Synthesis and Characterization of Biopolymer Coated Particles for the Removal of Tungsten from Drinking Water

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Abstract

This study investigates the removal of tungsten from simulated water using biopolymer coated particles (i.e. chitosan coated clay) and natural clay. The effects of initial tungsten concentration (from 20 to 500 ppm) and water pH (4, 5.5 and 6.4) on zeta potential and tungsten removal were studied for both chitosan coated clay and natural clay. It was found that the net surface charge of natural clay shifts from negative to positive upon coating with chitosan as confirmed with zeta potential measurements. The point of zero charge (PZC) of natural clay and chitosan coated clay are 2.8 and 5.8, respectively. The chitosan coating on clay was found to be stable over seven days. Zeta potential measurements show that the net surface charge of chitosan coated clay decreases with increased tungsten concentration in feed water since the positively charged sites are consumed due to adsorption of tungsten anions. Chitosan coated clay was found to be much more effective than natural clay for the removal of tungsten. The initial tungsten concentration and water pH significantly affect the removal of tungsten for both the use of chitosan coated clay and natural clay. High initial tungsten concentration and high pH decrease the tungsten removal efficiency of coated and natural clay.

1. Introduction

The presence of heavy metals in drinking water has been a source of various diseases all around the world. High levels of tungsten detected in water have become a source of concern for the city of Fallon, NV. The level of tungsten was found to be 25μg/L (ppb) in drinking water of Fallon, NV (CDC, 2003b). In 2003, Center for Disease Control and Prevention (CDC) conducted a urine analysis of the Fallon residents and the tungsten level of 0.97 ppb was observed in the urine of eight out of ten Fallon residents. This level is about eleven times higher than the level observed (0.09 ppb) for nationwide USA population (CDC, 2003b). Furthermore, sixteen child leukemia cases have been diagnosed in Fallon, NV and three children have died since 1997 (RGJ, 2003). Although there is no scientific evidence linking tungsten ingestion to the high rate of leukemia cluster found in children, local residences and authorities believe that the high tungsten level might be the main cause. Tungsten has also been identified in at least 6 of the 1636 hazardous waste sites that have been proposed to be included in the EPA National priority List (NPL) for clean up (HazDat, 2003). In addition, in August

2002, the CDC nominated tungsten to be investigated with high priority by the National Toxicology Program (NTP) (CDC, 2004).

Various techniques are available for the removal of heavy metals from contaminated water. However, the cost of these methods and the lack of information about tungsten limit their practical application. Information for the removal of tungsten from water is limited because the existence of tungsten in drinking water has not been regulated by the Unites States Environmental Protection Agency (U.S. EPA). Therefore, a detailed research of tungsten chemistry and the development of cost-effective removal methods are needed.

Tungsten occurs naturally in ground water if the aquifers are in contact with the tungsten ores. The most important tungsten minerals are scheelite ($CaWO_4$) and wolframite [(Fe, Mn)WO_4]. Elements such as sodium and potassium have been found near the formation of tungsten ores (Graupner et al., 1999). At ground water pH levels (between 6 and 9), these alkaline metals may interact with tungsten species to form soluble sodium or potassium tungstate salts and contribute to an increase in tungsten concentration in the aquifer (Graupner et al., 1999). Tungsten in water may also result from human activities such as the release of poorly treated effluents from tungsten mines or tungsten treating plants and the smelting of tungsten ores in open air.

Water treatment techniques such as ion exchange, coagulation, and membrane filtration are well known for heavy metal removal. However, the costs associated with their practical applications to remove trace amount of impurities stimulate the search to identify or develop cost-effective removal methods for tungsten-affected communities. For this study, the development and characterization of a low cost adsorbent for tungsten removal is targeted. This absorbent is made by coating clay (i.e., montmorillonite) with biopolymer (chitosan).

Montmorillonite is hydrated aluminosilicates characterized by the linking of silicates (SiO_4^{2-}) tetrahedral sheets with aluminates (AlO_4^{4-}) octahedral sheets in their structure (Krishna et al., 2000). With a market price of about $0.04-0.12/kg, montmorillonite is 20 times cheaper than activated carbon (Virta, 2002). Clays are widely used in industrial applications because of their high specific surface area, chemical and mechanical stability, and a variety of surface and structural properties (Lin and Juang, 2002). Studies have reported a high adsorption capacity for clay in the removal of dye from textile effluent (about 300 mg of methylene blue/g dry clay) (Bagane and Guiza, 2000). Due to its properties, montmorillonite exhibits the highest cation exchange capacity (Bagane and Guiza, 2000). Studies have demonstrated the effectiveness of montmorillonite on the removal of Zn^{2+}, Pb^{2+}, Cd^{2+} and Al^{3+} (Brigatti et al., 1996; Stauton and Raubaud, 1997). Studies of Zn^{2+} and Cd^{2+} sorption on montmorillonite have shown that the metal adsorption capacity was affected by the polarizing effect (Pradas et al., 1994). Consequently, Cd^{2+} (11.4 mg/g) with less polarizing effect to surface charge is adsorbed on montmorillonite at twice the amount of Zn^{2+} (4.54 mg/g). Clay minerals, at water pH level between 6 and 9 have a negative surface charge and have no affinity to anionic species such as WO_4^{2-}. For this reason, the clay surface charge should be modified prior to any anion adsorption attempts.

Several studies have been conducted to investigate the adsorption performance of chitosan for the removal of heavy metals from aqueous solutions (Chiou and Li, 2002; Jin and Bai, 2002; Sag and Aktay, 2002). Chitosan, a product derived from chitin by N-deacetilation, is a natural, non-toxic, biodegradable, and hydrophilic cationic polymer of high molecular weight. The adsorption capacities of chitosan for Hg^{2+}, Cr^{6+}, and Cd^{2+} were found to be 815, 273, and 250 mg/g, respectively (Babel et al.,

2003). The adsorption of tungsten on cross-linked chitosan has been performed at a pH level of between 1 and 5 and the maximum tungsten recovery was $97.4 \pm 6.7\%$ (Gao et al., 2000)

Although chitosan has metal binding properties, non cross-linked chitosan is soluble in acidic media. This represents the main disadvantage of chitosan for practical applications as an adsorbent. In order to overcome this issue and improve the chemical and mechanical stability of chitosan, various chemical modifications can be performed. Chitosan can be either cross-linked with a cross-linking agent such as epychlorohydrine or coated on other materials. A chitosan coated onto ceramic alumina for the removal of Cd^{2+}, Cr^{3+}, Cr^{6+}, Pb^{2+}, Hg^{2+}, Ni^{2+} was investigated and the adsorption capacity of coated biosorbent on a per gram basis of chitosan was found to be 13 mg Cd^{2+}/g, 75 mg Cr^{3+}/g, 154 mg Cr^{6+}/g, 130 mg Pb^{2+}/g, 370 mg Hg^{2+}/g and 75 mg Ni^{2+}/g (Boddu et al., 2004).

Taking advantage of the adsorption properties of both chitosan and clay, in addition to their availability, chitosan-coated clays may be a promising, effective, and efficient adsorbent for tungsten removal from drinking water. The objective of this study was to develop a low cost biosorbent (montmorillonite clay coated with cross linked chitosan) and investigate its efficacy to remove tungsten from drinking water.

2. Experimental

2.1. Materials

The low molecular weight chitosan was purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Sodium tungstate (99% purity), epychlorohydrin (99% purity) and bentonite K10 (montmorillonite) were purchased from Acros Organics (Gell, Belgium). Sodium hydroxide (1N), hydrochloric acid (1N) and glacial acetic acid (analytical grade) were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Min-U-Sil particles were obtained from Zeta-Meter, Inc, (Staunton, VA).

2.2. Methods

2.2.1. Coating clay particles with chitosan

Chitosan solution was prepared by following the procedure described by Boddu et al., 2003. Bentonite K10 was added to the chitosan solution and the mixture was stirred at 40 ºC for 10 to 12 hours. Next, epychlorohydrin as a cross-linking agent was added to the clay-chitosan mixture and stirred for 12 additional hours under the same stirring conditions and temperature of 50 ºC. Afterwards, the slurry was allowed to settle and the clear liquid was decanted. The coated clay particles were washed twice with double deionized water (DDI), filtered under vacuum with Watman 40 filter paper, and dried in an oven at 70 ºC for 24 hours (Despatch). Finally, coated clay particles were stored in bottles.

2.2.2. Zeta potential of clay and coated clay

The zeta potential values of clay and chitosan coated clay particles in DDI water and feed water (water spiked with tungsten) were determined at the pH of 4, 5.5, and 6.4 with Zeta-Meter 3.0+ (Zeta-Meter Inc., Staunton, VA). Prior to all zeta potential measurements, the accuracy of Zeta meter was

confirmed with a Min-U-Sil standard solution (between -52 and –56 mV as indicated by the manufacturer).

0.1 g of clay or coated clay particles were suspended in 100 mL of DDI water or feed water and the mixture was equilibrated at room temperature for a desired time period of between one day and seven days. During the equilibration period, the mixture was periodically hand shaken. Then, about 30 mL of air bubble free solution was poured into the electrophoresis cell and platinum cathode and molybdenum anode were mounted on the cell. Anode and cathode were connected to the DC voltage. According to the sample conductance, an appropriate voltage (75 – 300 V) was applied to the electrophoresis cell. Particles as they moved from cathode to anode or anode to cathode in the electrophoresis cell were detected and tracked by using an installed microscope and a tracker. The average zeta potential (ZP) of particles in mV, the standard deviation and the number of tracked particles were read from the Zeta Meter. ZP values were corrected for the temperature effect (Corrected ZP = C_t x ZP, where ZP is the value from Zeta meter 3.0+, C_t is the temperature correction factor and is equal to 1.03 at 21 ºC).

2.2.3. Removal of Tungsten from water using clay and chitosan coated clay

Simulated water spiked with tungsten was used for the tungsten removal experiments. Stock solution was prepared by dissolving 1.8122 g of sodium tungstate (i.e. 1 g of tungsten) in 1 L DDI water. This stock solution was diluted to the experimentally desired tungsten concentrations (i.e., 500, 250, 100, 50, 20 ppm) by step dilution and used as feed water.

Feed water (100 mL) and 2 g of clay particles or chitosan coated clay particles were combined in a 125 mL glass bottle. The solution pH was adjusted to the desired pH values (4, 5.5, and 6.4,) with sodium hydroxide or hydrochloric acid. Then, glass bottles were placed on the shaker (model G76, New Brunswick Scientific Co, Edison, NJ) and mixed at 520 rpm at room temperature (~25 ºC) for four days. Then, the solution was poured into a 50 mL centrifuge tube and centrifuged for 10 minutes at a speed of 5000 rpm using a Beckman Model J-2-21 centrifuge (Backman Instruments Inc., Palo Alto, CA). Next, the supernatant liquid (product water) were collected and analyzed for tungsten concentration.

The concentration of tungsten in the feed and product waters were determined according to the standard methods of EPA 200.7 (EPA, 1994a) and 200.8 (EPA, 1994b) with established guidelines outlined in our previous work (Gecol et al., 2004). EPA 200.7 was used for samples with tungsten concentration higher than 1 ppm. Samples with tungsten concentration lower than 1 ppm were diluted and analyzed according to the standard method of EPA 200.8. The mean of the three concentration values were reported.

3. Results and discussions

3.1. Zeta potential of natural clay and coated clay

The variation of the net surface charge on both natural clay and chitosan coated clay with respect to water pH has been studied in order to determine the effect of chitosan coating on the surface properties of natural clay. The results of the charge variation as a function of pH are shown in Figure 1. As seen in Figure 1, the net surface charge of natural clay is significantly changed upon coating with chitosan. The point of zero charge (PZC) increased from a pH of about 2.8 (natural clay) to 5.8 (chitosan coated clay), confirming a successful coating. Over a wide range of pH (up to about 5.8)

chitosan coated clay exhibit a net positive charge attributed to the protonation of the amino groups in chitosan at low pH values. Above the PZC, the chitosan coated clay shows a net negative charge due to lack of protonation and adsorption of OH⁻ ions. On the other hand, natural clay is negatively charged throughout a wide range of water pH (above a pH of 2.8). Therefore, it is expected that chitosan coated clay will adsorb oppositely charged tungsten anions more effectively than natural clay below a water pH of about 5.8.
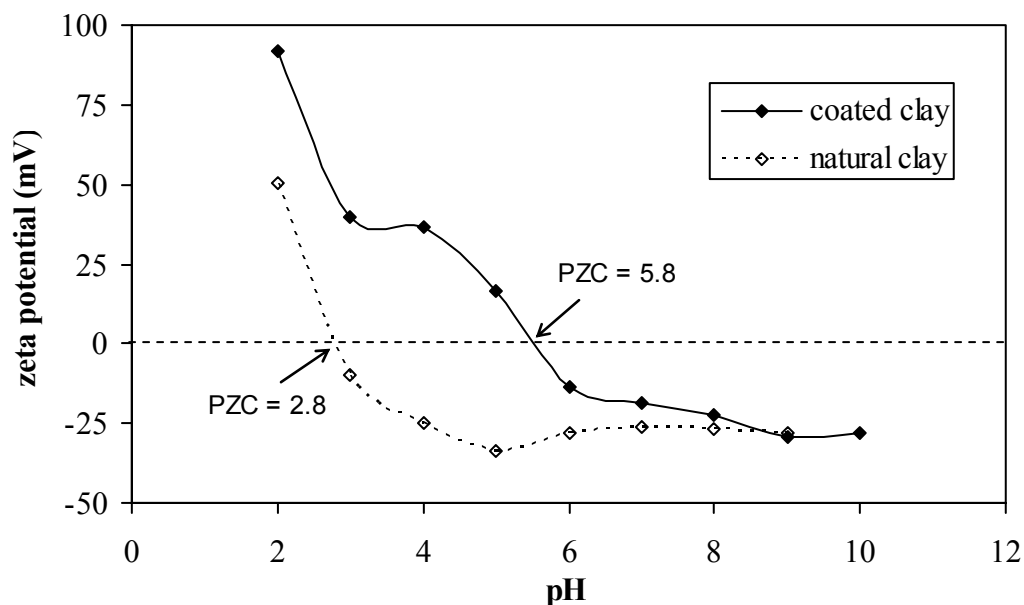

Figure 1. Zeta potential of coated clay and natural clay in DDI water as a function of pH.

The stability of the chitosan coating and the net surface charge are fundamental in understanding the behavior of these particles in solution and their binding capacity for tungsten. Therefore, further zeta potential studies with both coated clay and natural clay particles with respect to equilibration time for different water pH were conducted. Figure 2 shows the zeta potential values of coated clay and natural clay at pH 4, 5.5, and 6.4 equilibrated in DDI water. It is seen that the net surface charges for both coated and natural clay did not change for a period of 7 days. This is especially important for practical applications since it confirms that the chitosan coating is stable and that there is no significant bulk or surface erosion of the cross-linked chitosan.

In all cases, chitosan coated clay has a higher surface charge density than natural clay (around 45 ± 2 mV at a pH of 4 being the highest). It was found that the charge density significantly decreases with increasing water pH. It was reduced to 26 ± 2 mV at pH 5.5 and became negative at higher pH (-17 ± 2 mV at pH 6.4) above its PZC. On the other hand, the charge density of natural clay remained negative and the effect of water pH was less pronounced (Figure 2).

The change in charge density for coated clay at pH 4 was also studied in solutions containing tungsten. The effect of tungsten addition (20 and 50 ppm) on the charge density is shown in Figure 3. A slight decrease in the charge density with increasing tungsten concentration was observed, which is attributed to the consumption of positively charged sites due to adsorption of tungsten anions.
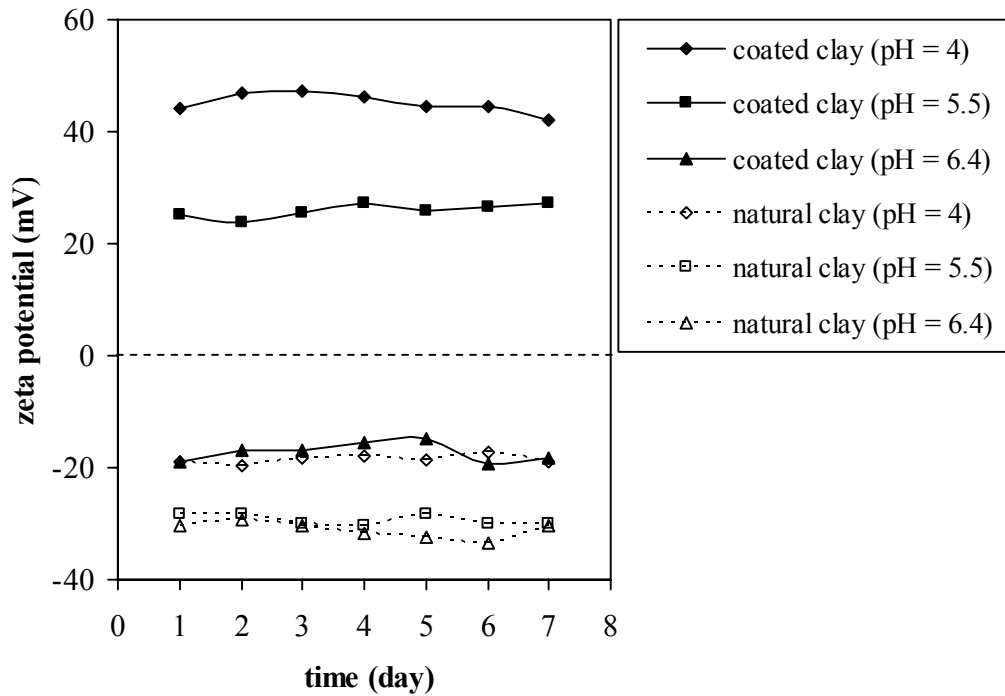
Figure 2. Zeta potential of coated clay and natural clay as a function of time and pH.
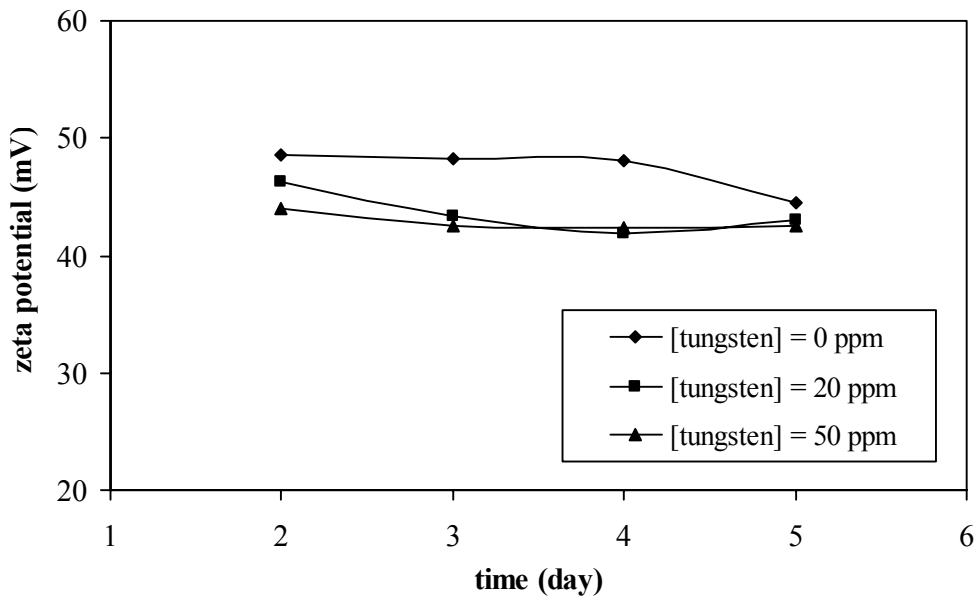
Figure 3. Zeta potential of coated clay as function of tungsten concentration and time.

3.2. Removal of Tungsten with chitosan coated clay and natural clay

The experimental results for the removal of tungsten with both coated clay and natural clay are shown in Table 1 and Figure 4. The effects of feed water tungsten concentration (20 to 500 ppm), and water pH levels on the removal of tungsten are shown in Figure 4. As seen in Figure 4, tungsten

removal is significantly higher with the use of chitosan coated clay at all pH levels studied. However, it decreases with increased initial tungsten concentration for both coated clay and natural clay and the decrease in tungsten removal efficiency with the use of natural clay is more pronounced.

Tungsten removal with both chitosan coated clay and natural clay is influenced by pH, with tungsten removal being the highest at pH 4 (Figure 4). For chitosan coated clay, this can be attributed to the fact that higher electrostatic attraction of tungsten anions to chitosan occur due to the increased protonation of amino groups in chitosan with decreased pH level (Gao et al., 2000). Furthermore, the adsorption of tungsten also depends on its aqueous chemistry. The valence state and the molecular form of tungsten ions greatly affect the adsorption mechanism. At water pH of 4, the dominant tungsten species exist in valence form of -3, and -6. On the other hand, when the pH level is higher than 4 but lower than 7, the positive valance tungsten species (+1 and +2) coexist with negative valance tungsten species (-1, -3, -4, -5, -6, and -10) in water (Lassner and Schubert, 1999). Therefore, the extent of adsorption will largely be influenced by the quantitative distribution of tungsten anions in solution.

Table 1. Removal efficiency of coated and natural clay (C_e is equilibrium concentration)

pH	C_o	$C_{e, natural clay}$	$C_{e, coated clay}$	Clay	Coated Clay
	20	0.4	0.2	98.2	99.2
	50	3.4	0.1	93.3	99.8
4	100	13.1	0.9	86.9	99.1
	250	136	2.0	45.6	99.2
	500	367	131	26.6	73.8
	20	4.9	0.7	75.4	96.6
	50	20.6	0.9	58.8	98.3
5.5	100	54.1	4.9	45.9	95.1
	250	201	75.1	19.6	70.0
	500	459	306	8.2	38.8
	20	10.1	1.4	49.5	92.9
	50	25.1	4.7	49.8	90.6
6.4	100	57.4	9.4	42.6	90.6
	250	184	66.6	26.4	73.4
	500	409	322	18.2	35.6

The Concentration (ppm) header spans C_o, $C_{e, natural clay}$, and $C_{e, coated clay}$ columns. The Removal (%) header spans Clay and Coated Clay columns.
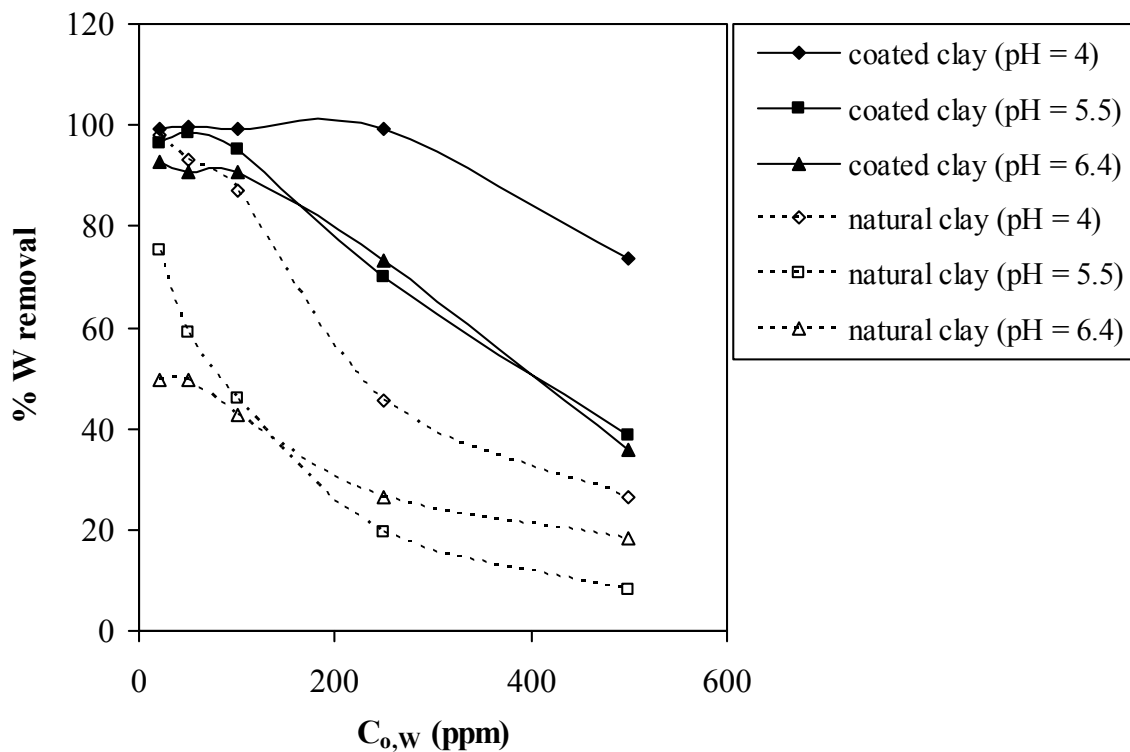
Figure 4. Removal efficiency as a function of initial tungsten (W) concentration.

Conclusion

The net surface charge of natural clay shifts from negative to positive upon coating with chitosan as confirmed by zeta potential measurements. The point of zero charge (PZC) of natural clay and chitosan coated clay was found to be 2.8 and 5.8, respectively. The chitosan coating on clay was found to be stable over seven days. Zeta potential measurements show that the net surface charge of chitosan coated clay decreases with increased tungsten concentration in feed water since the positively charged sites are consumed due to adsorption of tungsten anions. The removal of tungsten from simulated water using chitosan coated clay and natural clay was also investigated. Chitosan coated clay was found to be much more effective. The initial tungsten concentration and water pH significantly affect the removal of tungsten for both the use of chitosan coated clay and natural clay. Tungsten removal became decreases with the increase in initial tungsten concentration and high pH.

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