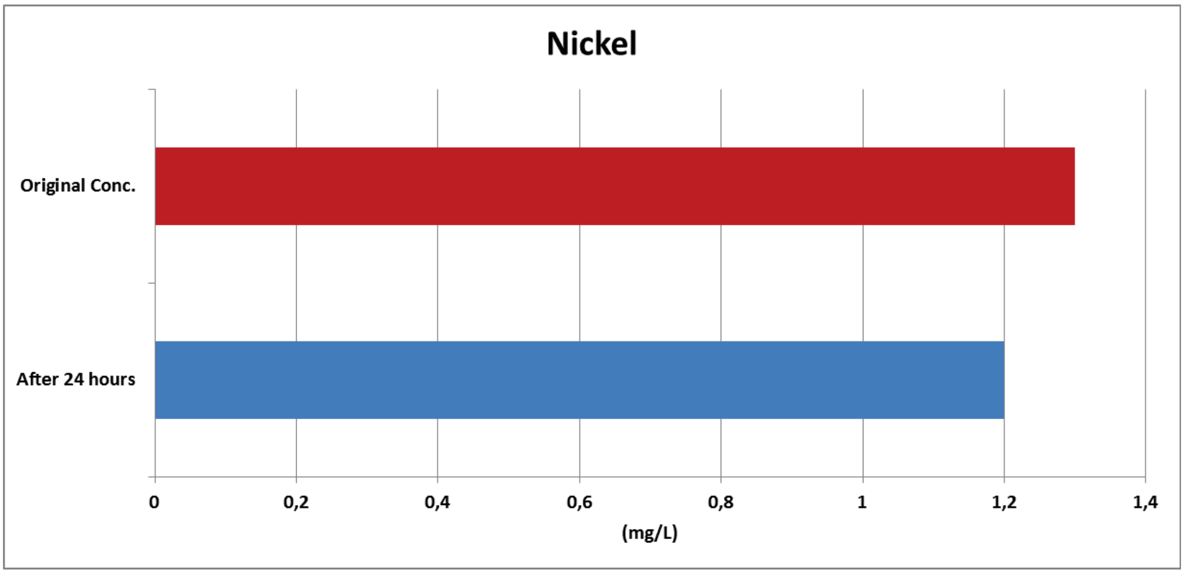


Figure A1: Sorption of Nickel to walls of container.

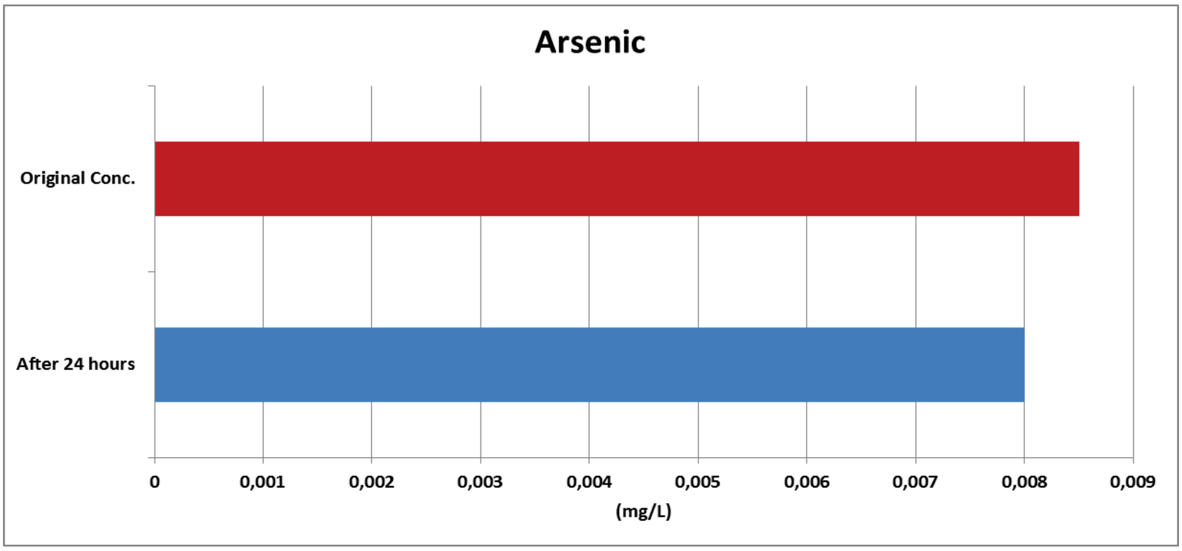


Figure A2: Sorption of Arsenic to walls of container.

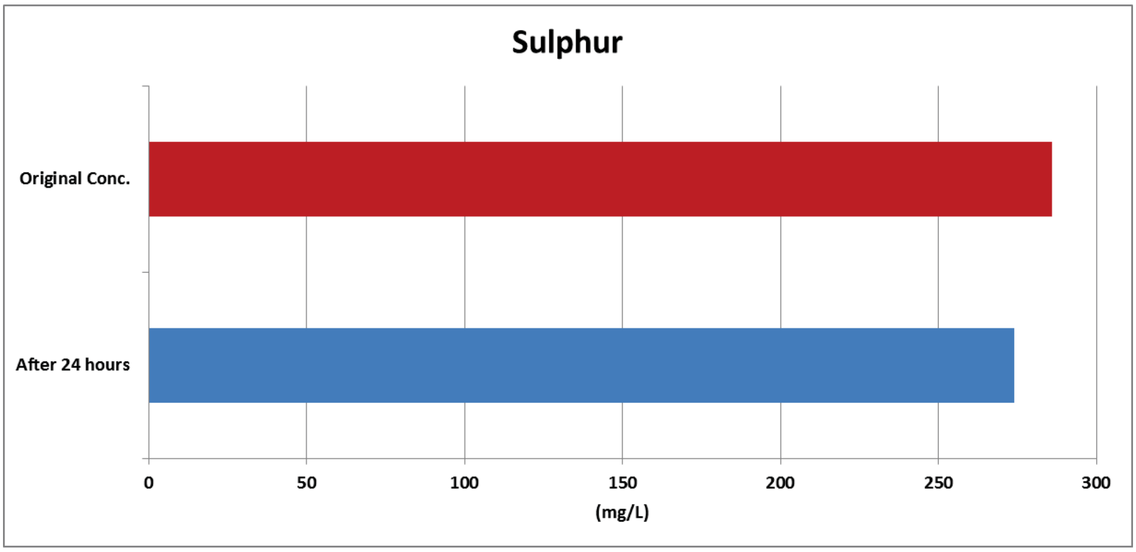


Figure A3: Sorption of sulphur to walls of container.

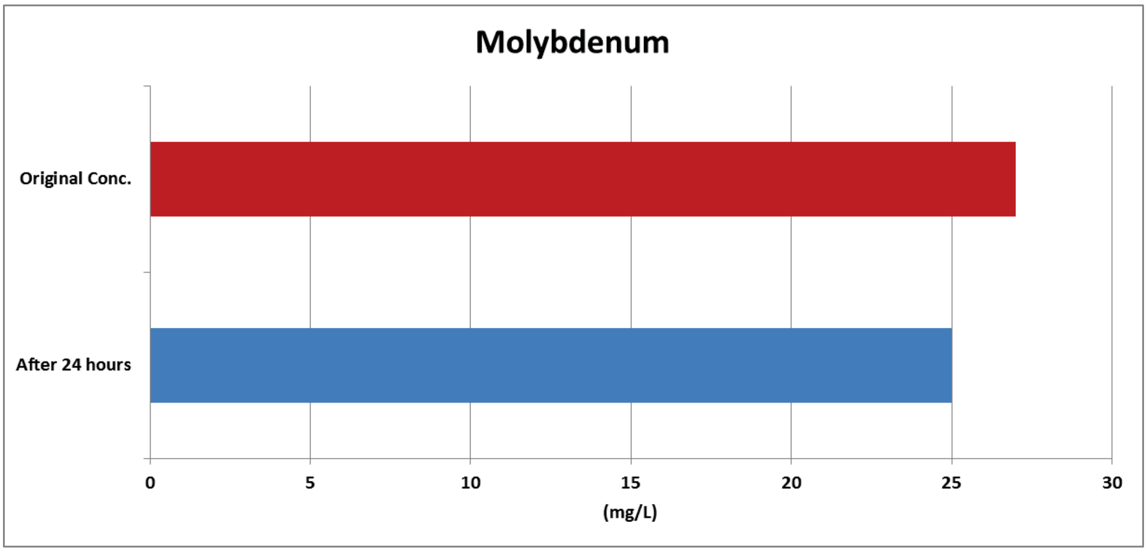


Figure A4: Sorption of molybdenum to walls of container.

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