Article

A Research Study on Cr(VI) Removal from Contaminated Wastewater Using Natural Zeolite

Sandhya BABEL and Tonni Agustiono KURNIAWAN

Environmental Technology Program, Sirindhorn International Institute of Technology (SIIT), Thammasat University, P.O. BOX 22, Pathumthani 12121, Thailand

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Abstract

In this research, the technical feasibility of zeolite for Cr removal from contaminated wastewater was investigated using batch studies. Chemical treatment of zeolite with NaCl was also conducted to improve its adsorption capacity on Cr. The removal performances of all types of zeolite were evaluated and statistically compared. It was evident that the chemically treated zeolite showed significantly better Cr removal capabilities (3.23 mg/g) than as-received zeolite (1.79 mg/g) at 20 mg/l of Cr concentration. It was also found that the adsorption capacities of NaCl-treated zeolite at 5 and 10 mg/l of Cr concentrations were found to be 7.37 and 6.66 mg/g, respectively.

1 Introduction

The generation of Cr-contaminated wastewater is one of the critical problems arising from the local electroplating industries in Thailand. Chromium is present in the electroplating wastewater as Cr(VI). Due to its high solubility, Cr(VI) is highly toxic to living organisms and can cause various disorders, such as nausea and hemorrhaging. Various treatment techniques can be employed for treating Cr(VI)-contaminated water, including chemical precipitation, ion exchange, and reverse osmosis. But, these methods are unattractive due to their high cost. Adsorption using commercial activated carbon (CAC) can remove metals from electroplating wastewater. It may be possible to meet the stringent standard of Cr effluent discharges (<0.25 mg/l) in Thailand using the adsorption treatment method. However, CAC remains an expensive material for metal removal. To replace CAC, various low cost adsorbents have been investigated to achieve the economically feasible and effective treatment of Cr-contaminated water. It has been reported that chitosan can bind chromium. Due to the presence of its negatively charged lattice, which are exchangeable with certain metals, recently zeolite has been developed for metal removal. Treatment using zeolite for Cr-contaminated wastewater appears to be economically appealing as its current price (US$ 0.69/kg) is one-tenth of the price of CAC (US$ 6.78/kg).

In this study, zeolite is treated with NaCl. Using synthetic wastewater with varying Cr concentration (5 to 25 mg/l), the Cr removal performances of as-received and NaCl-treated zeolite are statistically compared. Both Langmuir and Freundlich isotherms were used to understand the adsorption mechanism of Cr removal by zeolite.

2 Experimental

2.1 Materials

Commercial grade zeolite with surface area 780 m²/g was used in this study. Potassium dichromate was used as the source of Cr(VI) in synthetic wastewater. The Cr stock solution (500 mg/l) was prepared by dissolving 0.7071 g of K₂Cr₂O₇ in 500 ml of deionized water, while Cr concentrations were varied from 5 to 20 mg/l. The pH of Cr solution was measured using pH meter model pH PRO. Adjustment of pH was carried out using 0.1 N NaOH and/or 0.1 N H₂SO₄. Agitation of the system under
investigation was conducted on a rotary shaker type SserikerII PNP, while Cr concentration was analyzed by a spectrophotometer model CECIL/CE 1021.

2.2 Chemical treatment of zeolite with sodium chloride

Prior to the experiments, zeolite was treated with sodium chloride (NaCl) solution 2 M. The suspension was continuously mixed for 24 h using a rotary shaker. Zeolite was then separated from the supernatant using GF/C filters and the liquid was drained. The washing process was repeated to remove any excess NaCl on the surface of zeolite. Finally, the zeolite was dried for 3 h and stored until required for use.[4]

2.3 Batch adsorption experiments

To find the optimum dose, pH, agitation speed, and contact time, batch experiments were conducted using 20 mg/l of Cr concentration at ambient temperature. Adsorption isotherm tests were also carried out in the reaction mixture consisting of 1.5 g/l of zeolite and 0.1 l of Cr solution with varying Cr concentrations from 5 to 25 mg/l.

2.4 Chromium analysis

The change in Cr(VI) concentration due to adsorption was determined according to Standard Methods. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. Absorbance was measured at wavelength (λ) 540 nm.[5]

2.5 Statistical analysis

Statistical analysis with confidence interval 95% (p ≤ 0.05) was performed to evaluate if there was any significant difference in terms of chromium removal efficiency between as-received and NaCl-treated zeolite.

3 Results and discussion

3.1 Effect of chemical treatment on zeolite

Zeolite contains a complement of exchangeable Na⁺, K⁺, Mg2⁺, and Ca2⁺, with selectivity of metals as follows: K⁺>Mg2⁺>Ca2⁺>Na⁺. To prepare the zeolite in the homoionic form of Na⁺, zeolite was conditioned with NaCl, the most effective exchangeable ion for metal removal. It was reported that after treatment with NaCl, K⁺ and Ca2⁺ were strongly held by the zeolite in preference to Na⁺ and that Mg2⁺ was not exchangeable. Therefore, the contents of K⁺, Ca2⁺, Mg2⁺ in zeolite were ignored. [6]

3.2 Effect of dose

The results, presented in Fig. 1, show that the adsorption efficiency of as-received zeolite increased from 2 to 43% with an increase in the amount of dose to 25.5 g/l; beyond this dose, the adsorption efficiency of as-received zeolite on Cr was almost constant. Similarly, the removal efficiency of NaCl-treated zeolite also increased from 20 to 74% with increasing dose to 9 g/l. Therefore, 25.5 and 9 g/l of as-received zeolite and treated-zeolite, respectively, were selected for the remaining adsorption studies.

A remarkable difference of Cr removal efficiency was also seen for both types of zeolite (p ≤ 0.05; paired t-test). This may be due to the fact that treatment of zeolite with NaCl rendered the zeolite in the homoionic form of Na⁺. Consequently, the Na⁺ of zeolite could be replaced by Cr3⁺ in the solution.

3.3 Effect of pH

Knowledge of optimum pH is important since pH of solution affects the surface charge of the adsorbent. To find the effect of pH on the removal efficiency of Cr, the pH of solution was varied from 2.0 to 9.0.

In this study, the removal efficiency of zeolite on Cr was found to be strongly dependent on pH. In general, the adsorption curves are characterized by a gradual increase of removal efficiency up to pH 4.5 and then, a significant reduction occurs beyond
pH 6.5. It is indicated that adsorption by zeolite could not effectively occur at the pH greater than 7.00 as the removal efficiency of Cr significantly decreased from 73 to 27% and from 57 to 10% for treated-zeolite and as-received zeolite, respectively.

3.4 Effect of agitation speed

Effect of agitation speed was investigated by varying the speed from 90 to 190 rpm. The adsorption efficiency of treated-zeolite and as-received zeolite slightly increased from 69 to 76% and from 50 to 58%, respectively, with an increase in shaking speed from 90 to 150 rpm, indicating that the Cr removal efficiency of zeolite was not much affected by shaking speed (p>0.05; ANOVA).

A shaking speed of 150 rpm, giving the maximum removal efficiency of Cr, was selected as the optimum speed for both types of zeolite and used for the remaining study. An optimum shaking speed is essentially required to maximize the interactions between Cr$^{3+}$ and the adsorption sites of zeolite during equilibrium.

3.5 Effect of contact time

To find the effect of contact time on the removal efficiency of zeolite, a series of experiments with different contact time varying from 30 to 270 min, were carried out with a initial Cr concentration of 20 mg/l. This study was conducted at optimum conditions of dose, pH, and shaking speed, where maximum Cr adsorption occurred.

It was found that the equilibrium between Cr and adsorbent was attained within 210 min, where treated zeolite had a relatively higher Cr removal efficiency (82%) than as-received zeolite (66%). No significant increase of adsorption efficiency occurred after 210 min of contact time (p>0.05; paired t-test).

3.6 Adsorption isotherm

a. Langmuir isotherm

The nature of Cr adsorption on zeolite, represented by a linearized Langmuir isotherm, is shown in Fig. 2. The Langmuir constants, determined from the intercept and slope of the plot of $1/Qe$ and $1/Ce$, are listed in Table 1.

The above figure demonstrates that treated-zeolite has a better fitting model of Langmuir isotherm than as-received zeolite under the concentration range studied, indicating that Langmuir isotherm is more applicable for treated zeolite than as-received zeolite. The values of $R_L$ in Langmuir isotherm indicated that favorable adsorption (0<$R_L$<1) of Cr took place on the zeolite uptake surface (Table 1).

Table 1 Adsorption capacities (mg/g) of zeolite for Cr(VI) ions based on Langmuir isotherm.

<table>
<thead>
<tr>
<th>Type of zeolite</th>
<th>$Q_e$(mg/g)</th>
<th>$R^2$</th>
<th>$a_m$</th>
<th>$b$</th>
<th>$R_L$</th>
<th>Equation of $Q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>1.79*</td>
<td>0.7690</td>
<td>1.7931</td>
<td>0.5004</td>
<td>0.0740</td>
<td>$Q_e=1.793Ce/(1+0.5004Ce)$</td>
</tr>
<tr>
<td>Treated with NaCl</td>
<td>3.23*</td>
<td>0.9951</td>
<td>3.2323</td>
<td>0.2905</td>
<td>0.1210</td>
<td>$Q_e=0.9391Ce/(1+0.2905Ce)$</td>
</tr>
</tbody>
</table>

*significant difference (p ≤ 0.05; paired t-test) between as-received and treated zeolite

b. Freundlich isotherm

The results of Cr uptake by zeolite are also plotted for the Freundlich isotherm. As demonstrated in Fig. 3, the plot of log $Qe$ and log $Ce$ has a higher regression coefficient for NaCl-treated zeolite than that of as-received zeolite; thus, indicating that the Freundlich isotherm is also applicable for treated zeolite. The constant values ($n$) of the Freundlich isotherm lie between 3 and 7 suggests that adsorption of Cr on zeolite was favorable (Table 2).

Fig. 2 A linearized plot of Langmuir isotherm for Cr uptake by zeolite

Table 2 Freundlich isotherm

<table>
<thead>
<tr>
<th>Type of zeolite</th>
<th>$Q_e$(mg/g)</th>
<th>$R^2$</th>
<th>$a$</th>
<th>$b$</th>
<th>$R_L$</th>
<th>Equation of $Q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>0.3077</td>
<td>0.5049</td>
<td>0.3077</td>
<td>0.0476</td>
<td></td>
<td>$Q_e=0.3077Ce^{0.5049}$</td>
</tr>
<tr>
<td>Treated with NaCl</td>
<td>0.1598</td>
<td>0.0002</td>
<td>0.1598</td>
<td>0.0002</td>
<td></td>
<td>$Q_e=0.1598Ce^{0.0002}$</td>
</tr>
</tbody>
</table>

Fig. 3 Freundlich isotherm for all types of zeolite
Between the two isotherms, Langmuir was found to be more representative for zeolite than Freundlich. This can be attributed to the fact that zeolite has a smaller surface area for Cr adsorption. Consequently, only monolayer adsorption occurred on its surface, regardless of any chemical pretreatment.

Table 2 Adsorption capacities (mg/g) of zeolite on Cr\textsuperscript{VI} based on Freundlich isotherm.

<table>
<thead>
<tr>
<th>Type of zeolite</th>
<th>(Q_e) (mg/g)</th>
<th>(R^2)</th>
<th>(N)</th>
<th>Equation of (Q_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>1.00**</td>
<td>0.6085</td>
<td>6.2590</td>
<td>(Q_e = 1.0005 \times C_e^{0.1598})</td>
</tr>
<tr>
<td>Treated with NaCl</td>
<td>1.11**</td>
<td>0.9643</td>
<td>3.2503</td>
<td>(Q_e = 1.1158 \times C_e^{0.3077})</td>
</tr>
</tbody>
</table>

**No difference (p>0.05; paired t-test) between as-received and treated zeolite.

3.7 Removal performance of zeolite at lower chromium concentrations

Although zeolite was capable for Cr removal at 20 mg/l of concentration, further investigations show that as-received zeolite has better removal capacities at lower Cr concentrations (5 and 10 mg/l) with adsorption capacities of 4.20 and 3.55 mg/g, respectively, while the adsorption capacities of NaCl-treated zeolite at 5 and 10 mg/l of Cr concentrations were found to be 7.37 and 6.66 mg/g, respectively; thus, suggesting that zeolite is also suitable for the treatment of chromium effluents at lower concentrations (5 and 10 mg/l).

3.8 Mechanism of Cr(VI) removal by zeolite

There are two major steps for Cr removal by zeolite. The first step is concerned with the reduction of Cr(VI) to Cr(III) according to the following reactions:

\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} + 14 \text{H}^+ + 6e \leftrightarrow 2 \text{Cr}^{3+} + 8 \text{H}_2\text{O} \tag{1}
\]

Since the pH of synthetic wastewater ranged from 5-6, Cr existed not only as \(\text{Cr}^{3+}\), but also as \([\text{Cr(OH)}]^2+\).\n
\[
\text{Cr}^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{Cr(OH)}]^2+ + \text{H}^+ \tag{2}
\]

The second step controlling the Cr removal by zeolite is represented as follows:

\[
[\text{Cr(OH)}]^2+ + \text{Na}_n\text{A}_{z_0} + n \text{H}_2\text{O}(s) \leftrightarrow [(\text{Cr(OH)})]^2-\text{H}_n\text{A}_{z_0} + n \text{Na}^+ + n \text{OH}^-(s) \tag{3}
\]

where A represents adsorption sites on the zeolite, while subscripts s and z denote “solution” and “zeolite” phases, respectively. Equation (3) shows that Cr uptake by zeolite mostly occurred due to ion exchange. However, some Cr removal by zeolite might be due to adsorption also.

As pH increased to 4.5, the adsorption reaction shifted from left to right, which resulted in the production of more surface complex \([(\text{Cr(OH)})]^2-\text{H}_n\text{A})\) on zeolite. It was also found that the final pH slightly increased after adsorption due to the fact that the hydrolysis reaction of zeolite caused more OH\textsuperscript{-} release into the solution.

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References