Sorption of Cr(III) ion from aqueous solution by two kinds of modified diatomite
Er Li and Xiangying Zeng

ABSTRACT

Raw diatomite modified by microemulsion (DMM) and manganese oxide (MnD) were used for the removal of Cr(III) ions from aqueous solution. The characteristics and performance of these two types of modified diatomite on Cr(III) ion adsorption were compared. The results indicate that the Cr(III) ion adsorption capacities of diatomite were considerably improved after modifications by manganese oxide (MnO) and microemulsion. The surface area of MnD was increased because of the formation of MnO on the diatomite surface, and that of DMM was promoted owing to the existence of the hydrolyzed aromatic acid. Because of the stronger surface ionized function, the adsorption performance of Cr(III) ions in DMM was better than that in MnD. Within the experimental range of pH (i.e. 2.2–6.3), the Cr(III) ion removal of DMM (35–70%) was higher than that of MnD (33–59%) owing to the different electrostatic forces between the Cr(III) ion and the surface of the modified diatomite. The Cr(III) ion removal in MnD and DMM was improved with the increase of synthetic solution concentration in volumes from 0 to 2,500 mL.

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Key words | chromium removal, diatomite, manganese oxide modified, microemulsion modified

INTRODUCTION

With rapid growth of local industries such as plating, ceramics, mining, battery manufacturing, metal finishing and chromate preparation, heavy metal ion concentrations, especially that of the chromium (Cr), are increasing in water bodies and becoming a major concern for China. Normally the Cr(III) ion is very difficult to biodegrade and prone to accumulate in living organisms, causing ill-effects probably leading to diseases and disorders (Ijagbemi et al. 2009).

Despite conventional methods for the treatment of metal-containing wastes, such as chemical precipitation, membrane filtration, ion exchange, alum coagulation and adsorption tending to be the norm in the field, their safe and economical efficiencies especially their ability to eliminate Cr(III) ions are commonly in dispute (Ijagbemi et al. 2009; Rajfur et al. 2010). Therefore an alternative method with larger potential for better Cr(III) ion removals has been studied (Ijagbemi et al. 2009; Vega et al. 2009; Rajfur et al. 2010). Diatomite, consisting of a wide variety of shapes diatoms, in a structure containing up to 80–90% voids, is a pale-coloured, soft, lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae (Khokhotva & Waara 2010). Because of its highly porous structure, low density and high surface area, diatomite has been widely used in a number of industrial applications, e.g. as a filtration media for various beverages and inorganic and organic chemicals, and as an adsorbent for the treatment of oil spills (Ijagbemi et al. 2009). To enhance its capability to adsorb heavy metals from aqueous solution, the surface of diatomite should be modified (Ediz et al. 2010; Sari et al. 2010). Many modified methods for diatomite have been compared and as such two ways, microemulsion modified method and MnO modified method, have presented advantages. Microemulsion has been demonstrated quite efficiently in the recovery processes of metallic ions at a laboratory scale and MnO is verified to have high surface charge which is useful for modification (Aivalioti et al. 2010; Ediz et al. 2010; Sari et al. 2010).

In this paper, microemulsion and MnO have been used to modify diatomite. The aim of this study is to examine the effectiveness of local diatomite modified by microemulsion (DMM) and MnO for the removal of Cr(III) ions from aqueous solution. Furthermore, the comparison of their
characteristics and effect on the adsorption of Cr(III) ion is investigated.

MATERIALS AND METHODS

Adsorbent

In this study, raw diatomite was obtained through the National Territorial Resource Authority (NTRA) Suizhou, China. The samples were washed several times using deionized water and dried in an oven at 100°C overnight, then desiccated and stored in tightly stoppered glass bottles. Obtained by X-ray fluorescence (XRF), the detailed chemical composition of raw diatomite in mass percentage was: Al₂O₃ 13.26, SiO₂ 71.35, Fe₂O₃ 5.5, CaO 1.94, Na₂O 6.7, TiO₂ 0.08, MgO 0.15, K₂O 0.11, MnO <0.05, CuO <0.07. Raw diatomite was sieved into different Tyler sizes and the fraction passed through a sieve of 0.84 mm (+20 Tyler) and retained at 0.297 mm (−20 + 48 Tyler) used in the experiments.

Chemicals

Except for coconut oil and kerosene (chemical composition: paraffinic hydrocarbons ≥70%, aromatic hydrocarbons ≤20% and olefinic hydrocarbons ≤5%; density <1 g/mL; viscosity 2.7 St at 20°C; distillation range 150-300°C at 760 mmHg), all chemicals were analytical grade, and used without pre-purification.

Adsorbate

Heavy metal solutions containing copper, nickel and chromium with 2% NaCl were prepared in distilled water using sulfate salts. Based on the different conditions and requirements for each experiment, the solution concentration and pH were adjusted. The standard solutions were prepared in distilled water using potassium dichromate (500 mg L⁻¹), copper sulfate (100 mg L⁻¹) and nickel sulfate (500 mg L⁻¹). The concentration of heavy metal in aqueous solution were analyzed by flame atomic absorption spectroscopy (FAAS) using a VARIAN SpectrAA-10 PLUS in air-acetylene and nitrous oxide-acetylene flames.

Surface modification

The steps of raw diatomite surface modification with manganese oxide and microemulsion are shown as Table 1.

Surface area

The surface areas of MnD and DMM were estimated based on the Zn²⁺ adsorption method. A measure of 2 g samples of MnD and DMM was mixed with 25 mL of Zn²⁺ solution (2 M NH₄Cl, 0.1073 M ZnCl₂), stirred with a mechanical

Table 1 | Modification steps of MnD and DMM

<table>
<thead>
<tr>
<th>Step</th>
<th>MnD</th>
<th>DMM</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Sample of 15 g of raw diatomite immersed in 6 M sodium hydroxide at 90°C for 2 h.</td>
<td>Material prepared: 10 g of raw diatomite diatomite and 20 mL of microemulsion (its content: 20 wt% surfactant (saponified coconut oil); 20 wt% aqueous phase (deionized water); 30 wt% co–surfactant (isoamyl alcohol —99% P.A.) and 30 wt% oil phase (kerosene)).</td>
</tr>
<tr>
<td>2</td>
<td>The mixture was placed in 100 mL of 2.5 M manganese chloride (adjusted to pH 1–2 with hydrochloric acid) at room temperature, for 10 h.</td>
<td>The prepared diatomite and the microemulsion was mixed and shaken.</td>
</tr>
<tr>
<td>3</td>
<td>The manganese soaked diatomite was filtered and separated from the supernatant.</td>
<td>The mixture was placed dried at 65°C.</td>
</tr>
<tr>
<td>4</td>
<td>The solid was immersed in 6 M sodium hydroxide, at room temperature for 10 h to precipitate the manganese hydroxide.</td>
<td>The dried mixture was stored in tightly stoppered glass bottles.</td>
</tr>
<tr>
<td>5</td>
<td>The excess solution was decanted off and the diatomite left exposed to the air (to facilitate oxidation of manganese hydroxide to form a mixture of hydrated manganese oxide).</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>The samples were washed with deionized water, dried at 100°C, desiccated and stored in tightly stoppered glass bottles.</td>
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shaker for 24 h and then allowed to stand overnight. The supernatant solution was analyzed for Zn\(^{2+}\) content using atomic absorption spectroscopy.

**Adsorption isotherms**

Adsorption isotherms were obtained by adding 200 mL of a variable mass of sorbent into a fixed volume of chromium synthetic solution containing a constant metal-ion concentration (1.5 g L\(^{-1}\), pH 3.5). Experiments showed that equilibrium was reached after a contact time of 2 h. As a standard procedure, the mixtures were mixed by a thermostatic shaker at room temperature and samples withdrawn and filtered through a Whatman membrane filter (pore size 2.7 mm). The filtrate was analyzed by atomic adsorption spectroscopy. As one of the most common adsorption isotherm models, the Langmuir isotherm has been widely applied to many adsorption systems including organic and inorganic adsorbates. The model is applicable in cases where only one molecular layer of adsorbate is formed at the adsorbent surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration. This corresponds to complete coverage of the adsorbent surface by a monomolecular layer of adsorbate, which remains constant even at higher adsorbate concentrations (Ediz et al. 2010; Sari et al. 2010).

The quantity of adsorbed heavy metal ions on MnD and DMM was calculated as the difference between initial and equilibrium concentrations at equilibrium (mg mL\(^{-1}\)). The magnitude of the factor \(R_1\) indicates the nature of the interaction and the isotherm type: unfavourable \((R_1 > 1)\), linear \((R_1 = 1)\), favourable \((0 < R_1 < 1)\) and irreversible \((R_1 = 0)\) (Lourie & Gjengedal 2011).

**pH of a solution and surface charge density**

The pH of diatomaceous solution (pH\(_{\text{solution}}\)) was determined in 60 cm\(^3\) glass bottles where 2.5 g of modified diatomite and 25 cm\(^3\) of deionized water were added. The mixture was then agitated for 24 h and its pH was recorded using a pH meter. Furthermore, the surface charge of diatomite was estimated by following an alkali metric titration method (Rajfur et al. 2010).

**RESULTS AND DISCUSSION**

**Characterizations of MnD and DMM**

Based on the Zn\(^{2+}\) adsorption method, the surface areas of the MnD and DMM in this study, which depend on the solution acidity and the duration of the treatment, were estimated to be approximately 65 and 90 m\(^2\) g\(^{-1}\) in the same solution acidity (pH 4.3).

To show the effect of the two modified methods, Fourier transform infrared (FT-IR) was used. Figure 1 shows the FT-IR spectra of raw diatomite, MnD and DMM.

Figure 1 shows that the trend of spectra curve is similar at pH 4 and 5.2. Compared with the spectrum of raw diatomite, adsorption bands such as 486, 991, 1,383 and 3,602 cm\(^{-1}\) (Figure 1(a)) for MnD are replaced by 455, 1,015, 1,495 and 3,611 cm\(^{-1}\) (Figure 1(b)), respectively. The chemical interactions between the manganese oxide and the silanol groups on the diatomite surface may explain the absence of the bands. In addition the absence of adsorption bands at 507, 753, 1,536 and 3,687 cm\(^{-1}\) in the MnD spectrum (Figure 1(a)) and 515, 727, 1,605 and 3,725 cm\(^{-1}\) (DMM spectrum of Figure 1(b)) can be the response to the enlarged function of surfactant on the dissociation energy bond of silanol groups. The broad band at 3,630 cm\(^{-1}\) in the MnD spectrum of in Figure 1(a) and at 3,750 cm\(^{-1}\) in that of Figure 1(b) represent the O–H stretching of interlayer...
molecules and framework hydroxyl groups. The O–H reformation caused by the aromatic hydroxylation of the surfactant results in the broad band for DMM at 3,819 cm⁻¹ (Figure 1(a)) and 3,955 cm⁻¹ (Figure 1(b)). As shown in Figure 1(a), the different peak of the raw diatomite spectrum (the band at 821 cm⁻¹) and MnD spectrum (the band at 753 cm⁻¹) is caused by Mn–O stretching, and the corresponding difference of the raw diatomite spectrum (the band at 821 cm⁻¹) and DMM spectrum (the band at 806 cm⁻¹) is owed to the disturbance of the aromatic hydrocarbon of surfactant. A similar result can be drawn from Figure 1(b).

Surface charges for MnD and DMM

The surface charges of diatomite may arise from chemical reactions at the surface due to the presence of ionizable functional groups such as –OH, –COOH, –SH and –NH₃. The ionization of such groups results in electric charges (Vieira et al. 2010a, 2010b). For example, in the case of oxides and hydroxides, the surface charge is formed by the ionization of [MOH₂⁺] and [MO⁻]:

\[
[MOH_2^+] = [MOH] + [H^+]
\]

\[
[MOH] = [MO^-] + [H^+]
\]

The surface charge caused by these surface chemical reactions is known as the surface charge density, \(\sigma\). According to the above equations, \(\sigma\) is dependent on the degree of ionization and on the pH of the system. It is assumed that the H⁺ and OH⁻ ions are potential determining ions. Accordingly, the total negative charge can be determined from the amount of acid reacted, while the total positive charge can be determined from the total base consumed. Thus, the surface charge, \(\sigma\), can be calculated by applying Equation (6):

\[
C_A - C_B + [OH^-] + [H^+] = [MOH_2^+] - [MO^-]
\]

(6)

\(C_A\) and \(C_B\) represent the concentration of the base and acid added, while \([OH^-]\) and \([H^+]\) are the equilibrium concentration of the base and acid, respectively.

The concentrations of \([OH^-]\), \([H^+]\) are measured potentiometrically with a glass electrode and the final values are estimated by applying the following equation:

\[
pH = -\log[H^+] \text{ and } K_w = [OH^-][H^+] = 10^{-14}
\]

(7)

The mean surface charge, \(Q\) (mol/g), can then be calculated as a function of pH from the difference between the total added base or acid and the equilibrium OH⁻ and H⁺ ion concentration for a given quantity of the adsorbent:

\[
\frac{C_A - C_B + [OH^-] - [H^+]}{a} = Q
\]

(8)

If the surface area \(S\) (m²/g) of the adsorbent is known, the surface charges (C/m²) can be calculated:

\[
\sigma = \frac{QF}{S}
\]

(9)

where \(F\) is the Faraday’s constant (96,500 C/mol).

\(\sigma\) of the diatomite as a function of pH is shown in Figure 2. The intersection of the curve with the x-axis at surface charge density equals zero, defines the zero point.
of charge (pH\textsubscript{ZPC}). The total charges from the cations and anions at the adsorbent surface are equal to zero and these zero points of charge occur at pH 4.6 of MnD and pH 4.7 of DMM in Figure 1(a), and when pH 5.3 of MnD and pH 5.6 of DMM in Figure 1(b), respectively. The slight difference between the pH\textsubscript{ZPC} of MnD and DMM relate to their rather small differences in the quantity of activated proton (Vega et al. 2003; Khokhotva & Waara 2010). In addition the pH\textsubscript{ZPC} of both MnD and DMM are affected by the different quality of adsorbent. The hydroxyl groups present on the surface of the diatomite can gain or lose a proton, resulting in a surface charge that varies with changing pH. At low pH, surface sites are protonated and the surface becomes positively charged:

\[ \text{H}^+ + \text{MOH} \rightarrow \text{MOH}^+ \quad (10) \]

While at high pH, the surface hydroxides lose their protons, and the surface becomes anionic:

\[ \text{MOH} \rightarrow \text{H}^+ + \text{MO}^- \quad (11) \]

When the concentration of cationic MOH\textsuperscript{2+} sites equals the concentration of anionic MO\textsuperscript{-} sites, the average surface charge is neutral, at the zero point of charge (ZPC).

**Comparison of adsorption capacity for heavy metals: adsorption isotherms**

Normally Cr(III) ion tends to precipitate under alkaline solution conditions. In addition, diatomite powder is slightly unstable in higher pH conditions and filtration...
quality is improved at strong acidic pH (pH < 4). Therefore the batch isotherm studies are commonly conducted under the acidic conditions (pH ≤ 4). The equilibrium measurements focus on the determination of the adsorption isotherms. The relationship between the quantities of Cr(III) ions adsorbed by per unit mass of raw diatomite, MnD and DMM and the equilibrium concentration at the same temperature (23 °C) are shown in Figure 3. Due to $R^2 > 0.99$ ($R^2$-correlation coefficients for the Langmuir), all of the Cr(III) ion adsorption by raw diatomite, MnD and DMM could be described as an isotherm of Langmuir type. According to the results shown in Figure 3, the traditional observation that the number of sites on the diatomite surface is limited and the heavy metal forms a monomolecular layer on the surface at maximum capacity for the adsorbents is confirmed.

The Langmuir values of $q_0$ are calculated by the slope of each isotherm and $b$ is calculated based on the ordinate at the origin of each isotherm line. The results are shown in Table 1. According to the values of $R_l$ exhibited in Table 1, the adsorption behaviors of MnD and DMM are both extremely favorable ($R_l < 1$), and tend to be weakly irreversible adsorptions ($R_l = 0$) (Deliyanni et al. 2009; Vega et al. 2009; Vieira et al. 2010a, 2010b). On account of a lower value of $R_l$, the adsorption of DMM is more favorable than that of MnD. The maximum adsorption capacity ($Q$) reported in Table 2 demonstrates the lower adsorption capacity of MnD for Cr(III) ion removal than that of DMM.

Figure 3 and Table 2 demonstrate that the behaviors of both MnD and DMM for Cr(III) ion removal are distinctly superior to that of raw diatomite, and the Cr(III) ion adsorption by DMM is more significant than that by MnD. This can be owed to the increment in surface area of diatomite by different modification way. Furthermore as far as MnD is concerned, its surface charge results from the formation of manganese oxide onto the diatomite surface. Due to the large acidity constant of the manganese oxide surface, surface charge of MnO in solution is normally higher than that of other oxides, e.g. SiO$_2$, TiO$_2$ and Al$_2$O$_3$. This means that the surface ionizes at a low pH and carries a net negative charge which is greater than those of other oxides (Khokhotva & Waara 2010; Sari et al. 2010; Vieira et al. 2010a, 2010b). On the other hand, the improvement in performance of DMM can be attributed to the present aromatic

| Table 2 | Langmuir isotherm constants for adsorption of Cr(III) ion onto raw diatomite, MnD and DMM |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Type of diatomite | $Q$ (mg g$^{-1}$) | $b$ (dm$^3$ mg$^{-1}$) | $R_1 (×10^{-5})$ | $R^2$           |
| Raw diatomite   | Figure 3(a)     | Figure 3(b)     | 0.23            | 0.27            | 2.1             | 2.3             | 0.993           | 0.994           |
| MnD             | 18.18           | 20.16           | 0.23            | 0.27            | 2.1             | 2.3             | 0.993           | 0.994           |
| DMM             | 35.47           | 42.43           | 0.16            | 0.19            | 0.46            | 0.58            | 0.996           | 0.995           |
| Raw diatomite   | 49.85           | 58.13           | 0.08            | 0.11            | 0.33            | 0.42            | 0.991           | 0.994           |

Figure 4 | pH dependency of adsorption isotherms of DMM and MnD.
acid caused by hydrolysis (Vega et al. 2009; Khokhotva & Waara 2010; Vieira et al. 2009a, 2009b). This also leads to the surface charge increasing at a low pH. Because of the higher bond energy of aromatic compounds, the surface ionized function on DMM is much stronger than that on MnD (Khokhotva & Waara 2010; Sarı et al. 2010; Tomczak 2011).

Effect of pH on the heavy metal removal rate

The effect of pH on the removal percentage of Cr(III) ions from aqueous solution by MnD and DMM is illustrated in Figure 4. Within the experimental range of pH (pH 2.2–6.3), the Cr(III) ion removal of DMM varies from 35 to 70% in Figure 4(a) and from 55 to 81% in Figure 4(b), and that of MnD varies from 33 to 59% in Figure 4(a) and from 43 to 71%. This indicates that the increase of the mass of adsorbent will improve the removal of Cr(III) ions. Figure 4 also shows the maximum removal percentage by MnD and DMM take place at nearly pH 4 (pH 3.8 in Figure 4(a) and pH 3.6 in Figure 4(b)), and as expected the removal rates decline with pH > 4. Figure 4 exhibits that the Cr(III) ion removal by MnD and DMM are proximate at low pH ranges (i.e. pH < 3) but larger removals by DMM than those by MnD occur when 3 < pH < 6.3. The cause may be the different electrostatic forces between the Cr(III) ion and the surface of MnD and DMM (Vega et al. 2009). When σ decreases with an increment in pH of the solution, the electrostatic gravitation between Cr(III) ion and the surface of MnD (negative charge) is lowered, which results in reduced adsorption rates. In contrast the electrostatic repulsion between the Cr(III) ion and the surface of DMM (positive charge) while also lowered, will lead to the increased removals (Vega et al. 2009).

Comparison of heavy metal solution concentration

Cr(III) ion removal by DMM and MnD at pH 3.6 and 4 when equilibrium time = 24, 36, 48 and 64 h for adsorption is shown as Figure 5 (the solution volume varies from 0 to 2,500 mL). The results show that the removal by both MnD and DMM increase with the synthetic solution concentration. In addition, 36 and 24 h for MnD and DMM, respectively, showed optimum equilibrium time for maximum removal.

CONCLUSIONS

1. Compared with raw diatomite, the removal capability of the manganese oxide modified (MnD) diatomite and microemulsion modified diatomite (DMM) for Cr(III) ion are improved which is to be attributed to the increment of the surface areas.
2. The capacity for the sorption of Cr(III) ion of DMM is higher than that of MnD on account of the stronger surface ionized function.
3. The increasing pH has positive effect on the Cr(III) ion removal of DMM, and negative one on that of MnD.
4. The chromium synthetic solution concentration affects both of the removal for Cr(III) ion by MnD and DMM.

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