



**KTH Land and Water
Resources Engineering**

CHITOSAN BIOPOLYMER AS AN ADSORBENT FOR DRINKING WATER TREATMENT

Investigation on Arsenic and Uranium

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SAMMANFATTNING

I många länder världen runt (även i Sverige) orsakar metallers toxicitet besvärliga vattenkvalitetsproblem och utgör ett hot mot människors hälsa. Bland de toxiska metaller som finns i svenska vatten utgör arsenik och uran i dricksvatten allvarliga hälsorisker vid långvarig exposition då de kan orsaka cancer och neurologiska problem. Flertalet brunnar är installerade i kristallint berg och sedimentära bergarter och vattnet kommer vanligen från sprickor i berggrunden. Hanteringen av sådant vatten kan kräva reduktion av expositionen för arsenik- och uraninnehåll genom förbättrade processer och teknologier. Detta är ett angeläget problem som kräver en säker, pålitlig och ekovänlig teknologi att tillämpas innan vattnet distribueras. En rad olika behandlingssystem är tillgängliga men många av dem är inte lämpliga beroende på deras höga kostnad, den komplicerade tillämpningen och problem med hanteringen av restprodukter. I denna studie has biopolymeren chitosan, den näst vanligaste polymeren efter cellulosa, konstaterats vara en möjlig adsorbent för att avlägsna arsenik(V) och uran(VI) från vatten. Karakterisering av adsorbenten har också genomförts genom XRD, FTIR, SEM, UV och strålning i synligt ljus samt TGA/DTA undersökningar. Batch-tester i bänskala har genomförts med användning av chitosan (DDA-85%) som adsorbent för att bestämma dess förmåga att avlägsna arsenik(V) och uran(VI) genom att variera fyra parametrar, nämligen kontaktid, pH, dos av chitosan och halt av föroreningen. Adsorptionsdata vid optimala förhållanden bestämdes genom tillämpning av Langmuir, Freundlich och Dubinin-Radushkhevic (D-R) isotermer. Vidare tillämpades Lagergrens pseudo-first-order och pseudo-second-order kinetiska modell för att undersöka adsorptionsprocessen. Karakteriseringen av materialet visade förefintligheten av effektiva amino- (N-H), hydroxyl- (O-H) samt karboxylgrupper (C=O) i chitosan-polysackariden och att det är lätt nedbrytbart. Preliminära resultat visar att reduktionen av arsenik(V) och uran(VI) var 100 respektive 97,45 % efter 300 minuters kontaktid med optimalt pH på 6,0 respektive 7,0. De optimala doserna av adsorbent och den initiala koncentrationen var 60 och 80 g/L och 100 och 250 µg/L. Adsorptions process beskrevs bäst av Freundlich-isotermen för arsenik(V) ($R^2 = 0,9933$) och med Langmuir-isotermen för uran(VI) ($R^2 = 0,9858$) jämfört med andra isotermer vilket var en viktig indikation på en homogen monolager-adsorption. För både arsenik(V) och uran(VI) beskrev pseudo-second order adsorptionen bättre än pseudo-first-order. Second-order kinetiska regressionskoefficienten (R^2) var 0,9959 och 0,9872 respektive. De ovanstående resultaten visar sammanfattningsvis att chitosan (DDA-85%) kan användas som en billig, pålitlig och miljövänlig behandlingsmetod av vatten för arsenik(V) och uran(VI).

Nyckelord: Chitosan, Biopolymer, Karakterisering, Bionedbrytbar, arsenik(V), uran(VI), Adsorption, Isoterm, Kinetisk modell

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LIST OF APPENDED PAPERS

Paper I

M. Annaduzzaman, P. Bhattacharya, M. Ersoz, Z. Lazarova, P.C. Deshpande (2015). Evaluation and optimization of chitosan biopolymer as an adsorbent for arsenic(V) in drinking water treatment (Manuscript).

Paper II

M. Annaduzzaman, P. Bhattacharya, P.C. Deshpande, M. Ersoz, Z. Lazarova (2015). Chitosan biopolymer: a treatment option for uranium(VI) removal from drinking water (Manuscript)

LIST OF NOT APPENDED PAPERS

- I. Annaduzzaman, M., Bhattacharya, Prosun; Ersoz, Mustafa and Lazarova, Zdravka. Removal of arsenic from contaminated water using chitosan biopolymer as an adsorbent derived from shrimp or crab shells Vol. 337-10, GSA Annual Meeting and Exposition (GSA2014), Vancouver, BC, Canada (19-22 October), 2014.
- II. Annaduzzaman, M., Bhattacharya, Prosun; Ersoz, Mustafa and Lazarova, Zdravka. “Arsenate removal using chitosan biopolymers: A study on sorption behavior and kinetics through batch experimental studies.” 5th International Congress of Arsenic in the Environment (As2014), Buenos Aires, Argentina (11-16 May), 2014.

ABSTRACT

In many countries over the world (including Sweden), metal toxicity in freshwater resources causes a severe drinking water quality problem and poses a threat to the environment and human health. Among the different toxic metals in the water resources of Sweden, arsenic and uranium are the biggest threats to health. These elements, over long time consumption, may even lead to cancer and/or neurological disorder. Most of the wells are installed in crystalline and sedimentary bedrock and the received water comes from water bearing fractures in the bedrock. The handling of such water is an issue and there is a need to reduce the arsenic and uranium exposure by improving processes and technologies. It is a very serious problem demanding a safe, sustainable and eco-friendly arsenic and uranium removal technology prior to drinking water supply. Different treatment systems are available, but many of them are not suitable due to their high cost, operation complexity and waste management issues. Through this study, chitosan biopolymer the second largest abundant polysaccharide on earth after cellulose, was verified as a potential adsorbent for arsenic(V) and uranium(VI) removal from water solution. Adsorbent characterizations were also conducted by XRD, FTIR, SEM, UV-visible spectrum and TGA/DTA investigations. Bench-scale batch experiments were conducted using chitosan biopolymer (DDA-85%) as an adsorbent to determine the arsenic(V) and uranium(VI) removal efficiency, by allowing four important effective parameters e.g. chitosan dosages, pH, contact time and contaminant concentration. The adsorption data at optimum conditions were fitted with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm and Lagergren pseudo-first-order and pseudo-second-order kinetic model to investigate the adsorption process. The characterization of materials assured the presence of effective amino, hydroxyl, and carboxyl groups of chitosan. Another advantage is that the materials are bio-degradable. The results show that the arsenic(V) and uranium(VI) removal efficiency was 100% and 97.45% after 300 minutes with optimum pH of 6.0 and 7.0 respectively. The optimum adsorbent dosages and initial concentration were 60 and 80g/L and 100 and 250 µg/L respectively. The adsorption process was suitably described by Freundlich isotherm ($R^2 = 0.9933$) and Langmuir isotherm ($R^2 = 0.9858$) correspondingly for arsenic(V) uranium(VI) compared to other isotherms. This is an important indicator of homogeneous monolayer adsorption of metals. For both of arsenic(V) and uranium(VI), pseudo-second-order explained the adsorption kinetics better than pseudo-first-order and the second-order kinetic regression coefficient (R^2) were 0.9959 and 0.9672 correspondingly. Connecting to the above mentioned results, it can be summed up that the chitosan biopolymer (DDA 85%) can be used as an inexpensive, sustainable and environment-friendly treatment option for arsenic(V) and uranium(VI) contaminated drinking water.

Key words: Chitosan Biopolymer, Characterization, Biodegradable, Arsenic(V), Uranium (VI), Adsorption, Isotherm, Kinetic model

1. INTRODUCTION

1.1. Background

The United Nations (UN) has stated that safe drinking water accessibility is a prime human right. Only a small portion of accessible water in the earth crust can be considered as potable, which can be accessible from either surface water or groundwater.

Unluckily, a number of organic and inorganic pollutants contaminate water by both natural and anthropogenic sources. As a result, safe drinking water has become limited (Rahman, 2009; Annaduzzaman, 2012). In many countries all over the world, groundwater is extracted for drinking purposes. About 2 billion people around the world rely on groundwater as their main

drinking water source (Buamah *et al.*, 2008). Compared to surface water sources, contamination of groundwater by anthropogenic waste is less prevalent. However, natural weathering of aquifer materials may release organic and inorganic contaminants in the aquifer system. Arsenic is an extremely poisonous element, occurs randomly in the earth's crust and causes contamination of drinking water in many countries, including (not restricted to) Argentina, Bangladesh, Bolivia, Canada, China, Ghana, India, Myanmar, Nepal, Nicaragua, Pakistan, Romania, United State of America (USA) and some parts of Europe including Hungary, Finland, Germany and also Sweden (Smedley and Kinniburgh, 2002; Bhattacharya *et al.*, 2007; Bhattacharya *et al.*, 2010; Löf, 2012 Annaduzzaman, 2012). According to the World Health Organization (WHO) report in 2001, approximately 130 million people worldwide were exposed to elevated levels of arsenic through drinking water. Long time consumption of arsenic contaminated drinking water may cause both carcinogenic and non-carcinogenic health disorders. It has been proven in the past that arsenic contaminated ($\geq 50 \mu\text{g/L}$) drinking water is prone to increase risks of skin lesions, lung and bladder cancer. Consumption of arsenic also leads to disturbance of the cardiovascular and nervous system functions and eventually leads to death (Boudda *et al.*, 2008). Besides arsenic, uranium is a radioactive element which poses significant health disorders including kidney failure. Drinking water contaminated with a high level of uranium gets much attention for its toxic and radioactive properties. Long term exposure to uranium may cause severe human health problems including renal failure (Löf, 2012), irreversible kidney damages, deficiency of calcium in the bones (Svensson *et al.*, 2005), and bone cancer (Suc & Ly, 2011). It has also been discovered that uranium can accumulate in the brain and cause symptoms of depression and agitation (Lestaevel *et al.*, 2005). Arsenic and uranium in drinking water are regulated world-wide including Sweden; but they need further optimized

treatment technologies for contaminated water sources. In Sweden, 1.2 million people depend on private wells where about 800 000 people have their own drilled wells (SGU, 2008). However, most of the well owners are not concerned about the risk of elevated concentrations of contaminants like arsenic, uranium and other metals (Karlsson, 2010). It was identified that the private wells exceeded the guideline value of arsenic ($10 \mu\text{g/L}$) in Västerbotten, Öland, Bålsta, and around Sollefteå (Löf, 2012). In Sweden, around 17% of the private drilled wells have elevated concentration of uranium; over $15 \mu\text{g/L}$ and 2% have uranium concentration beyond $100 \mu\text{g/L}$ (Löf, 2012). Most of the wells are installed in crystalline and sedimentary bedrock and the received water comes from water bearing fractures in the bedrock (Ek *et al.*, 2008). The management of such water is an issue and there is need to reduce the arsenic and uranium exposure by improving processes and technologies. It is a very serious problem demanding a suitable arsenic and uranium removal technology to protect human health.

Considering the significant human health impacts of elevated levels of arsenic and uranium in drinking water supplies, a number of methods and technologies are commonly applied to such water. Ion exchange, chemical precipitation, solvent extraction, membrane processes, adsorption, coagulation and flocculation are the most commonly used methods. However, application of these methods may not be economically or sensibly feasible. Generally, the adsorption process is very effective at low concentrations of the contaminants. Adsorption of contaminants (arsenic and uranium) onto different solids is essential from environmental, purification and hazardous waste product disposal point of view (Mellah *et al.*, 1992; Saleem *et al.*, 1992; Gavrilescu, 2004; Mellah *et al.*, 2005; Benavente, 2008). Many researchers, used a number of materials as adsorbents, such as activated charcoal (Kutahyali & Eral, 2004), Coir pith (Parab *et al.*, 2005), smectits (Chisholm-Brause *et al.*, 2004), olivine rock (El Aamrani

et al., 2002), kaolinite (Payne *et al.*, 2004), bentonite (Missana *et al.*, 2004), montmorillonite (Catalano & Brown, 2005), goethite (Missana *et al.*, 2003), polymeric materials (Zhang *et al.*, 2005) and biomass (Kalin *et al.*, 2004). The two most important factors that determine adsorption are efficiency and treatment cost. Recently, natural products have been proven as novel and alternative adsorbent materials for heavy metal and radioactive contaminants (Bailey, 1999).

Chitin and its derivative form chitosan are two biopolymers that come from exoskeletons of shellfish like crabs and shrimps, and have the ability to sorb a great range of heavy metals and radionuclides (Guibal, 2004; Muzzarelli, 2011). The metal sorption capacity of chitosan depends on its crystallinity, affinity for water and deacetylation degree (amino group content). The sorption process likewise is governed by the physicochemical features of the aqueous solutions (e.g. pH, temperature, pE metallic ion concentration and the species in the solution) (Guibal, 2004; Benavente, 2008). It is observed that the removal of arsenic(V) is greater than the arsenic(III) onto chitosan biopolymer depending on the aqueous solution pH, redox potential and temperature (Boddu *et al.*, 2007; Dambies *et al.*, 2002).

The design of chitosan biopolymer filter for metal ions removal from contaminated aqueous solutions requires equilibrium and kinetic data for the system. A number of studies have been conducted and confirmed that chitosan biopolymer possesses a significant metal ions sorption capacity with favorable kinetics. Very few reports have been published on removal of arsenic and uranium from wastewater (not drinking water) with modified and unmodified chitosan derivatives. Moreover, treatment of drinking water contaminated with arsenic and uranium is still in research phase. Therefore, there is no case study as of now for large scale application of chitosan derivatives and its influence on the removal of drinking water contaminants. It is necessary to investigate the feasibility of chitosan biopolymer

as an adsorbent for mass scale drinking water treatment application.

1.2. Objectives

The objectives of the present study has been to test the sorption performances of chitosan biopolymer as sorbent media for arsenic and uranium removal on laboratory scale as a baseline of technical feasibility

- Characterize the chitosan biopolymer adsorbent by XRD, FTIR, SEM, UV and TGA/DTA techniques
- Investigate the sorption efficacy of the adsorbent media considering the influence of water quality parameters (contact time, pH, adsorbent dose, initial ion concentration)
- Evaluate arsenic and uranium sorption isotherms (Langmuir, Freundlich and Dubinin-Radushkevich (D-R)) and Lagergren pseudo-first-order and pseudo-second-order kinetics models
- Design support criteria for selection and design of an effective performing sorbent media for arsenic and uranium in the drinking water sources

2. ARSENIC AND URANIUM IN NATURAL WATER

2.1. Arsenic

Arsenic is a ubiquitous element present in the environment and found at different concentration levels, in natural water it varies from less than 0.5 µg/L to more than 5000 µg/L. According to the WHO guideline value, drinking water is safe when the concentration level is below 10 µg/L. Groundwater with high level of arsenic is rarely found. However in high arsenic regions, up to 90% of the drinking water wells show arsenic concentration levels exceeding 50 µg/L. This high level of arsenic occurs mainly in two types of groundwater environment; firstly, in strongly reduced aquifers and secondly, inland and in closed basins in arid and semi-arid areas. Both of the environments formed by geologically young sediments and flat low-lying areas and have slow groundwater flow and sluggish turn over (Smedley *et al.*, 2002; Westergren, 2006; Bhattacharya *et al.*, 2007). Arsenic could also be found in the areas with

mining activity, geothermal activity and also in the area of sulphide oxidation mineral activity.

2.1.1. Aqueous speciation and mobility

In natural waters, arsenic can be found in different oxidation states (-3, 0, +3 and +5). However it is mostly found as trivalent arsenite [As(III)]. The different oxidation states fully depend on redox conditions and pH of the natural waters.

According to Figure 1, under the different oxidation conditions, H_3AsO_4^- and $\text{H}_2\text{AsO}_3^{2-}$ are the dominating arsenic species at pH under 6.9 and at higher than 6.9 correspondingly. In extremely acidic and alkaline conditions arsenic may be present in the form of H_3AsO_4 and AsO_4^{3-} respectively. In the phase of reducing condition ($\text{pH} < 9.2$) the dominating species is the uncharged arsenite (H_3AsO_3^0) (Westergren, 2006).

Among other heavy metalloids and oxyanion elements (Se, Sb, Mo, Cr, and U), arsenic poses critical sensitivity to mobilization with groundwater at pH level of 6.5 to 8.5 by reducing and oxidizing conditions (Smedley

et al., 2002). Toxic metals are generally available as cations in the solution (e.g. Pb^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+}) and these are insoluble with increase in pH. The mobility of metal cations in most groundwater is severely limited by precipitation and co-precipitation at nearly neutral pH. Depending on other certain conditions these ions can persist in water at relatively high concentrations even at neutral pH, and therefore these oxyanions (Se, Sb, Mo, Cr, and U) are the most common trace elements in groundwater. Out of these oxyanions, arsenic is likely to be a more problematic contaminant since it has high mobility over wide range of reducing and oxidizing conditions (Smedley *et al.*, 2002). Among different mechanisms, there are two different triggers that have been identified as responsible for arsenic release in groundwater:

- $\text{pH} > 8.5$ act as a catalyst for high evaporation and weathering rates in arid and semi-arid environments and causes desorption of arsenic from mineral composition (especially from Fe-oxides) and prevents arsenic adsorption onto mineral surfaces.

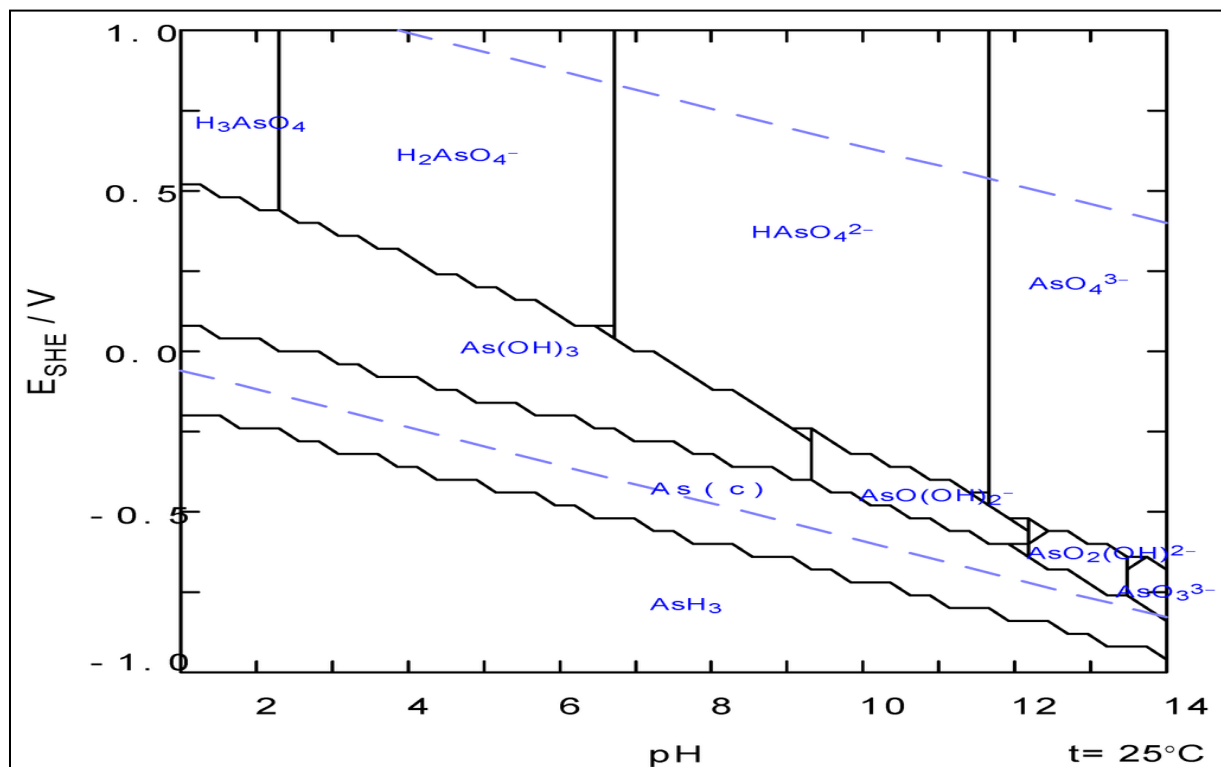


Figure 1. *pe-pH diagram for the As speciation in aqueous system As-O₂-H₂O at 25°C with 1 bar total pressure (Smedley *et al.*, 2002).*

- Extremely reducing condition even at neutral pH, helps to arsenic desorption from mineral oxides including reductive dissolution of Fe and Mn oxides.

In high arsenic regions, there is a strong correlation among arsenic(III), iron(II) and low sulphate concentrations. In some places, large concentration of biocarbonate, silicate, phosphate and some organic material may enhance the arsenic desorption due to competition for adsorption sites (Westergren, 2006).

2.1.2. Toxicity

Arsenic toxicity highly depends on the species of arsenic in water. Inorganic arsenic compounds, As(III) is similarly toxic as arsenic(V) for human health (Castrode Esparza, 2006). Pontius *et al.* (1994) scale up the arsenic species according to their toxicity in the following order:

Inorganic As(III) > Organic As(III) ≥ Inorganic As(V) > Organic(V) > Elemental As

Metal toxicity to human health is rather limited; however arsenite is about 60 times more toxic to human health than other forms of arsenic (oxidized) (Jain and Ali, 2000). The organic arsenic compounds are less toxic (almost 100 times) compared to inorganic arsenic. Inorganic arsenic methylation has been explained as valuable detoxification process in the human health due to reduction affinity of the compounds in tissues (Vahter and Marafante 1988).

2.2. Uranium

Uranium is a naturally occurring chemical element available in the environment and found at different concentration levels in natural water and it may vary from 0.5 µg/l to more than 400 µg/l. According to the WHO guideline value, drinking water is safe when the concentration level is below 15 µg/l. Groundwater with high level of uranium is found in the bedrock (silicate rich), such as granite, pegmatite and syenite. In common practice, wells are seldom located in the alum shale since the water quality is generally low (Birke *et al.*, 2010; Löf 2012). The most common uranium bearing minerals are uranite, autunite, pitchblende, coffenite

and uranophane, commonly these are comparatively rare and restricted to uranium mineralized zones. Approximately 5% of all these minerals contain uranium (Smedley *et al.*, 2006). Uranium minerals are soluble in the pH range of 5-8.5 (during adsorption of mineral is highest). Uranium can be concentrated in cracks due to hot water circulation through the pluton and dissolves, finally precipitates along the cracks with other elements (Marshak, 2005).

2.2.1. Aqueous speciation and mobility

Uranium in groundwater originates from weathering of bedrock and from anthropogenic sources (uranium mining) (Prat *et al.*, 2009). The dominating uranium species in groundwater are influenced by several parameters including pH, redox state, low adsorption capacity and presence of uranium ores (Bucher *et al.*, 2008; Birke *et al.*, 2010). The most common uranium bearing minerals (uraninite) produces equilibrium and limits the uranium concentration in groundwater to 0.06 µg/L in anoxic conditions (Smedley *et al.*, 2006). Three different uranium oxidation states are common in groundwater depending on redox conditions uranium(IV), uranium(V), and uranium(VI). Practically, uranium becomes immobile in reducing waters due to insolubility of uraninite and coffenite at normal groundwater pH 4-8 (Langmuir, 1978; Smedley *et al.*, 2006; Löf, 2012). Redox state, generally define by p_e , where low p_e is an indication of reducing conditions and elevated p_e is used for oxidizing conditions. Figure 2 gives the indication of different uranium species under various pH and redox conditions.

The most commonly available uranium ion is the hexavalent and usually available as UO_2^{2+} to form complexes with ligands and organic matter in natural aqueous media. Carbonate is a significant uranium ligands in natural water system and form carbonate complexes with the greater solubility of uranium(VI) ions. The carbonate complexes formation can change the uranium(VI) stability fields and these complexes may be available in alkaline conditions and higher carbonate concentrations in reducing conditions (Ivanovich and Harmon, 1982; Allard, 1983;

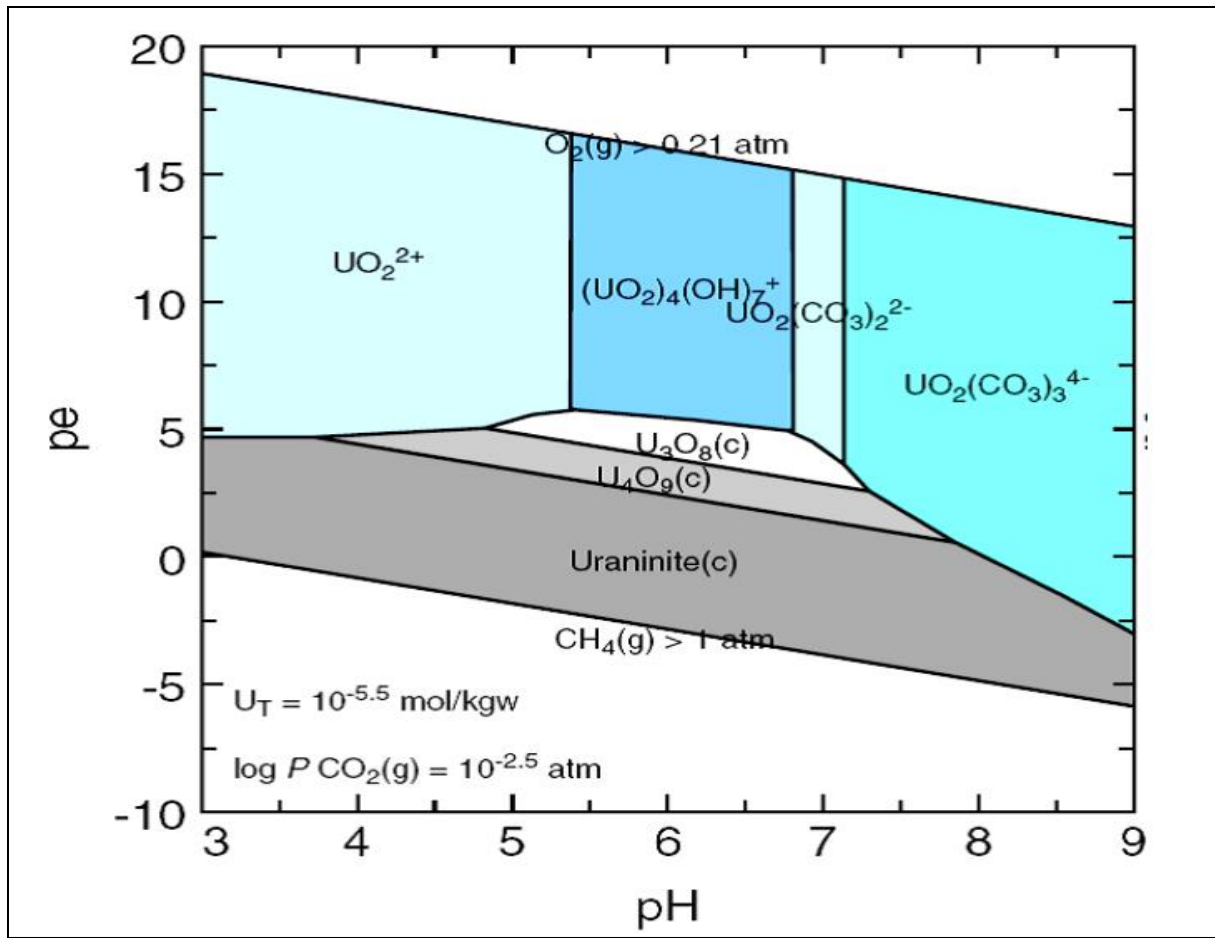


Figure 2. *pe* vs. *pH* plots for uranium at 10°C, *p*CO₂ = 10^{-2.5}atm. (Smedley *et al.*, 2006).

Ervanne, 2004). According to Figure 3, under the different oxidation conditions, the uranium complexes are highly dependent on pH of aqueous solution and the ion compositions. In uranium rich water, uranyl-hydroxides are predominant at all pH ranges and with the basis of uranium concentration, polynuclear species will be predominating (Langmuir, 1978; Vaaramaa, 2003; Grenthe *et al.*, 2004; Löf, 2012). At pH>10.5 uranyl-hydroxide (positively charged) will dominate the system (Swedish Health Authorities, 2006).

2.2.2. Toxicity

Uranium toxicity is not as so severe as arsenic for human health and according to the WHO, radioactive properties of uranium are not a major concern for human health while the chemical toxicity is. Many of the studies have been carried out on exposure of uranium and its effect on rats (Kurtion *et al.*, 2002; Svensson *et al.*, 2005; Prat *et al.*,

2009). According to these studies, uranium is nephrotoxic and has harmful effects on kidneys. Uranium contaminated drinking water (giving exposure leading to 10-25 mg/body weight) that's comes from drilled wells can cause acute renal failure and irreversible kidney damages (Kurtio *et al.*, 2002). Exposure to low dosages of uranium (0.004-8.5 µg/kg body weight) causes the increase of uranium in urine and long term exposure to uranium will interfere with the functionality of kidneys (Zamora *et al.*, 1998; Löf, 2012). When the uranium reaches to blood stream, it forms complexes with bicarbonate, proteins and red blood cells. Conversely, 66% of the uranium (reaches to blood cells) comes out from the body through the urine and the remaining fraction adsorbed by kidney (12-15%), bones (10-15%) and soft tissue (Svensson *et al.*, 2005; Prat *et al.*, 2009).

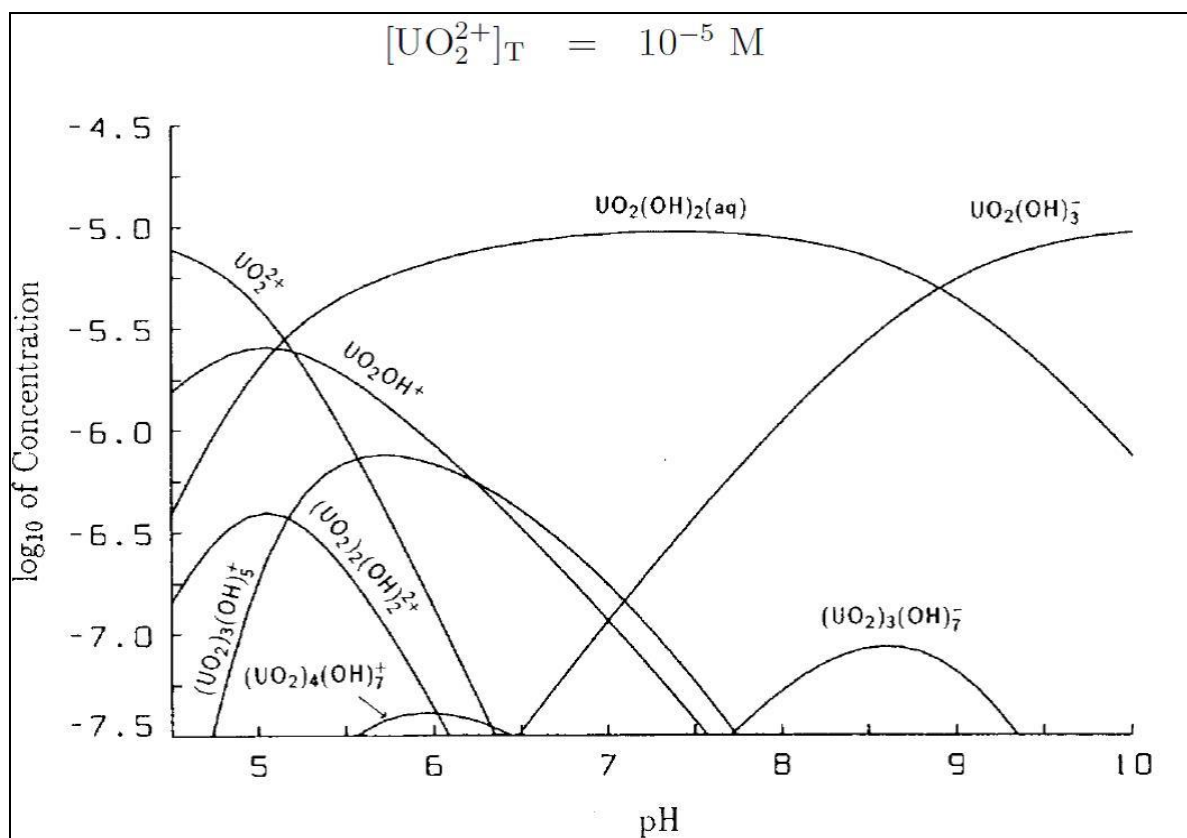


Figure 3: Species distribution of the dioxouranium(VI) hydroxide system at 25°C in the range $4.5 < \text{pH} < 10$. The precipitation of solid phases is suppressed (Grenthe et al., 2004).

2.3. Arsenic and uranium removal methods

The chemistry of arsenic and uranium (As(V) and U(VI)) is different compare to other toxic metals, which are usually found as cations in drinking water. Thus the conventional precipitation removal option is not sufficient. Along with this, the treatment and management of such water is an issue to reduce both the arsenic(V) and uranium(VI) exposure by improving processes and technologies. It is an essential problem demanding a suitable removal technology for arsenic(V) and uranium(VI) to protect human health.

2.4. Adsorption

Adsorption is a process where adsorbates (contaminant chemical elements in aqueous media) are attracted by bonding (chemical or physical) to the solid surface (adsorbent) during contact to each other. Compared to different chemical sorption methods, adsorption process depends on experimental data

of the solid-liquid interaction for the system design.

The important characteristics of the adsorbent materials are a high porosity along with irregular geometries to deliver a large surface area. Adsorption characteristics are gradually more utilized for separation or purification of different contaminants. The important characteristics of adsorbents are the availability of materials and low cost (Ruthven, 1984; Benavente, 2008).

It is important to understand the adsorption process in the design of adsorption equipment. The knowledge of the equilibrium isotherm and kinetics are two important properties to understand the mechanism, in which adsorption isotherms determine the adsorption capacity and the kinetics used to determine the adsorption velocity.

2.5. Adsorption isotherm

Adsorption isotherms are used to describe the solute adsorption by the adsorbent at a given temperature, and also to evaluate the applicability of the adsorption process as a

unit operation to explain the physicochemical features of the adsorbent (Vadivelan and Kumar, 2005; Wang and Chen, 2009). The most repeatedly used isotherms for adsorption studies are Langmuir, Freundlich and Dubinin-Radushkhevic (D-R) isotherms due to its simplicity in applications and in order to evaluate the applicability of different adsorption processes.

2.5.1. Langmuir isotherm

The Langmuir isotherm model was first used to describe the adsorption of gas molecules on metal surfaces (Chegrouche *et al.*, 1997; Chegrouche *et al.*, 2009; Gok & Aytas, 2009). This model has also been successfully proven for many other sorption processes. Langmuir isotherm depends on several assumptions, which includes (Coulson and Richardson, 2002; Benavente, 2008):

- The energy is equally distributed over the adsorbent surface
- Contaminant molecules gets adsorbed on specific sites and will not migrate over the surface
- The adsorption will take place in the monolayer surface of the adsorbent material and
- Adsorbent molecules will not interact with each other.

The Langmuir isotherm's shape is a progressively positive curve which flattens to a constant value. This method has been widely used to describe the adsorption mechanism of the adsorbent materials. The Langmuir isotherm model can be given by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \dots \dots \dots (1)$$

In which q_e is the adsorption capacity of the chitosan biopolymer, q_m is equal to the monolayer adsorption capacity ($\mu\text{g/g}$), K_L is Langmuir equilibrium sorption constant ($\text{L}/\mu\text{g}$) and C_e ($\mu\text{g/L}$) is equilibrium contaminant concentration in solution.

2.5.2. Freundlich isotherm

The Freundlich isotherm model is one of the oldest used pragmatic equations to describe

adsorption equilibrium data, which is used to describe a non-linear sorption process. This is also used to explain the initial surface adsorption tracked by condensation effect which occurs due to strong solute-solute interactions in the system. To explain the non-ideal adsorption on heterogeneous surfaces, the Freundlich isotherm model is widely used; it also used to describe the multilayer sorption mechanism (Milmile *et al.*, 2011). Freundlich model can be expressed by the following equation

$$\text{Log}(q_e) = \frac{1}{n} \text{Log}(C_e) + \text{Log}(K_F) \dots \dots \dots (2)$$

In which q_e ($\mu\text{g/g}$) is the adsorption capacity of chitosan biopolymer, C_e ($\mu\text{g/L}$) is equilibrium contaminant concentration in solution, n is the Freundlich constant which indicates the degree of favorability of adsorption and K_F is isotherm constant.

2.5.3. Dubinin-Radushkhevic (D-R) isotherm

The Dubinin-Radushkhevic (D-R) isotherm is used to explain the adsorption process on a specific type of identical pores on the basis of Gaussian energy distribution on a heterogeneous surface (Kilislioglu and Bilgin, 2003; Nuri and Mustafa, 2006; Gunay *et al.*, 2007). The D-R isotherm can be represented by the following equation:

$$q_e = q_m \exp(-k\mathcal{E}^2) \dots \dots \dots (3)$$

This can be linearized as follows:

$$\ln(q_e) = \ln(q_m) - k\mathcal{E}^2 \dots \dots \dots (4)$$

In which \mathcal{E} (Polanyi potential) can be calculated from $[RT \ln(1 + (1/C_e))]$, q_e ($\mu\text{g/g}$) is the adsorption capacity of the adsorbent material, q_m is the adsorption capacity ($\mu\text{g/g}$) and k is the R-D adsorption energy constant ($\text{mol}^2/\text{kJ}^{-2}$). On the other hand, R , T and C_e represent the gas constant (8.314 J/molK), absolute temperature (K) and equilibrium concentration (mg/L) respectively.

2.6. Kinetic studies

Reaction and the mass transfer steps are the main influencing factors for metal sorption kinetics. These two steps are also important to govern the transfer of metal ions from bulk solution to the adsorption sites. This mechanism depends on the physical formation (particle size), intrinsic structure of the adsorbent (for chitosan- degree of deacetylation, crystallinity, molecular weight, viscosity and ash content), and the nature of contaminants in the solution and adsorption process conditions (temperature and pH). The simplified Lagergren pseudo-first-order and pseudo-second-order model are widely used to explain the metal ions sorption of adsorbent materials.

2.6.1. Pseudo-first-order kinetics

The Lagergren pseudo-first-order rate equation was the first rate equation for the sorption (liquid/solid system) based on solid capacity (Ho and McKay, 1999), this equation can be represented by (Lagergren and Svenska, 1898),

$$\log(q_e - q_t) = -\frac{K_1}{2.303}t + \log q_e \dots \dots \dots (5)$$

In which q_e and q_t represents the metal concentration ($\mu\text{g/g}$) at equilibrium and at any time, t (h) correspondingly.

This kinetic model is suitable to explain the adsorption mechanism, although it has the following disadvantages Gerente *et al.*, (2007).

- The above mentioned equation does not provide the theoretical q_e values that come from practical q_e values and
- The plots are linear up to approximately first 30 minutes and beyond this period of time, the theoretical results and experimental data do not correlate well as expected.

2.6.2. Pseudo-second-order kinetics

The Lagergren pseudo-second-order rate linear equation can be given as

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 \cdot q_e^2} \dots \dots \dots (6)$$

In which q_e (1/slope), and K_2 (slope /intercept) are the equilibrium contaminant concentration and second order adsorption

rate constant correspondingly, and these values were calculated from t/q_t versus t plot. This model is suitable to determine an effective q_e , since q_e and K_2 is calculated from the slope and intercept of the plot.

2.7. Chitin and chitosan

Chitin and its derivative form chitosan are the second most abundant polymer in nature coming from crystalline microfibrils forming structural components. This biopolymer that originates from exoskeletons of shellfish like crabs and shrimps has the ability to fix a great range of heavy metals and radio-nuclides (Guibal, 2004; Muzzarelli, 2011). Chitin was first isolated by Braconnot (1811) as fungine and later, in 1823, Odier discovered it in insects and named as chitin. Currently, chitin is mostly produced from shrimp and crab shells as they are dumped as waste product from seafood industry. These shells contain 30-50% calcium carbonate, 30-40% protein and the rest 20-30% is chitin (dry mass) (Johnson and Peniston, 1982).

2.8. Structure of chitin and chitosan

Chitin is generally a hard, inelastic, white and inert solid, which is greatly hydrophobic and insoluble in water and organic solvents. However it is soluble in hexafluoroisopropanol, hexafluoroacetone and chloroalcohols in synthesis with aqueous solutions (Ravi Kumar, 2000; Benavente, 2008). Chitin is a homopolymer and the chemical structure consists linear chain of β -(1, 4)-lined 2-acetamino-2-deoxy- β -D-glucopyranose with 2-amino-2-deoxy- β -D-glucopyranose units. And the metals uptakes ensured by large number of active amino group (NH_2) and hydroxyl group (OH) present in the chitosan polymer chain, by interacting with various metallic species through chelation or ion exchange mechanism (Sureshkumar *et al.*, 2010). The molecular weight, purity and crystal morphology are fully dependent on their sources and it is generally available in three crystalline polymorphic forms (α -, β - or γ - chitin) which can be defined by the basis of crystalline chain packing regions (Salmon and Hudson, 1997; Rudall, 1963). α -consist with anti-parallel chains, β - has two

parallel chains (stack structure) and Y- has one anti-parallel chain in the structure. In both α - and β -chitins structure, $C=O \cdots H-N$ intermolecular hydrogen bonds is present, but $-CH_2OH$ groups are present only in α - chitin but not in β -chitin. For which β - chitin can easily swells in water and produces hydrates which is unlikely to α -chitin. β -chitin are generally found in squid and marine diatoms and it found very rarely. One the other hand α - chitin is mostly found in crustaceans, insects and fungi. Chitosan generally prepared from most available α -chitin (Blackwell *et al.*, 1978).

2.9. Chitosan

Chitin is a semi-crystalline polymer which includes inter-and intra-molecular hydrogen bonds which reduce the dissolved properties in organic solvents and dilute acids. Chitin with deacetylation degree over 60% can easily dissolve in dilute acidic aqueous solutions, which is known as chitosan. Thus chitosan is a collective name of the polymer that comes from deacetylated chitin. Since chitosan has versatile physical and chemical properties, cationic nature, biodegradability, compatibility, antimicrobial activity and non-toxicity, it has an extensive wide range of applications including food processing, cosmetics, biotechnology, agriculture, fiber formation, pharmaceuticals, medical application, paper production, wastewater and

drinking water treatment with other different applications (Ravi Kumar, 1999; Li *et al.*, 1997; Brine *et al.*, 1992; Bahmani *et al.*, 2000; Hudson and Smith, 1998; Momin, 2008).

Commercially chitosan can be produced through alkaline deacetylation of chitin with the aim to make it easily soluble in dilute acetic acid. Deacetylation is a process that includes the reaction of chitin with 40-50% NaOH aqueous solution at 100°C or more for at least 30 minutes to hydrolyze the N-acetyl groups. By the repetition of the process, deacetylation degree can be achieved up to 98% since complete deacetylation is difficult with the heterogeneous process.

The production of chitin from crab or shrimp shells depends on several consecutive process including (a) chemical or enzymatic desprotenization, (b) demineralization by acidic treatment to remove calcium carbonate and other minerals and finally (c) decolouration to remove residual pigments. In industrial scale, chitosan is generally produced by chemical deacetylation of chitin using sodium hydroxide, which can also be done by enzymatic deacetylation of chitin (Cai *et al.*, 2006).

2.9.1. Degree of Deacetylation (DDA)

Deacetylation is a process of acetyl groups removal from chitin molecular structure. The deacetylation degree is defined as the number of D-glucosamine units per 100 monomers and is expressed in percentage. It

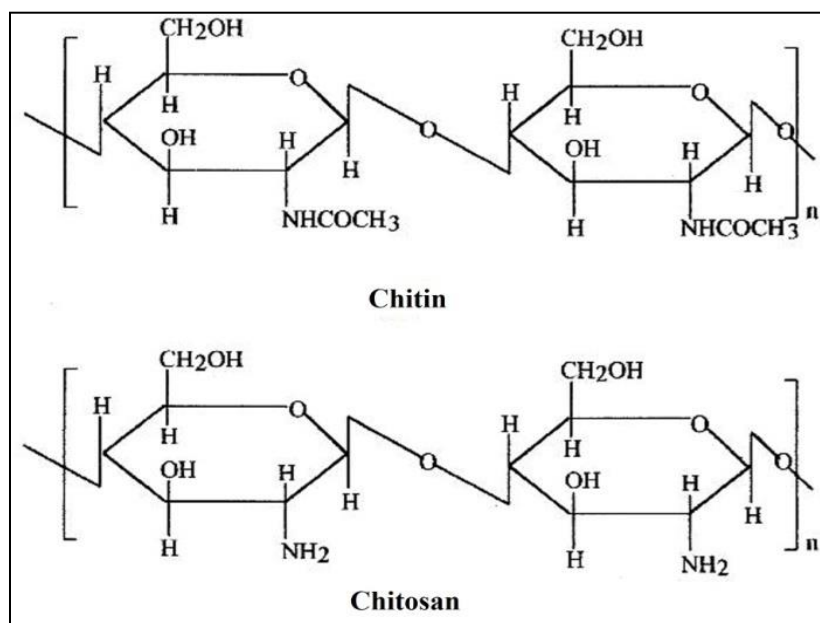


Figure. 4. Chemical structure of chitin and chitosan (Nair and Laurencin, 2007; Ghanbarzadeh and Almasi, 2013).

is also used as an indicator for free amino groups ($-NH_2$) in the chitosan as an important chemical characteristics that influence the physicochemical properties, biological properties, antibacterial activity and also application of chitosan (Momin, 2008). The degree of deacetylation depends on the production methods and species used. Generally the available chitosan have a degree of deacetylation in the range of 56%-99%. However, good quality (solubility) chitosan should have at least 85% of deacetylation degree (No and meyers, 1995).

2.9.2. Viscosity

Viscosity of chitosan solution is another important property to determine the commercial applications which may be affected by degree of deacetylation, molecular weight, concentration, ionic strength, pH and temperature. With the increase of molecular weight and concentration of chitosan, viscosity can be increased and by decrease in pH. Viscosity is an important characteristic of chitosan for antibacterial activities.

2.9.3. Ash Content

Ash content of chitosan is an important indicator of the effective demineralization (DM) step for calcium carbonate removal. The ash content of chitosan may affect the solubility or other important characteristics of the final products. The high quality chitosan grade is also defined by the ash content and it should be less than 1% (No *et al.*, 1995). No and Meyers (1995) reported less than 1% ash content in chitosan that comes from crab shells, and crawfish chitosan contained less than 1% ash (range of 0.2% to 0.9%). Usually the commercial chitosan product has less than 2% ash content (Fernandez-Kim, 2004).

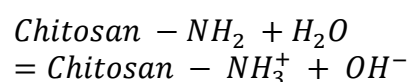
2.10. Chitosan Biosorption

The metal sorption capacity of chitosan depends on its cristanility, affinity for water and deacetylation degree (amino group content). Chitosan biopolymer chelates metals from solution five to six times more than the chitin due to presence of free amino groups in chitosan chain. This property is widely used for environmental

purposes to uptake, separation or recovery processes of valuable metals. The application of chitosan is limited in industrial applications due to materials cost, variability in characteristics and availability of resources (Guibal, 2004). The adsorption properties of chitosan biopolymer is attributed with its functional group including increase of hydrophilicity by hydroxyl groups of the polymer, which also helps to enhance the diffusion of polymer networks and allows to adsorption of metals from aqueous solutions. In a number of different ways, the hydroxyl and amino groups of chitosan biopolymer can react with solutes in the aqueous solutions. Amino groups of chitosan are very important for adsorption processes compared to hydroxyl group, for which degree of deacetylation is an important parameter to evaluate the quality of the chitosan biopolymer (Crini, 2005; Westergren, 2006). Instead of these favorable properties of chitosan biopolymer, there are some problems that can occur during the chemical process of the adsorption system including solubility of chitosan in acidic medium, for which it is not favorable to use as an insoluble sorbent under acidic conditions (Varma *et al.*, 2004). The stability of chitosan biopolymer under acidic and alkaline condition can be enhanced by crosslinking reactions; however this process may reduce the adsorption properties.

2.11. Sorption process on chitosan biopolymer

The presence of high nitrogen content in the chitosan biopolymer works as active sites for different chemical reaction in water solutions. The amine groups present in chitosan biopolymer are weak enough to deprotonate water according to the following expression (Westergren, 2006)



Chitosan, in contact with water increases pH of the solution due to the pKa of 6.3 (Elson *et al.*, 1980). The adsorptions on chitosan biopolymer depend on solution pH by the direct consequence of acid-base reaction.

The amine groups in the deprotonated form of chitosan biopolymer act as binding site for metals by chelation mechanisms. Chitosan biopolymer may also possess electrostatic properties to adsorb metals by ion exchange mechanism (Crini 2005; Westergren, 2006).

3. MATERIALS AND METHODS

3.1. Materials

Chitosan biopolymer (Degree of Deacetylation, DDA-85%, Viscosity=1000 mPas and Ash content 1%) was used as adsorbent which was collected from **BioLog Biotechnologie und Logistik GmbH, Germany**. Other chemicals like 10 mg/L of arsenic and uranium solution were bought from Spectra-scan (Teknolab AB, Sweden) to use as a starting stock solution. The stock solution was further diluted to prepare working solutions. Distilled water (Millipore Ultra-Pure Water System) was used for the entire investigations. The pH meter was calibrated with standard buffer solutions (pH 4, 7 and 9) and the initial pH of the test solution was adjusted to the required value with diluted HNO₃ and NaOH solutions.

3.2. Instrumentation for characterization

Characterization of chitosan biopolymer was carried out using X-ray diffraction (XRD) with a two-dimensional VÅNTEC-500 detector (BRUKER Corporation, Germany). The FTIR spectrum was obtained using a FTIR Spectrophotometer (BRUKER Corporation, Germany); the surface morphological images by a Scanning Electron Microscope (SEM) (Zeiss Company), Ultra-violet (UV) spectroscopy which performed by UV-NIR (HITACHI Mark//Model: 1J0-0016) in the wave length range from 200 nm to 900 nm, and changes in the physical properties were identified by a thermal gravimetric analysis (TGA/DTA) (Setaram). The pH was determined by standard pH meter (SensION™+ PH31, HACH, manufactured by SCAND iNOVATA AB). The initial and final contaminant concentration in aqueous solutions was determined by ICP-OES (iCAP-6000, Thermofisher AB).

3.3. Batch adsorption method

The arsenic(V) and uranium(VI) containing aqueous solutions were prepared in the following way:

Triplicate aqueous solutions containing 100 µg/L were mixed with 5-90 g/L chitosan powder. The samples were shaken for 24 hours in a temperature controlled (22 °C) water bath using an orbital circulation mode (200 rpm). The treated water samples were filtered through 0.45 µm Sartorius syringe filters. The filtrates were analyzed to determine the residual arsenic(V) and uranium(VI) concentration using ICP-OES (iCAP-6000); pH using a standard pH meter (SensION™+ PH31, HACH, manufactured by SCAND iNOVATA AB). The average value of the corresponding parameter was selected as a reporting value. The percentage of adsorption (%) was calculated from the following equations:

$$\text{Ads (\%)} = [(C_i + C_f)/C_i] \times 100 \dots \dots (7)$$

In which C_i and C_f , are the arsenic(V) and uranium(VI) concentrations in the initial and final solutions of the batch experiments in µg/L.

3.4. Effect of adsorbent dose

The effect of adsorbent doses was investigated using 100 ml solution of 100 µg/L arsenic(V) and uranium(VI) with predetermined pH at 22°C, the chitosan doses were varied from 5 to 90 g/L and the agitation was carried out for 360 min to ensure the optimal removal condition. The adsorbent and solution were separated using centrifuge and filters, the concentration of arsenic(V) and uranium(VI) in the filtrates were determined by ICP-OES.

3.5. Effect of pH

The effect of pH on adsorption capacity of chitosan biopolymer was also examined using 100 ml solution of 100 µg/L arsenic(V) and uranium(VI) with the pH range of 5-9 (groundwater pH level) at 22°C correspondingly. And the predetermined chitosan doses were added in 100 ml of 100 µg/L arsenic(V) and uranium(VI) solutions. Flasks were agitated in a thermostated shaker for 360 min to ensure optimal removal state.

Finally, the adsorbent and solution were separated by filters and the filtrates were further analyzed to determine the remaining contaminant concentrations.

3.6. Effect of contact time

The batch experiments were conducted at different contact times using the initial arsenic(V) and uranium(VI) concentration of 100 µg/L and predetermine chitosan biopolymer doses in 100 ml solution in a water bath at a fixed temperature of 22°C. The adsorbent and solution were separated at pre-determined time intervals and the filtered solution was scrutinized by ICP-OES to determine the remaining arsenic(V) and uranium(VI) concentrations.

3.7. Effect of initial concentration

Finally the effect of initial contaminant concentration on removal capacity was also investigated using 100 ml arsenic(V) and uranium(VI) solutions with different initial concentration level (50 µg/L to 250 µg/L) at temperature of 22°C by considering other predetermined constant parameters (e.g. doses. pH and time).

3.8. Adsorption isotherm and kinetic studies

The sorption isotherms and kinetic studies were conducted using arsenic(V) and uranium(VI) solution of 50, 100, 150, 200 and 250 µg/L concentrations. 100 ml of arsenic(V) and uranium(VI) solution was agitated with required amount of adsorbent by considering different contact time ranging from 30 to 360 min at pH of 6.0 ± 0.1 and 7.0 ± 0.1 respectively for arsenic(V) and uranium(VI). The adsorbent was separated from aqueous solution by filtration and the filtrates were analyzed by ICP-OES to determine remaining arsenic(V) and uranium(VI) in the solutions.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of chitosan biopolymer

4.1.1. X-Ray Diffraction (XRD)

The XRD patterns of the chitosan biopolymer materials are illustrated in the Figure 5. From the figure, two significant characteristics diffraction peaks at $2\Theta = 10^\circ$ and 20° are found which are typical

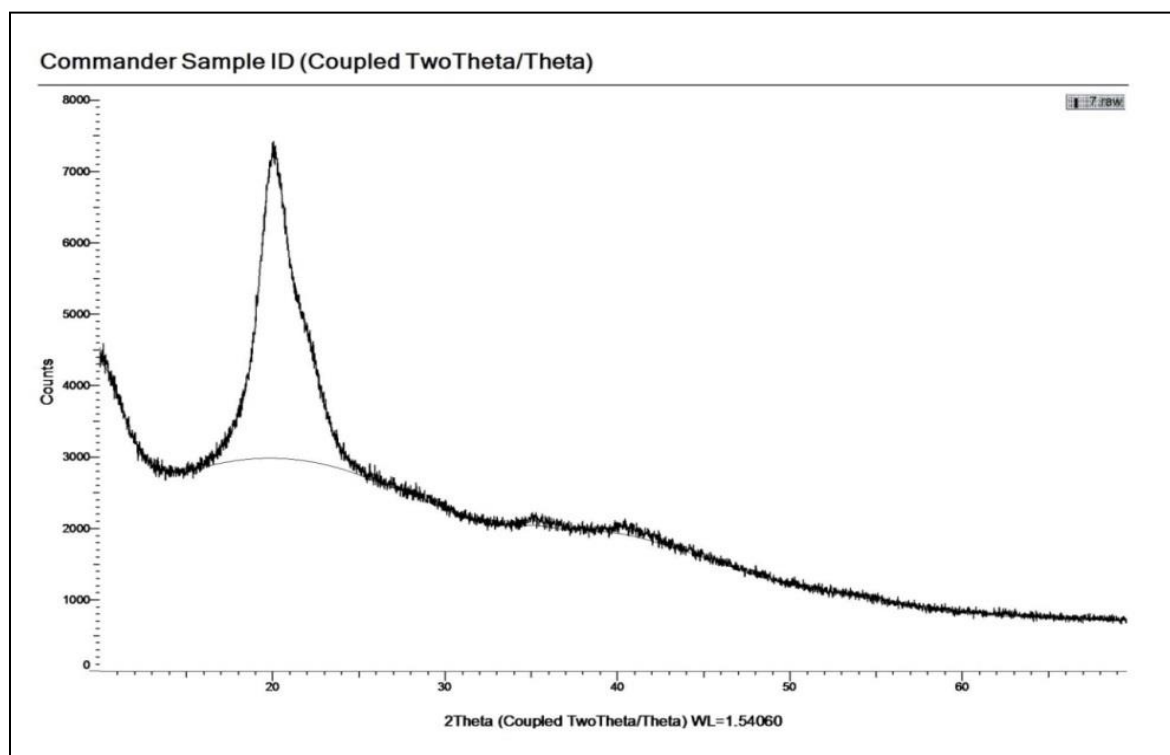


Figure 5. X-Ray diffraction pattern of chitosan biopolymer.

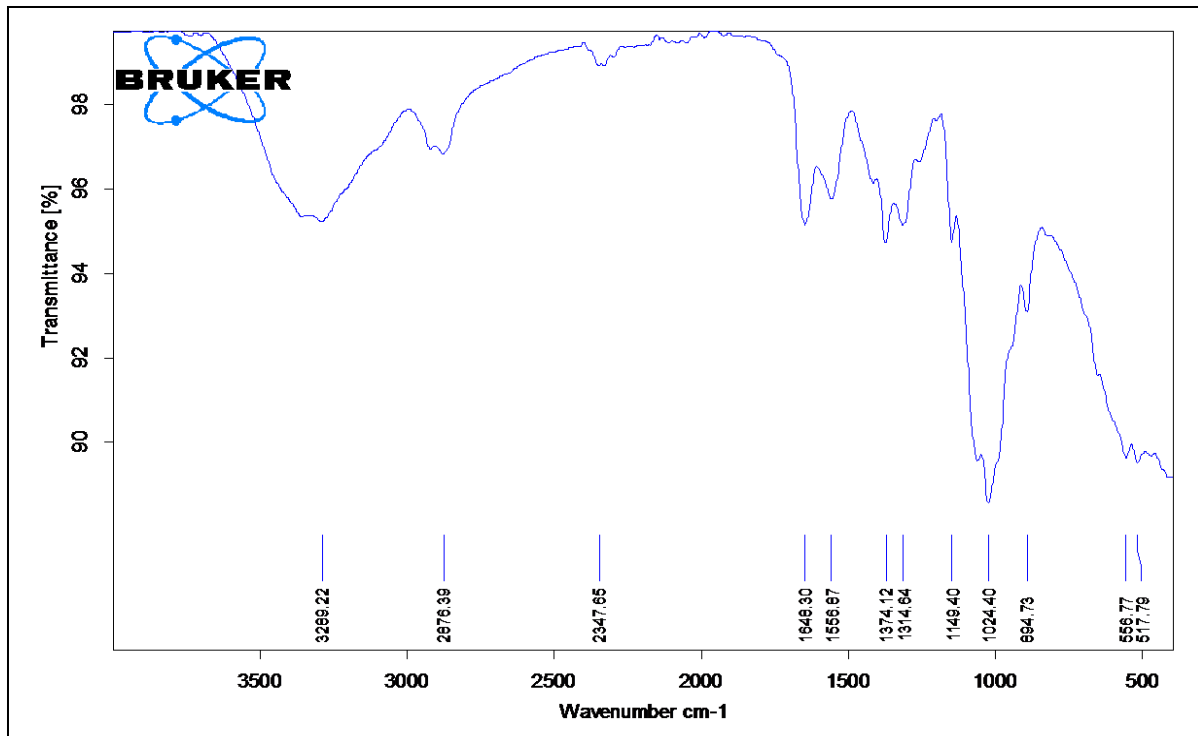


Figure 6. FTIR spectra of chitosan biopolymer

fingerprints of semicrystalline chitosan (Bangyekan *et al.*, 2006). According to Yen and Mau (2007), chitosan produced from fungi had two crystalline reflections at 9.7° and 19.9°, however in the case of shrimp chitosan it was reported that it has two major peaks at $2\theta = 9.9$ to 10.7° and 19.8 to 20.7° (Prashanth *et al.*, 2002). The peaks around $2\theta = 10^\circ$ and 20° are related to crystal I and crystal II in chitosan structure (Ebru *et al.*, 2007; Marguerite, 2006) and both of these peaks attributed a high degree of crystallinity to the proposed chitosan biopolymer (Julkapli and Akil, 2007). The of

crystallinity development within a polymer depends on its structural regularity, and the influencing factors of crystallinity include polarity, presence of hydrogen links and also the capacity to pack polymer chains (Canevarolo Junior, 2002; Rotta, 2010)

4.1.2. Fourier-transform infrared (FTIR) spectra

FTIR spectra of the chitosan biopolymer are illustrated in Figure 6. Caused by the chitosan cross linking, a peak at 3000 cm^{-1} to 3500 cm^{-1} bands was observed, which corresponds to the stretching vibration of N-H

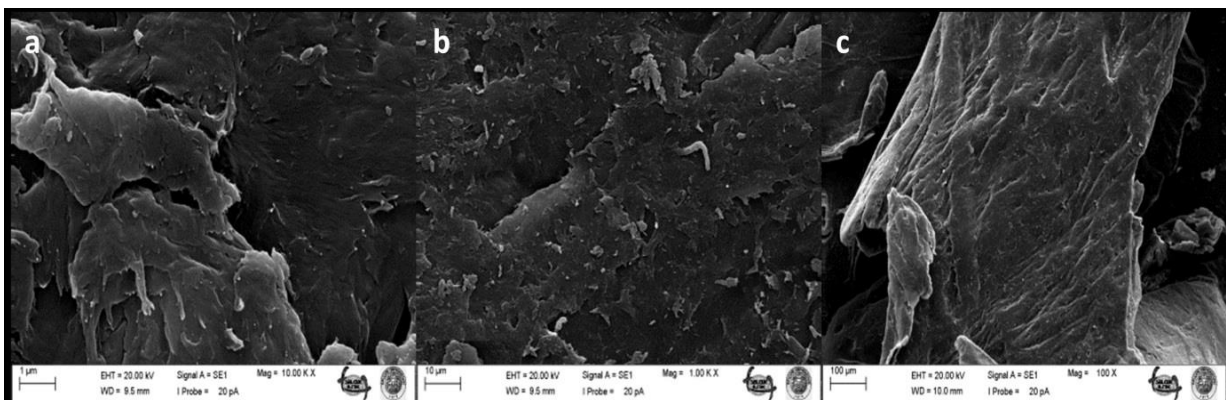


Figure 7. SEM of chitosan biopolymer (powder).

bonds (1650 cm^{-1} bands corresponds to C=N stretching bond). This peak is an indication for the formation of Schiff's base due to reaction among the carbonyl group of the glutaraldehyde and the amine group of the chitosan chains. The peaks in the spectrum of chitosan around 2950 , 2347 , 1641 , 1578 , 1425 , 1300 to 1025 cm^{-1} are due to the stretching vibrations of 3-methylbenzyl chloride, ethyl sorbet, chlorogenic acid hemihydrate, 3-nitrophenol, 3-methoxypropio-nitrile, phenylethylene glycol, 4-chlorobenzophen-one respectively (Nakamoto, 1978; Annaduzzaman *et al.*, 2014).

4.1.3. Surface morphology of chitosan biopolymer by Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) analysis gives information about the surface structure of the chitosan sorbent. Figure 7 shows different magnifications SEM image of different areas of chitosan biopolymers. It was observed that the chitosan biopolymer has porous (not so significant), rough and fibril structures. SEM micrographs indicate good homogeneity.

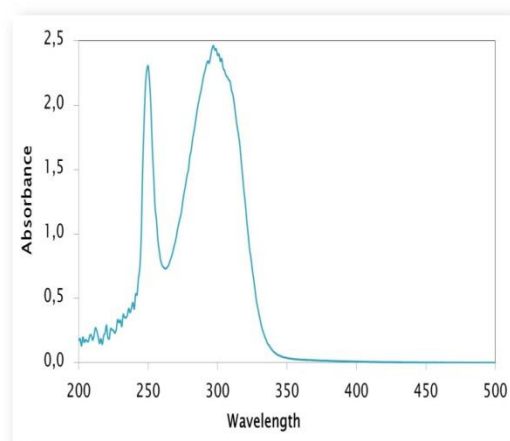


Figure 8. UV-visible spectrum of chitosan biopolymer.

4.1.4. UV-visible spectrum

UV spectra of chitosan biopolymer was recorded in the range of 200-500 nm and shown in Figure 8. The peaks are located at 250 and 300 nm which can be attributed to dissolution of chitosan with $n-\sigma^*$ transition. In case of substitution of aldehydes, the amine groups of chitosan are coupled along with conjugated phenolic group of aldehyde and this conjugated nitrogen atom and electrons steam comes from aldehyde, which is the main reason for decreasing of energy

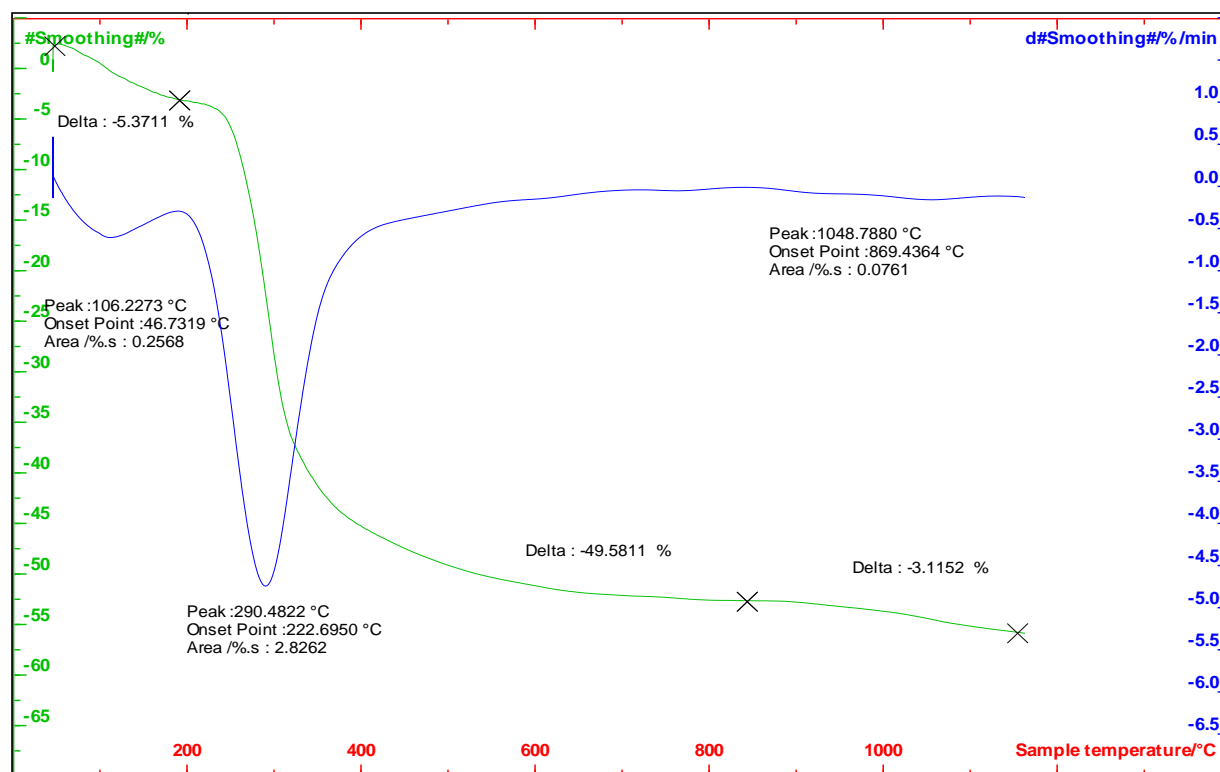


Figure 9. TGA/DTA of chitosan biopolymer.

level for σ^* (Soliman *et al.*, 2013). These peaks are also an indication of less dissolved properties and have high degree of polymerization.

4.1.5. TGA/DTA

Thermo-gravimetric analysis of the chitosan biopolymer was conducted in the temperature ranges from the room temperature to 1150°C (Figure 9). The native chitosan weight loss curves in the range of 250°C to 450°C can be associated with decomposition of the chitosan. The remaining weight of the chitosan during TGA analysis was 50%, 48% and 47% after 450°C, 650°C and 850°C correspondingly. The TGA analysis data showed that the chitosan (DDA 85%) material is sufficiently stable and appropriate for water treatment processes (Desai *et al.*, 2008; Thirumavalavan *et al.*, 2013).

4.2. Adsorption Study

4.2.1. Effect of adsorbent dose

The sorption of arsenic(V) and uranium(VI) as a function of adsorbent dose was studied by considering constant temperature (22°C), time, pH, and concentration. The chitosan biopolymer doses were varied from 5 g/L to 90 g/L. The results (Figure 10) illustrate the effect of the adsorbent doses on arsenic(V) and uranium(VI) adsorption from aqueous solution. They reveal that the increase in adsorbent doses positively affect the adsorption percentage up to a certain limit. The maximum removal percentage was attained 98.95% for arsenic(V) at a dose of 60 g/L and 100% for uranium(VI) in both doses of

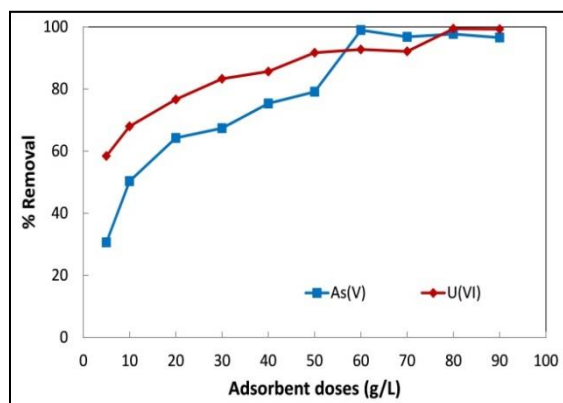


Figure 10. Effect of adsorbent doses on arsenic(V) and uranium(VI) removal from aqueous solutions.

80 and 90 g/L. By economic consideration and optimal use of materials, 80 g/L was considered as the optimum dose for uranium(VI) removal. Further increase in dose has no significant effect in removal percentage.

4.2.2. Effect of pH

The effects of pH on contaminants removal are studied with the pH ranges of 5.0 ± 0.2 to 9.0 ± 0.2 (drinking water pH ranges) with keeping other parameters constant. The effect of pH on both arsenic(V) and uranium(VI) ions sorption are presented in Figure 11. The percentage adsorption increases with increase in pH up to 6.0 ± 0.2 and 7.0 ± 0.2 correspondingly for arsenic(V) and uranium(VI) and then decreases with increase in pH. The arsenic(V) and uranium(VI) adsorption mechanism was affected by pH of the aqueous solutions through the hydrolysis of arsenic(V) and uranium(VI) ions.

At low pH (<6.0), the amine groups of chitosan biopolymer are ionized, for which the lower adsorption capability can be recognized with the competitive binding of arsenic(V) ions and H^+ to the amine groups (Alakhras *et al.* 2005). Chitosan biopolymer degrades to a smaller chain at acidic pH and becomes soluble in the aqueous solution. At pH >6.0, the As(V) removal efficiencies are lower. At higher pHs (>6.0), the aqueous As(V) speciation is controlled by $H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$; $pK_a = 7$ (Boddua *et al.*, 2008; Reed *et al.* 2000). Therefore, pH 6.0 was selected as the optimum pH for the

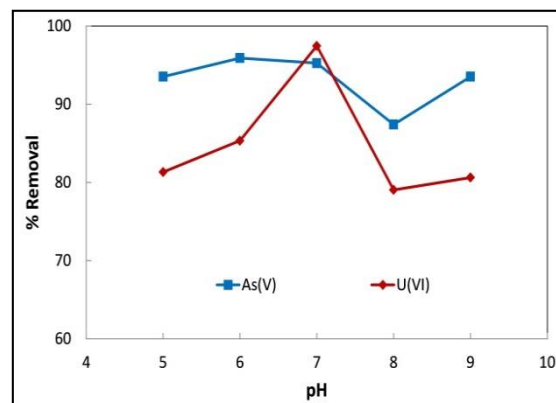


Figure 11. Effect of initial pH on arsenic(V) and uranium(VI) removal from aqueous solutions.

assessment of the arsenic(V) adsorption by the chitosan biopolymer. According to the XPS studies performed by Dambies *et al.*, (2000), the anion sorption occurs at the amine functional groups, which identified the sorption site involved as well as the forms of the species sorbed on the biopolymer.

The biomass enriched with high amounts of carboxyl groups that comes from manuronic and guluronic acids on the polysaccharides cell wall, for which biosorption is influenced by solution pH. Uranium(VI) removal percentage achieved 97% at pH 7.0 ± 0.2 . At low pH, primarily uranyl exists as a mononuclear aqueous ionic species. Uranyl hydrolyzes and produces oligomeric solution species during increase in pH (Chisholm-Brause *et al.*, 2001; Sari *et al.*, 2008; Gok & Aytas, 2009). Uranium cation UO_2^{2+} hydrolyzed in aqueous solutions with increase in pH, makes the ion exchange mechanism much more complex. At pH level of acidic to neutral, UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, UO_2OH^+ and $(\text{UO}_2)_3(\text{OH})_5^+$ hydrolysed complex ions exist in the solutions (Khani *et al.*, 2006). The removal percentage of UO_2^{2+} by chitosan biopolymer increases with increase of the system up to pH 7.0 ± 0.2 , since the hydrolysed species sorbed better than the free hydrated ions (Collins & Stotzky, 1992), and this was selected as working pH for further experiments.

4.2.3. Effect of Contact time

Arsenic(V) and uranium(VI) adsorption has been investigated as a function of time onto chitosan biopolymer. Figure 12 represents the sorption percentage variation of arsenic(V) and uranium(VI) ions with shaking time. The initial sorption percentage is higher compared to long time duration. After 15 minutes, the adsorption of arsenic(V) and uranium(VI) were 96 and 84% respectively. This initial rapid phase sorption occurs mainly due to both presence of high vacant site as well as concentration gradient among adsorbent surface and adsorbate in solution. Afterwards the removal capability decreases slightly and constant due to low vacant site available in addition to

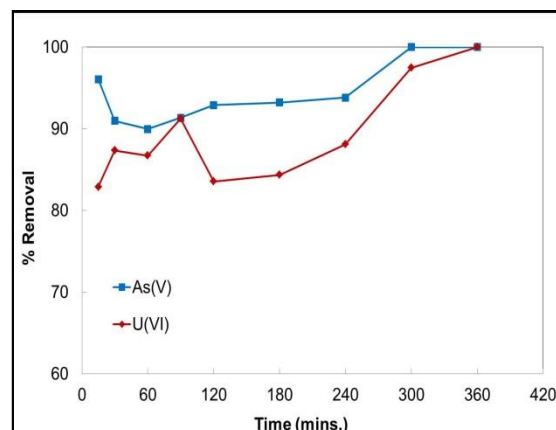


Figure 12. Effect of contact time on arsenic(V) and uranium(VI) removal from aqueous solutions.

desorption of arsenic(V) and uranium(VI). The maximum removal of arsenic(V) and uranium(VI) were 100% after 300 and 360 min respectively.

4.2.4. Effect of initial concentrations

The percentage removal of the contaminants as a function of initial concentration, was conducted at 22°C with achieved optimum pH of 6.0 ± 0.2 and 7.0 ± 0.2 , chitosan dose of 60 and 80 g/L for arsenic(V) and uranium(VI) respectively (Figure 13).

For arsenic (V), during the experiment with varying initial contaminants concentrations (50-250 $\mu\text{g/L}$), the removal percentage increases from 36.64% to 69.97% (at 100 $\mu\text{g/L}$). Afterwards the removal percentages were decreasing. In general, the removal percentage increases with increase in the initial concentration of the adsorbate (Ayoob and

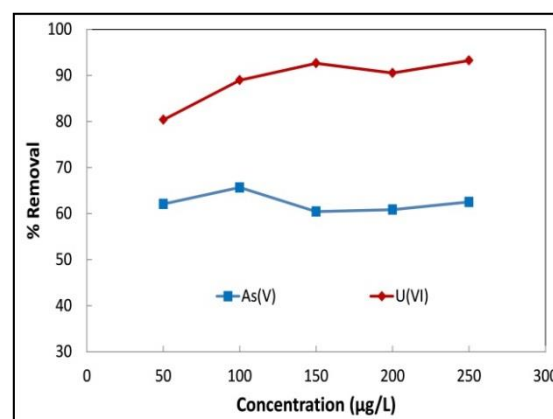


Figure 13. Effect of initial concentration on arsenic(V) and uranium(VI) removal from aqueous solutions.

Gupta, 2006; Srivastav *et al.*, 2013). The arsenic(V) removal was found to be around 70%, when initial concentration is in the range of 50-100 µg/L arsenic(V); elsewhere the removal decreases. In the low concentration range, there are enough sites on the sorbent surface for arsenic(V)-ions in the solution. However, with increase in the arsenic concentration, arsenic(V) species are not able to come in contact with the active sites of the adsorbent.

On the other hand, for uranium(VI), the removal percentage increases with increase in concentration level. The highest uranium(VI) removal percentage was found at 250 µg/L of initial concentration and the value was 93.28%. This is an indication that the absolute amount of uranium(VI) uptake by chitosan biopolymer is greater at the higher uranium(VI) concentrations.

4.2.5. Adsorption isotherm

The sorption data has been investigated using different sorption isotherms to evaluate the applicability of adsorption process as a unit operation to explain the adsorbent's physicochemical features (Vadivelan and Kumar, 2005; Wang and Chen, 2009). The adsorption isotherms for arsenic(V) and uranium(VI) using chitosan biopolymer (as an adsorbent) at optimum pH are shown in Figure 14. The adsorption experiments were performed under controlled pH of 6.0 ± 0.2 and 7.0 ± 0.2 , chitosan dose of 60 and 80 g/L for arsenic(V) and uranium(VI) respectively.

The adsorption isotherm studies were modelled using Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm due to its simplicity in applications and to test the adsorption behavior.

4.2.6. Langmuir isotherm

The plots (Figure 14a) indicates that the adsorption process could be well defined by the Langmuir adsorption isotherm model. The parameters and the correlation coefficient calculated from models are presented in Table 1. According to the results, the adsorption was a complex process including chemical and physical adsorption, and the adsorption processes by chitosan could be

reflected as homogeneous monolayer adsorption.

The separation factor (R_L), a dimensionless constant, can be used to explain the adsorption mechanism. The separation factor R_L is defined as

$$R_L = 1/(1 + K_L C_0) \dots \dots \dots (8)$$

In which K_L is model constant (L/µg) and C_0 is initial concentration (µg/L). The value of R_L is classified as unfavorable ($R_L > 1$), Linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Zhai *et al.*, 2004; Liu *et al.*, 2011). The value of R_L (Table 1) was within $0 < R_L < 1$ for both of arsenic(V) and uranium(VI), which means that the uptake was favorable for chitosan biopolymer.

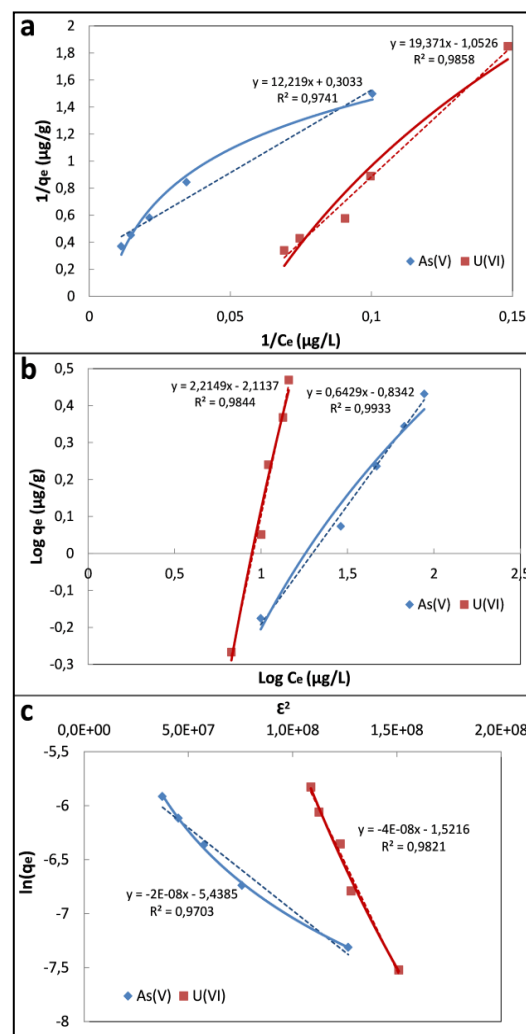


Figure 14. Langmuir (a), Freundlich (b) and D-R (c) isotherm plots for arsenic(V) and uranium(VI) adsorption by chitosan biopolymer.

Table 1. Adsorption parameters derived from the Langmuir, Freundlich and D-R isotherms of arsenic(V) and uranium(VI) adsorption by the chitosan biopolymer.

Isotherms	Parameters	Arsenic(V)	Uranium(VI)
Langmuir	q_m ($\mu\text{g/g}$)	3.3	0.951
	K_L ($\text{L}/\mu\text{g}$)	0.025	0.054
	R^2	0.9741	0.9858
	R_L	0.286	0.07
Freundlich	K_F	0.147	0.008
	n	1.56	0.45
	R^2	0.9933	0.9844
D-R	q_m ($\mu\text{g/g}$)	4.35	2.18
	k (mol^2/kJ^2)	2×10^{-8}	4×10^{-8}
	E (kJ/mol)	5	3.5
	R^2	0.9703	0.9821

4.2.7. Freundlich isotherm

The results from Freundlich isotherm analysis of arsenic(V) and uranium(VI) adsorption on chitosan bio-sorbent were evaluated (the correlation coefficient R^2 , Freundlich constants K_F and n) from the plots (Figure 14b) and tabulated Table 1. The value of the Freundlich constant n is within 1 to 10, which was an indication for the beneficial adsorption of the ions (Islam *et al.*, 2010).

4.2.8. Dubinin-Radushkevich (D-R) isotherm

According to Dubinin-Radushkevich (D-R) isotherm, the values of q_m and k were calculated (Table 1) from the intercept and slope of the $\ln(q_e)$ versus E^2 plots (Figure 14c). The mean free energy, E (kJ/mol) for arsenic(V) and uranium(VI) adsorption, were calculated from the following equation:

$$E = (-2k)^{-0.5} \dots \dots \dots (9)$$

From the plots of D-R model, q_m , k , R^2 and E were determined as $4.35 \mu\text{g/g}$, $2 \times 10^{-8} \text{ mol}^2/\text{kJ}^2$, 0.9703 and 5 kJ/mol and $2.18 \mu\text{g/g}$, $4 \times 10^{-8} \text{ mol}^2/\text{kJ}^2$, 0.9821 and 3.5 kJ/mol for arsenic(V) and uranium(VI) correspondingly (Table 1). According to Kilislioglu and Bilgin, (2003), if E value is within 8 and 16 kJ/mol , then the adsorption can be described as ion exchange. Since, the E value (5 and 3.5 kJ/mol) were not in the range of 8-16 kJ/mol , the adsorption mechanism were physiosorption, for both arsenic(V) and uranium(VI).

4.3. Kinetic studies

To understand the controlling mechanism of arsenic (V) and uranium(VI) adsorption by chitosan biopolymer, the most commonly used kinetic model pseudo-first-order and

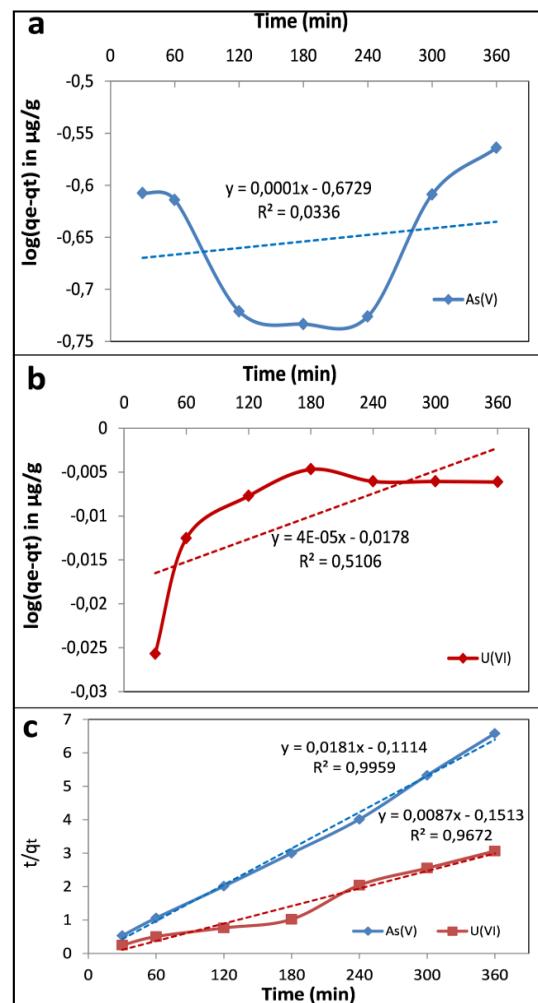


Figure 15. Pseudo-first-order (a,b) and Pseudo-second-order kinetic plots for arsenic(V) and uranium(VI) adsorption on chitosan biopolymer.

Table 2. Kinetic parameter for removal of arsenate by chitosan biopolymer.

Kinetic models	Parameters	Arsenic(V)	Uranium(VI)
Pseudo-first-order	$K_1(\text{hr}^{-1})$	-0.014	-0.005
	$q_e (\mu\text{g/g})$	0.213	0.964
	R^2	0.0336	0.5106
Pseudo-second-order	$K_2 (\text{g} \cdot \mu\text{g}^{-1} \text{hr}^{-1})$	10.575	0.0
	$q_e (\mu\text{g/g})$	0.923	1.961
	R^2	0.9959	0.9672

pseudo-second-order were tested to interpret the adsorption data with an assumption that the measured concentration are equal to the surface concentrations.

4.3.1. Pseudo-first-order and second-order kinetics

According to the Lagergren pseudo-first-order rate equation (Lagergren and Svenska, 1898) and $\log(q_e - q_t)$ vs. t plots slope (Figure 15a,b), the rate constant K_1 was calculated as -0.014 and -0.0046 hr^{-1} for arsenic(V) and uranium(VI) respectively (Table 2) which indicates that the adsorption of ions by chitosan biopolymer was not following pseudo-first-order kinetics.

The Lagergren pseudo-second-order results (Figure 15c and Table 2) indicate that the adsorption of arsenic(V) and uranium(VI) onto chitosan biopolymer follows pseudo-second-order kinetic model where the second-order rate constants were calculated as 10.575 and $0.0 \text{ g} \cdot \mu\text{g}^{-1} \text{hr}^{-1}$ with the regression coefficient (R^2) of 0.9959 and 0.9672 respectively. These results indicated that the sorption reaction kinetic among ions and chitosan biopolymer depends on the concentration of contaminants in the batch solution, and the adsorbent doses needed to sorb the maximum at equilibrium.

5. CONCLUSIONS

Based on the experimental study results of chitosan biopolymer application as an adsorbent for the removal of arsenic(V) and uranium(VI) from aqueous solutions, the following important conclusions can be made:

- Chitosan with deacetylation degree of 85% has a potential for the removal of arsenic and uranium from contaminated drinking water.

- Characterization of the chitosan biopolymer (DDA 85%) using XRD pattern analysis indicates a semi-crystalline structure of the materials.
- The FTIR analysis indicates the presence of NH_2 and OH groups on the surface of the chitosan biopolymer which is an indication of biodegradable properties.
- The UV spectra of the chitosan used reveal that the chitosan biopolymer with $n \rightarrow \sigma^*$ transition and the amine groups of chitosan are coupled with conjugated phenolic group with less dissolved properties and has a high degree of polymerrization.
- TGA analysis of adsorbent reveals that the chitosan biopolymer material is sufficiently stable and appropriate for drinking water treatment processes.
- The experimental results are fitted by Langmuir, Freundlich and D-R adsorption isotherms, where Langmuir adsorption isotherm indicates the adsorption of arsenic(V) and uranium(VI) takes place in a homogeneous monolayer of the biosorbent. The D-R isotherm indicates that the adsorption process is a physisorption and the adsorbent material (chitosan biopolymer) can be regenerated after the treatment process.
- The adsorption kinetic of chitosan followed the pseudo-second order-kinetic model more obviously than the pseudo-first-order-kinetic model for both of arsenic(V) and uranium(VI).

Finally, the natural chitosan biopolymer material can be used as a sustainable, alternative, and environment friendly adsorbent for arsenic(V) and uranium(VI) free drinking water production.

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