Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.934724

56 (2015) 232–238
September

Taylor & Francis
Taylor & Francis Group

Removal of tungsten from electroplating wastewater by acid- and heat-treated sepiolite

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Received 6 November 2013; Accepted 2 June 2014

ABSTRACT

In this study, the removal of tungsten from electroplating wastewater by adsorption on sepiolite has been investigated. To improve its performance, the natural sepiolite, was treated using H_2SO_4, followed by a heat treatment. The results obtained from the adsorption experiments showed that the acid- and heat-treated sepiolite had much higher adsorption for tungsten compared to the untreated (natural) sepiolite. The pH and temperature were important parameters in the adsorption process: the tungsten adsorption onto the acid- and heat-treated sepiolite increased at a lower pH and higher temperature, and the maximum adsorption capacity of 48.3 mg/g was obtained at pH 4.0, 55˚C, initial concentration of tungsten of 300 mg/L, and the sepiolite to liquid ratio of 0.5 g/100 mL. The acid- and heat-treated sepiolite was applied to electroplating industrial wastewater containing 265 mg/L tungsten, under the conditions of pH ≤ 6, 25–55˚C, more than 98% of tungsten was removed. It was concluded that the acid- and heat-treated sepiolite is a potential adsorbent that can be commercially used to remove the residual tungsten in industrial wastewater.

Keywords: Tungsten; Electroplating wastewater; Sepiolite; Acid and heat treatment

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1. Introduction

Heavy metals are common pollutants found in various industrial effluents. The strict environment regulation on the discharge of heavy metals makes it necessary to develop effective technologies for their removal [1]. Tungsten (W) is a heavy metal that is widely used in industry, such as steel, aerospace, and electronics industries [2]. The negative effects of tungsten to the receiving environment have been discussed by Strigul et al. [3]. Tungsten has also been identified in at least six of the 1,636 hazardous waste sites that have been proposed to be included in the EPA National Priority List for clean up. In China, a large amount of electroplating wastewater containing tungsten is discharged, which has received much public attention. In this context, China has imposed an emission limit of 2 ppm for the discharge of wastewater containing tungsten to the environment. However, there is limited information about techniques for removal of tungsten. Therefore, there would be an urgent need to develop economical/practical solutions.

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Water treatment techniques such as ion exchange, coagulation, and membrane filtration are well known for heavy metal removal. However, these treatment techniques are infeasible to remove trace amounts of impurities due to the costs associated with their practical application. Adsorption has been found to be an efficient and economic method to remove heavy metals. Various adsorbents, e.g. activated carbons, artificial adsorbents, and natural adsorbents have been extensively used to remove heavy metals from wastewater [4–6]. Sepiolite is a natural fibrous morphology clay mineral with a theoretical formula of $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4{\cdot}8H_2O$ [7]. It has fine microporous channels of dimensions 0.37 × 1.06 nm running parallel to the length direction of fibers [8]. Its structure has provided sepiolite with good adsorption properties. Sepiolite can have a very high specific surface area, as much as 900 m^2/g in theory [9], which is much larger than other natural adsorbents such as kaolinite, vermiculite, montmorillonite, bentonite, and zeolite. Compared with activated carbons and artificial adsorbents, the cost of sepiolite is much lower, about US$ 0.04–0.07/kg. Sepiolite has been studied as an effective and economical sorbent material for wastewater treatment, including the removal of dyes and pigments [10–17], the adsorption of surfactants [18], the adsorption of pesticides [19], and the removal of heavy metal ions [1,20–22].

There are several studies regarding the removal of heavy metal ions from wastewater using sepiolite as an adsorbent found in the literature, while that applied for the tungsten removal in the industrial wastewater was less. To improve its adsorption capacity, various surface modification methods like heat and acid treatment are applied to treat natural sepiolite by many researchers [16,19]. In this study we firstly investigated the effect of acid and heat treatment on the structure and the adsorption capacity for tungsten by the acid- and heat-treated sepiolite, then the removal of tungsten from electroplating wastewater by adsorption of the treated sepiolite was investigated.

2. Materials and methods

2.1. Materials

Sepiolite sample used in this study was obtained from Guangda Co. in Hunan, China. The chemical compositions of the sepiolite sample, determined by X-ray fluorescence spectroscopy, are presented in Table 1. The specific surface areas, pore volume (V_{pore}) and pore diameter (D_{pore}) of the natural sepiolite based on the BET equation, were determined from the N_2 adsorption isotherm on a surface area analyzer (Micromeritics ASAP 2400) [23] and the results are shown in Table 2.

Synthesized wastewater sample was prepared by dissolving 2.6913 g of sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$) (i.e. 1.5000 g tungsten) in 5 L of deionized water, and it was used for the adsorption experiments. The concentration of tungsten was 300 mg/L.

Electroplating wastewater containing tungsten used in this study was obtained from an electronics factory in Guangdong, China. Its pH was about 9.0, tungsten was in the form of tungstate anion (WO_4^{2-}). The concentration of tungsten was 265 mg/L, as determined using ICP-OES (Agilent 720).

2.2. Acid and heat treatments of the sepiolite sample

First, 20.0 g natural sepiolite sample was mixed with deionized water (400 mL) and stirred for 3 h at room temperature, which was then filtered under vacuum and washed several times using deionized water. Subsequently, the sample was dried at 60℃ in an oven for 24 h. Then the sepiolite was mixed with 1.0 mol/L H_2SO_4 in solid–liquid ratio of 1 g/10 mL [19,24,25], and the mixture was stirred continuously for a specified time at 25, 40, or 60℃, subsequently the sepiolite solid was filtered under vacuum and washed several times, and then dried. Thus the obtained sample was denoted as the "acid treated sepiolite" sample. The Mg^{2+} removal was determined using ICP-OES (Agilent 720).

The acid treated sample was subjected to the heat treatment under the conditions of 200℃ for 3 h to obtain the acid- and heat-treated sample. These heat treatment conditions were recommended in earlier studies [16,24,26].

2.3. Adsorption experiments

Sorption studies were performed by the batch technique to obtain the equilibrium data [16]. Adsorption experiments were carried out using 100 mL of synthesized sample and 0.5 g of sepiolite samples in a series of 200 mL glass bottles. The pH was adjusted to the desired pH (4, 6, 8, and 10) using sodium hydroxide or hydrochloric acid solution. The glass bottles were then placed on the shaker, which was set at 200 rpm at a specified temperature for 1 h. At the end of the adsorption period, the solution was centrifuged for 15 min at 3,000 rpm, the supernatant was collected and the concentrations of the residual tungsten were determined using ICP-OES (Agilent 720). The amounts of tungsten adsorbed (Q_e) (mg/g) were calculated as Eq. (1):

Table 1
Chemical compositions of the natural sepiolite and acid and heat treated sepiolite samples

	Weight/(%)	
Chemical composition	Natural sepiolite	Acid and heat treated sepiolite
SiO_2	56.82	73.96
MgO	21.69	12.33
CaO	7.25	2.51
Al_2O_3	0.071	0.045
Fe_2O_3	0.046	0.039
K_2O	0.037	0.026
Na_2O	0.018	0.012
MnO_2	0.0021	—
Ignition loss (%)	13.67	9.85

Table 2
Characteristics of the natural sepiolite and acid- and heat-treated sepiolite samples

Sample ID	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{pore} (nm)
Natural sepiolite	125.2	0.228	1.983
Acid treated sepiolite	382.6	0.529	2.186
Acid- and heat-treated sepiolite	415.8	0.576	2.197

$$Q_e = (C_0 - C_e)V/w \tag{1}$$

where C_0 and C_e, were the initial and equilibrium concentrations of tungsten in the aqueous phase in mg/L, respectively; V was the volume of the solution in liter (L); and w is the amount of dry adsorbent used in gram (g).

2.4. Removal of tungsten from the electroplating wastewater sample

The sample of 1 L was transferred to a beaker. The pH was adjusted to the desired pH using sodium hydroxide or hydrochloric acid solution. With the required amount of sepiolite addition, the content in the beaker was continuously stirred at 200 rpm for 1 h in a temperature bath. Then sepiolite was filtered, and the concentration of the residual tungsten in the filtrate was determined using ICP-OES (Agilent 720). The removals of tungsten (%) were then obtained.

2.5. Zeta potential measurements

The zeta potential of sepiolite suspensions was measured using a zeta meter (Ankersmid Zeta Meter 4.0, Netherlands) equipped with a microprocessor unit according to the literature [13,16].

3. Results and discussion

3.1. Acid and heat treatment of sepiolite

Several studies on acid and heat treatment of natural sepiolite have been studied to improve its adsorption capacity [16,19,24–27]. The acid treatment of sepiolite removes Mg^{2+} in its structure, thus greatly increasing its surface area [28,29], which also led to its structure changes. The soaking time and temperature can affect the structural changes during the acid treatment.

The magnesium ion removal is important for obtaining the desired properties of the treated sepiolite. Fig. 1 shows the effect of the soaking time on the magnesium ion removal at different soaking temperatures. With increase in the soaking time, the removal percentage of Mg^{2+} increased, and the higher the soaking temperature, the faster the Mg^{2+} removal. From Fig. 2, it can be seen that the specific surface areas of sepiolite reached the maximum at the Mg^{2+} removal of about 53%, which was 383 m^2/g. Similar observations were reported by Esteban–Cubillo [30] and Sabah et al. [31].

During the acid treatment, Mg^{2+} ions are displace by H^+, and silicon hydride bunches on the surface of sepiolite are converted to siloxanes [32]. As shown in Fig. 3, the Si–O–Mg–O–Si functions in sepiolite are changed to two Si–O–H groups during the acid treatment process. As a result, the number of micropores decreases, while the number of mesopores increases, the pore volume and the mean pore diameter are increased, consequently resulting in an increase in the specific surface area. If the removal of Mg^{2+} becomes excessive, the number of macropores increases, leading to the collapse of the crystalline structure, thus, a drastic decrease in its specific surface area [23,30,33]. Based on the results in Figs. 1 and 2, it was concluded that the optimal acid treatment time was about 125 min at 25℃, about 85 min at 40℃, and about 60 min at 60℃.

The characteristics of the acid treated, and acid- and heat-treated sepiolite are given in Table 2. A significant increase in the specific surface area, pore volume, and pore diameter was observed (Table 2). After the acid treated sepiolite was calcined (acid- and heat-treated sample), the specific surface area further increased from 382.6 to 415.8 m^2/g, and the pore volume and the pore diameter also increased. These can be explained by the removal of the zeolitic water during the calcination process [31].

As discussed above, acid- and heat-treated sepiolite removes Mg^{2+} ions from its original structure and resulting in the formation of many highly active silanol groups (Si–OH) [34], which can be potential adsorption sites. These treatments also changed the pore structure and physico-chemical properties of sepiolite structure. The adsorption capacity of the treated sepiolite for tungsten, and its comparison with that of the natural sepiolite, is shown in Fig. 4. As can be seen, the acid- and heat-treated sepiolite had much higher absorption capacity for tungsten than the natural sepiolite, in fact more than 2-fold increase than that of the natural sepiolite. Therefore, it can be concluded that the acid and heat treatment were beneficial to enhance the adsorption capacity of sepiolite for tungsten.

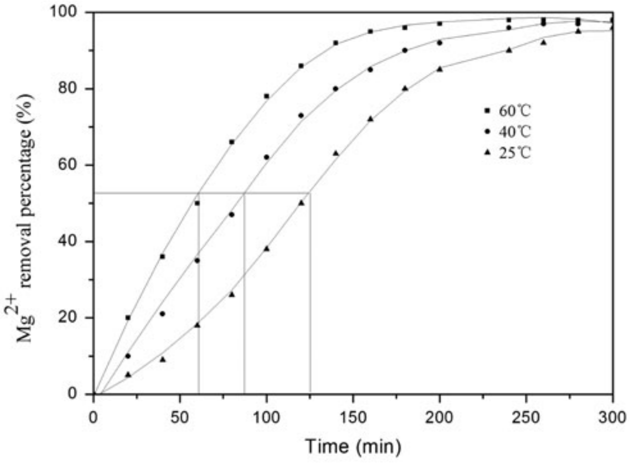

Fig. 1. Removal of Mg^{2+} during the acid treatment as a function of time at different temperatures. Conditions: 1.0 mol/L H_2SO_4 and solid–liquid ratio of 1 g/10 mL.

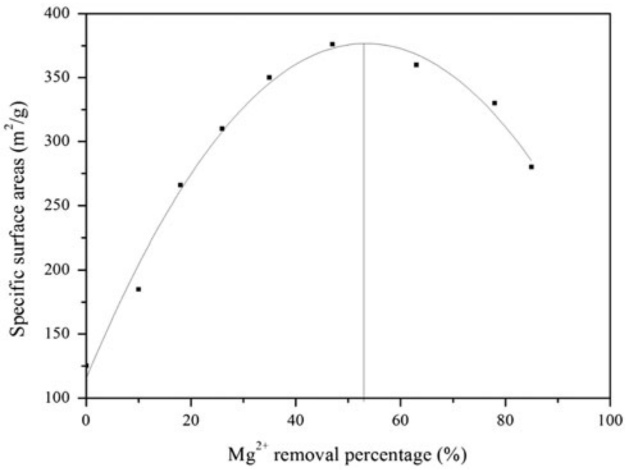

Fig. 2. Development of specific surface areas of sepiolite as the function of the Mg^{2+} removal. Conditions: temperature 40℃ and time 150 min.

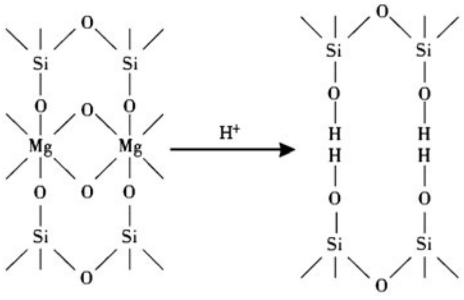

Fig. 3. Schematic of magnesium ion removal during the acid treatment of sepiolite.

3.2. *The adsorption capacity of acid- and heat-treated sepiolite for tungsten*

The pH and temperature are two important factors affecting the adsorption process. In order to study the influence of pH and temperature on the adsorption capacity of treated sepiolite, experiments were performed in a pH range of 4–10, and a temperature range of 25–55℃. Table 3 shows the results.

The pH affects the surface charge of the adsorbents as well as the degree of ionization of different adsorbates [10,35]. The results in Table 3 support the conclusion that the adsorption is highly dependent on the pH, and the adsorption capacity of acid- and

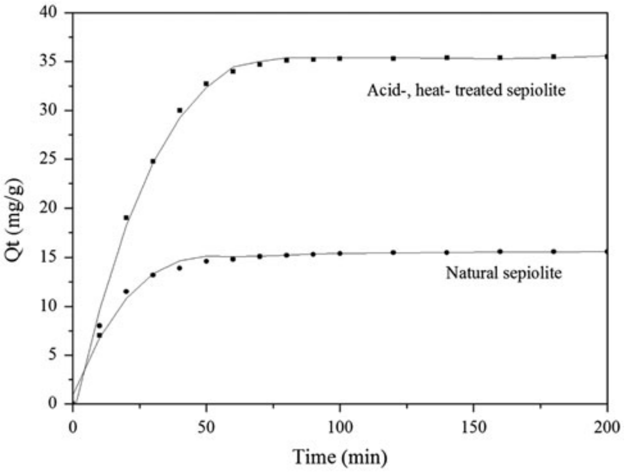

Fig. 4. Comparison of the adsorption capacity of acid- and heat-treated and natural sepiolite samples for tungsten. Conditions: temperature 25℃, pH 4.0, initial concentration of tungsten 300 mg/L and the sepiolite to liquid ratio 0.5 g/100 mL.

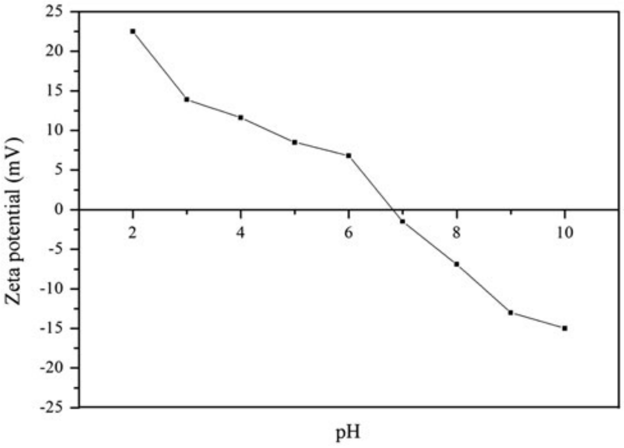

Fig. 5. The zeta potential of treated sepiolite as a function of pH. Conditions: the sepiolite to liquid ratio of 1.0 g/100 mL, 0.0001 M KCl and 25℃.

heat-treated sepiolite decreases with increasing in pH. Similar observations have been reported by others for adsorption of anionic pollutants on sepiolite [12,15,26], while the opposite is true for adsorption of cationic heavy metals [22,36] and other cationic pollutants [37]. According to previous studies [38], at pH of 4, the dominant tungsten species exist in valence form of −3 ($[HW_6O_{20}]^{3-}$) and −6 ($[H_2W_{12}O_{40}]^{6-}$). At $pH \geq 6.2$, tungsten is in the form of the tungstate oxyanion ($WO_4{}^{2-}$). At pH higher than 4 but lower than 6.2, the tungsten species mainly exist in the forms of $[W_6O_{20}(OH)_2]^{6-}$, $[HW_4O_{12}(OH)_4]^{3-}$, $[W_4O_{12}(OH)_4]^{4-}$ and $[HWO_4]^{-}$.

The zeta potential of acid and heat treated sepiolite as a function of pH is given in Fig. 5. As can be seen, the acid- and heat-treated sepiolite has an isoelectric point at around pH 6.8. In this case, the acid- and heat-treated sepiolite has a positive zeta potential below pH 6.8, and a negative zeta potential above pH 6.8. At pH lower than 6.8, the positive charges develop on the surface of treated sepiolite to form $S\text{–}OH_2{}^{+}$ groups due to protonation of silanol. At pH below 6.8, tungsten anions, such as $[HW_6O_{20}]^{3-}$ and $[H_2W_{12}O_{40}]^{6-}$ interact with positively charged sepiolite surface as follows (Eqs. (2) and (3)) [38,39]:

$$3S\text{–}OH_2^{+} + [HW_6O_{20}]^{3-} \longleftrightarrow (S\text{–}OH_2)_3[HW_6O_{20}] \quad (2)$$

$$6S\text{–}OH_2^{+} + [H_2W_{12}O_{40}]^{6-} \longleftrightarrow (S\text{–}OH_2)_6[H_2W_{12}O_{40}] \quad (3)$$

The above strong electrostatic interaction between the positively charged sepiolite surface and tungsten anions, would then be responsible for the high adsorption capacity of tungsten onto sepiolite.

With increasing pH, the protonation of silanol gradually decreases; and at pH higher than 6.8, the sepiolite surface appears negatively charged, leading to the ionic repulsion between the negatively charged sepiolite surface and the anionic tungsten. The above

Table 3
The adsorption capacity of acid- and heat-treated sepiolite for tungsten at various pH and temperature

pH	Temperature (℃)	Sorbent dosage (g)	Initial concentration of tungsten (mg/L)	Q_e (mg/g)
4	25	0.5	300	35.2
6	25	0.5	300	26.5
8	25	0.5	300	9.7
10	25	0.5	300	5.3
4	35	0.5	300	39.7
4	45	0.5	300	45.1
4	55	0.5	300	48.3

Table 4
Removal of tungsten from electroplating wastewater at various operating conditions

pH	Temperature (℃)	Sorbent dosage (g)	Initial concentration of tungsten (mg/L)	Residual concentration of tungsten (mg/L)	Tungsten removal (%)
4	55	5.5 (7.5)	265	18 (2)	93.2 (99.2)
4	25	7.5 (10.5)	265	22 (4)	91.7 (98.5)
6	25	10.0 (13.0)	265	23 (5)	91.3 (98.1)

explains the decreased adsorption capacity of sepiolite for tungsten [40].

The effect of temperature on the adsorption capacity of acid- and heat-treated sepiolite for tungsten was investigated at 25, 35, 45, and 55℃. As can be seen in Table 3, the adsorption capacity of acid- and heat-treated sepiolite gradually increases with increasing temperature, from 35.2 mg/g at 25℃ to 48.3 mg/g at 55℃. It indicates that the sorption of tungsten on sepiolite is promoted at higher temperature. Hence, the adsorption reaction is endothermic. Similar observations have been reported in previous studies [10,13,36].

In addition, with increasing the temperature, the diffusion rate of the adsorbates into the internal pores of sepiolite increases. Furthermore, the internal structure of the sepiolite swells at higher temperature. Both of the above favor the adsorption of tungsten onto sepiolite.

3.3. Removal of tungsten from electroplating wastewater

The acid- and heat-treated sepiolite was applied to treat an electroplating wastewater sample for removing tungsten. The results are shown in Table 4. The sorbent dosage was based on the absorption capacity established in Table 3 for complete removal of tungsten in the industrial sample. For example, at the condition of pH 4.0 and 55℃, the adsorption capacity of treated sepiolite for tungsten was 48.3 mg/g, if tungsten in 1 L electroplating wastewater was completely removed, the required sepiolite was about 5.5 g. As can be seen in Table 4, at the theoretical sepiolite dosage, tungsten removal was in the range of 91.3–93.2%, which may be explained by the presence of other anionic species in the industrial sample. With increasing the sepiolite dosage beyond the theoretical dosage (by 2–3 g/L), the tungsten removal was enhanced, reaching more than 98% in all three conditions studied.

The initial pH of the electroplating wastewater was about 9.0, which should be adjusted to the desired pH, and a higher temperature will be also favored.

4. Conclusion

Tungsten is a significant pollutant in the industrial waste water, such as that from the electroplating industry, this is particular true in China. Therefore, there would be an urgent need to develop economical/ practical solutions. In this project, the removal of tungsten from electroplating wastewater by the acid- and heat-treated sepiolite has been investigated. The results showed that the acid- and heat-treated sepiolite can be a potential absorbent for the tungsten in the industrial electroplating waste water. The acid and heat treatment enhanced the performance of sepiolite for this purpose. The results showed that the acid treatment using H_2SO_4, can increase the specific surface area, pore size, and pore volume. The subsequent heat treatment further improves these properties. Furthermore, it was found that the pH and temperature were important parameters in the adsorption of tungsten anions onto the treated sepiolite: it increased with decreasing pH and increasing temperature, and the maximum adsorption capacity of 48.3 mg/g was obtained at pH 4.0 and 55℃ at the initial tungsten concentration of 300 mg/L and the sepiolite to liquid ratio of 0.5 g/100 mL.

Acknowledgment

The authors wish to thank the National Basic Research Program of China (973 Program) of 2010CB732205, for financial support of this study.

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