Silica Ceramic as Potential Adsorbent of Cadmium Removal from Aqueous Solutions

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Abstract: The removal of cadmium ions from contaminated water using silica ceramic was conducted in batch conditions. The effects of initial cadmium concentrations, contact time, adsorbent dose, particle size and temperature on the cadmium adsorption by silica ceramic have been studied. The process of cadmium adsorption follows a first-order rate expression. Result revealed that the Langmuir model provided a better fit to the experimental data in comparison with the Freundlich equation. Langmuir adsorption capacity was found 0.65 mg g⁻¹. It was found the adsorption of cadmium was slightly endothermic. Cadmium adsorption capacity at the equilibrium increases with the decrease of particle sizes and adsorbent doses.

Key words: Adsorption, cadmium, isotherms, kinetics, removal, silica ceramic

INTRODUCTION

Industrial wastewaters containing heavy metals are major source of environmental pollution. The main trace elements considered as most harmful for public health included Cd, Pb, Cu, Hg, Cr, Ni, As and Zn. These toxic metals are released into the environment in various ways. The major sources of cadmium (Cd) released into the environment are electroplating, smelting, alloy manufacturing, pigments, plastic (Tsekes, 2001) battery, forest fires, volcanic eruptions, mining activities and refining processes (Holan et al., 1993; Cheng and Volesky, 1995). The most significant contemporary source results from the production of nickel-cadmium batteries (Jarup et al., 2000).

Cadmium has been well recognized for its negative effects on the environment where it accumulates readily in living systems. Due to cadmium intake through food, water or smoke can cause chronic health problems, such as serious damage to human enzyme tissues specially kidneys and bones (Hasan et al., 2006), lung edema, renal dysfunction, liver damage, anemia and hypertension (Waalkes, 2000). It is well known that chronic cadmium toxicity has been the cause of Japanese Itai-Itai disease and renal abnormalities, including proteinuria and glucosuria (Nogawa et al., 2004).

Methods proposed for Cd removal from wastewaters are those employed for most heavy metals. A variety of processes exists for the removal of cadmium ions from industrial wastewaters. The conventional methods for the treatment of wastewater from mining, electroplating and metal finishing industry include physicochemical treatments such as: filtration, flocculation, vacuum evaporation, solvent extraction, membrane filtration, reverse osmosis, chemical precipitation.

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coagulation, ion-exchange, ultra-filtration or electrochemical deposition (Pacheco et al., 2006; Kentish and Stevens, 2001). Most of these technologies have strong limitations: some of them are pH dependent, which reduces the efficiency and variety of metal ions that can be removed; in other cases these can remove neither at very low nor at very high metal ions concentrations (Aksoy, 2005; Sawyer et al., 2004). However, cadmium is very difficult to remove because conventional methods employed for heavy metal removal such as chemical precipitation are either too expensive or unsuitable when confronted with the large discharge volume, low concentration wastewater runoff (Ullmanu et al., 2003). In this way, adsorption method stands out for its effectiveness to remove cadmium even at low concentrations over a wide range of pH values. Until now, many researches about cadmium adsorption have been conducted and the interest tends to be focused upon the use of low-cost, effective sorbents (Chun et al., 2001; Gabaldon et al., 2006). In this regard, various biomaterials and inorganic materials have been studied as sorbent. The biomaterial sorbents are mostly algae (Holm et al., 1993), fungi, sugar cane bagasse (Peterleme et al., 1999), rice husk, wheat barn (Nouh et al., 2007), pine bark, olive cake (Deyrunum and Celik, 2006), coconut husk, chitin (Benguella and Benaissa, 2002) etc. The inorganic sorbents are commonly iron hydroxides andoxyhydroxides (Mustafa et al., 2004), aluminium hydroxides and oxides (Bell and Saunders, 2005), clays, zeolite, calcite, manganese nodule residue (Agrawal and Sahu, 2006), peat (Hasan et al., 2006), peat (Gabaldon et al., 2006), activated carbon (Jusoh et al., 2007) etc. Some of those are suitable for cadmium adsorption. However, silica ceramic is an inorganic artificial material that is prepared by mountain sand powder, waste glass powder and seashell powder which containing mostly SiO₂, Na₂O, Al₂O₃, CaO and K₂O. A recent study found using different type of silica ceramic can remove As (III) (Salim et al., 2007) from contaminated water. So far, the study of sorption properties of this artificial sorbent for its application in the purification of cadmium containing water has not been studied yet.

The purpose of this research was to study sorbent behavior of silica ceramic with respect to cadmium, to investigate the efficiency of cadmium adsorption capacity through batch kinetics and equilibrium system and to explore the possibility of using this material for the purification of cadmium containing water. Although modeling of metal adsorption are usually carried out using linear regression analyses, first order kinetic model, Langmuir and Freundlich isotherms were used in the present study. During the experiments under this study, effects of different parameters such as initial concentration of cadmium, adsorbent dose, adsorbent size, temperature were also studied.

MATERIALS AND METHODS

The study was carried out during January 2007 to July 2007 at the relevant laboratory of Kochi University in Japan.

Chemicals

The reagents and acids used in this study were of analytical grade and used without further purification. The synthetic cadmium standard stock solutions for the present study were prepared from atomic absorption spectroscopy reference solutions for cadmium. All standard solutions were prepared by using distilled water. The reference solutions of atomic absorption spectroscopy contained cadmium metal as solute dissolved in 0.1 mol L⁻¹ nitric acid solvent. The chemicals were obtained from Kanto Chemical Inc. Ltd., Japan. Solutions of the 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

Adsorbent

The silica ceramic was obtained from EKOAIRANDO Co. Ltd. Kochi, Japan. This ceramic was made by various types of sand, seashell powder and waste glass powder with controlled temperature
Table 1: Physio-chemical properties of the silica ceramic

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value/Kind</th>
<th>Elements/Components</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle form</td>
<td>Granular</td>
<td>SiO₂</td>
<td>61.23</td>
</tr>
<tr>
<td>Color</td>
<td>Gray-Asht</td>
<td>Na₂O</td>
<td>8.47</td>
</tr>
<tr>
<td>Particle size (μm)</td>
<td>0.42-0.82</td>
<td>Al₂O₃</td>
<td>5.54</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>1.67</td>
<td>CaO</td>
<td>5.48</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.37</td>
<td>K₂O</td>
<td>1.40</td>
</tr>
<tr>
<td>Pore volume (cm³ g⁻¹)</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and pressure. The major components of chemical compositions of the silica ceramic are SiO₂, Na₂O, Al₂O₃, CaO and K₂O. The details physio-chemical properties are shown in Table 1. All batch experiments reported here with this silica ceramic having a 0.42-0.82 mm particle size.

Equipments

The experiments on adsorption by batch techniques were conducted in temperature-controlled shaker. The pH measurement was done using pH meter [Model: SevenGo pH, Mettler Toledo, Switzerland]. The chemical composition was determined by X-ray diffraction (XRD) [Model: X’Pert, Philips, Netherlands] and SEM-EDS [Model: JEOL-JSM 6500F]. The concentration of Cd determined by Atomic Absorption Spectrometer [Model: AAAnalyst200, Perkin Elmer, Singapore] at a wavelength of 228.80 nm. The instrument was calibrated by using Cd (II) standard solution of 0.6, 0.3 and 0.1 mg L⁻¹.

Batch Adsorption Studies

Adsorption experiments of Cd on silica ceramic were carried out in batch method. The experiments were conducted for optimum dose, equilibrium time, effect of concentrations, development of adsorption isotherms and effects of temperature. Silica ceramic was added as per dose requirements to glass conical flasks of 150 mL capacity with 100 mL of Cd solutions of desire concentration and pH and were shaken in a mechanical shaker at 140 rpm. The temperature was fixed at 25°C during all relevant experiments. The samples were taken at predetermined intervals.

The amount of the cadmium adsorbed per unit mass of silica ceramic (qₑ, mg g⁻¹) and the removal efficiency (Rₑ determined as the Cd removal percentage relative to initial concentration) of the system, was calculated as:

\[ qₑ = \frac{(C₀ - Cₑ) \times V}{M} \]  \hspace{1cm} (1)

\[ Rₑ(\%) = \frac{(C₀ - Cₑ)}{C₀} \times 100 \]  \hspace{1cm} (2)

Where:

- \( C₀ \) and \( Cₑ \) = Initial and equilibrium (or at any time) ion concentration (mg L⁻¹), respectively
- \( V \) = Volume in liter of solution
- \( M \) = Mass (g) of the silica ceramic

The effect of contact time was studied using 5 mg L⁻¹ of Cd concentration, particle size 0.42-0.82 mm, dose 20 g L⁻¹ (ceramic amount 2 g in 100 mL Cd solution) and shaking time 24 h. The effect of adsorbent doses was investigated using 10-100 g L⁻¹ (ceramic amount 0.5, 1, 1.5, 2, 3, 3.5, 4 and 5 g in 50 mL Cd solution), initial metal concentration 5 mg L⁻¹, particle size 0.42-0.82 mm and shaking time 4 h. The effect of solute concentrations was studied using 5, 10, 15 and 20 mg L⁻¹ of Cd
concentrations, particle size 0.42-0.82 mm, dose 20 g L\(^{-1}\) (ceramic amount 2 g in 100 mL of Cd solution) and shaking time 24 h. The effect of particle size was studied using three particle size groups; they were 0.075-0.42, 0.42-0.82 and 0.82-1.2 mm. In this study following things were used such as the adsorbent dose 20 g L\(^{-1}\) (ceramic amount 2 g in 100 mL Cd solution), initial metal concentration 5 mg L\(^{-1}\) and shaking time 12 h. The effect of temperature of Cd adsorption was carried out using temperature of 15, 25, 35 and 45°C, dose 20 g L\(^{-1}\) (ceramic amount 2 g in 100 mL Cd solution), particle size 0.42-0.82 mm, initial metal concentration 5 and 10 mg L\(^{-1}\) and shaking time 12 h.

**Isotherms Studies**

The equilibrium isotherms were determined by conducting constant mass 2 g of silica ceramic with solutions of different concentrations 10-80 mg L\(^{-1}\) of cadmium. The silica ceramic and cadmium solution were agitated in a series of 250 mL conical flasks with equal volume of solution of 100 mL for period of 24 h at 25°C constant temperature.

**RESULTS AND DISCUSSION**

**Effect of Contact Time**

There is a rapid increase in the adsorption in the initial stages as seen in the curve (Fig. 1). Maximum adsorption occurs at the 8th hour after which the adsorption remains uniform, represented by the accomplishment of equilibrium (Fig. 1). The amount of cadmium (II) adsorbed at this point is the maximum 0.25 mg g\(^{-1}\) under the particular operating conditions. Therefore, the removal of cadmium ion can be happen in two different stages such as one is comparatively fast and other is slower than previous. These observations are in similar with the works of Benaisa (2006) and Benguella and Benaisa (2002) with other metal ion-biometal systems. The time variation curve is smooth and continuous and this indicates the sorption capacity and formation of monolayer coverage on the outer interface of the sorbent under the operating conditions.

**Effect of Metal Initial Concentration**

To evaluate the effect of initial cadmium concentration on adsorption, the studied were conducted with initial cadmium concentrations of 5 to 20 mg L\(^{-1}\) of 100 mL solution with 2 g of silica ceramic was stirred at ambient 25°C temperature. These results indicated that the curves have the same shape (Fig. 2). Adsorption amount \(q_c\) (mg g\(^{-1}\)) increased with increase in cadmium concentration and remained constant after equilibrium time. It is clear from Fig. 3 that the adsorption of cadmium at different

![Graph](image)

Fig. 1: Effect of contact time on Cd(II) removal on silica ceramic (Contact time, 0-26 h; adsorbent dose, 20 g L\(^{-1}\); Cd(II) concentration, 5 mg L\(^{-1}\); temperature, 25°C and solution pH 5.6)
**Adsorption Dynamics**

The study on kinetics of adsorption is quite significant in wastewater treatment as it describes the solute uptake rate, which in turn controls the residence time of adsorbate uptake at the solid solution interface. It was found that the uptake of Cd increases with the lapse of time. However, the adsorption of Cd was rapid in first 6 h after which the rate slowed down as equilibrium approached. In order to determine the rate constant for adsorption, the first-order kinetics model has been used. A simple first-order kinetic model is represented by the Lagergren equation (Gupta et al., 1988) as given below:
Table 2: First order adsorption rate constant

<table>
<thead>
<tr>
<th>Cadmium concentration (mg L⁻¹)</th>
<th>Kads (L min⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.53×10⁻⁳</td>
<td>0.9937</td>
</tr>
<tr>
<td>15</td>
<td>5.99×10⁻³</td>
<td>0.8834</td>
</tr>
<tr>
<td>10</td>
<td>5.30×10⁻³</td>
<td>0.9884</td>
</tr>
<tr>
<td>5</td>
<td>9.67×10⁻³</td>
<td>0.9924</td>
</tr>
</tbody>
</table>

Fig. 4: Effect of adsorbent dose on cadmium adsorption (adsorbent dose, 10-100 g L⁻¹; temperature, 25°C, solution pH 5.6, Cd(II) concentration, 5 mg L⁻¹)

\[ \log(q_e - q_t) = \log q_e - \left( \frac{K_{st}}{2.303} \right) t \]  

(3)

Where:

- \( K_{st} \) = Rate constant of adsorption
- \( q_e \) and \( q_t \) = Amounts of Cd (II) adsorbed (mg g⁻¹) at time \( t \) (min) and at equilibrium time, respectively

Linear plots of \( \log (q_e - q_t) \) versus \( t \) on silica ceramic suggest the applicability of Lagergren kinetic model. The \( K_{st} \) values calculated from the slopes of these plots (Fig. 3) for different cadmium concentrations. The correlation coefficients for the first-order kinetics model were greater that 0.9834 at all the concentration studied. This shows that the adsorption process follows the first order rate expression (Table 2).

Effect of Adsorbent Dose

The sorbent dose was varied from 10 to 100 g L⁻¹ at a fixed initial cadmium concentration of 5 mg L⁻¹. The general trend indicates that 10-30 g L⁻¹ of sorbent dose uptake large amount cadmium, rapidly and 40-100 g L⁻¹ dose uptake little amount but slowly (Fig. 4). The amount of metal adsorbed per unit mass of sorbent decreases with increase in sorbent amount. The result suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remain constant even with further addition of the dose of adsorbent. A fixed amount of adsorbent can only adsorb a certain amount of metal due to particle interaction, such as aggregation, resulting from high adsorbent concentration. This aggregation would lead to a decrease in the total surface area of adsorbent (Ghodbane et al., 2007). Thus with increasing sorbent mass, the amount of cadmium sorbed onto unit weight of sorbent gets reduced, therefore causing a decrease in sorption capacity with increasing sorbent mass concentration (Nouri et al., 2007).
Effect of Particle Size

The experiments of effect of particle size have been carried out with a constant cadmium concentration of 5 mg L\(^{-1}\). The particle size ranges of silica ceramic were used 0.075-0.42, 0.42-0.82 and 0.82-1.2 mm. Figure 5 shows that the effect of contact time curves with different adsorbent particle size. It can be seen from the Fig. 4 that percent of cadmium adsorption within 2 h was 54.4 for 0.82-1.2 mm size, 64 for 0.42-0.82 mm size and 86.9 for 0.075-0.042 mm size. That means the cadmium adsorption capacity at the equilibrium increases with the decrease of silica ceramic sizes. The differences in particle size to reach the equilibrium showed have an influence on the contact time. Consequently, when employed particle sizes 0.075 mm required time was about 4 h to reach the saturated completely. While particle sizes 0.42-0.82 and 0.82-1.2 were applied, the saturated time required was about 10 h. Therefore, increasing particle size increases the time needed to reach equilibrium. Through these investigations, it is determined that particle size of silica ceramic affected the adsorption of cadmium from the solutions. The smaller particle size of the adsorbent attained the higher adsorption level (Izandoo and Nasseri, 2005; Beraissa, 2006), which may not be discrete to the fact that smaller particle provide large surface areas. There is tendency that smaller particle produce shorter time to equilibrate (Agrawal and Saha, 2006).

Effect of Temperature

To investigate the effect of the temperature of cadmium adsorption by silica ceramic, the temperatures were used 15, 25, 35 and 45°C. The amounts of adsorbent used 20 g L\(^{-1}\), contact time 12 h were kept for this experiment. Figure 6 showed the effect of temperature on the batch adsorption of 5 and 10 mg L\(^{-1}\) of cadmium. The rise in temperature the caused to increase the of adsorption of Cd 100% at 25°C of 5 mg L\(^{-1}\) and 92% at 45°C for 10 mg L\(^{-1}\), respectively (figure not shown).

The results obtained in Fig. 6 showed that an increase of the temperature from 15 to 45°C deals with increase in capacity cadmium adsorption. That means the removal of Cd is favored at high temperature. Similar results have been reported for the sorption of cadmium and lead using olive cake in aqueous solution at four temperatures 20, 25, 30 and 35°C (Doyunur and Celik, 2006) and using spent grain in aqueous solutions at temperatures 15, 28, 35 and 55°C (Low et al., 2000). In general, an increase in temperature is followed by an increase in the diffusivity of the ion and consequently by an increase in the sorption rate if diffusion rate is the rate controlling step.
Adsorption Isotherm

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Several isotherm equations are available and the two popular isotherms are selected in this study, the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherms assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption process of monolayer adsorption. The Langmuir adsorption isotherm can be written as:

\[ q_e = \frac{q_m b C_s}{1 + b C_s} \]  

(4)

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from Eq. 4:

\[ \frac{C_s}{q_e} = \frac{1}{b q_m} + \frac{C_s}{q_m} \]  

(5)

The Freundlich isotherm is an experimental equation in use to describe heterogeneous systems:

\[ q_e = K C_e^\frac{1}{n} \]  

(6)

The linearized form of Freundlich equation is:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]  

(7)

Where:
- \( q_e \) = Adsorbent amount (mg g\(^{-1}\)) of the Cd
- \( C_s \) = Equilibrium concentration of the Cd in solution (mg L\(^{-1}\))
- \( q_m \) = Monolayer adsorption capacity (mg g\(^{-1}\))
- \( b \) = Constant related to the free energy of adsorption (L mg\(^{-1}\))
- \( k_f \) = Freundlich adsorption isotherm constants (mg g\(^{-1}\))
- \( n \) = Freundlich adsorption isotherm constants
Table 3: Langmuir and Freundlich isotherm constant for adsorption of cadmium by silica ceramic

<table>
<thead>
<tr>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>q_e</td>
<td>b</td>
</tr>
<tr>
<td>0.6125</td>
<td>1.76231</td>
</tr>
</tbody>
</table>

Fig. 7: Cadmium adsorption on silica ceramic at 25°C with following conditions (Initial pH 5.6, adsorption dosage, 20 g L⁻¹; Initial Cd(II) concentration, 10-80 mg L⁻¹; equilibrium time 24 h)

Fig. 8: Langmuir plots for Cd(II) adsorption by silica ceramic (Initial pH 5.6, adsorption dosage, 20 g L⁻¹; Initial Cd(II) concentration, 10-80 mg L⁻¹; equilibrium time 24 h)

Based on Eq. 5 and 7 the isotherms were fitted to the adsorption data obtained. In Table 3, calculated correlation coefficients for these isotherms have been shown. As seen in Fig. 7, the Langmuir isotherm yielded best fits to the experimental data (Fig. 7). The Langmuir and Freundlich adsorption exponents q_e, b, K_s and n are determined from the linear plots of C_e/q_e versus C_s and Log q_e versus log C_s, which are shown in Fig. 8 and 9, respectively and respective data, are shown in Table 3. The values of the Langmuir and Freundlich constant were calculated from the slopes and intercepts of the plots. It has been reported similar trends of lead and cadmium adsorption by olive cake (Doyuran and Celik, 2006).
Table 4: Dimensionless equilibrium parameter $R_c$ values for cadmium sorption by silica ceramic at different initial concentration

<table>
<thead>
<tr>
<th>Concentration (mg L$^{-1}$)</th>
<th>$R_c$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.0070</td>
<td>1.76231</td>
</tr>
<tr>
<td>70</td>
<td>0.0080</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.0094</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.0112</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.0140</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.0186</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0276</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0537</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9: Freundlich plots for Cd(II) adsorption by silica ceramic (initial pH 5.6, adsorption dosage, 20 g L$^{-1}$; Initial Cd(II) concentration, 10-80 mg L$^{-1}$, equilibrium time 24 h)

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter $R_c$ was determined by using the following equation (Budinova et al., 1994; McKay et al., 1985):

$$R_c = \frac{1}{1 + bC_0}$$  \hspace{1cm} (8)

Where:
- $C_0 = $ Initial concentration
- $b = $ Langmuir isotherm constant

According to the values of $R_c$, the isotherm shape may be interpreted as $R > 1$ unfavorable, $r = 1$ linear, $0 < r < 1$ favorable and $r = 0$ irreversible. The results given in Table 4 shows that the $R_c$ values 0.007-0.0537 lie between 0 and 1 indicating a highly favorable adsorption.

**CONCLUSIONS**

This study results suggest that silica ceramic can remove cadmium ion from aqueous solution. It has been established to be a potential sorbent for Cd under batch conditions. This results also indicates that adsorption of cadmium was found to be dependent on contact time, temperatures, initial metal concentrations, adsorbent size and doses. The isotherm study indicates that adsorption data can be satisfactorily modeled by the Langmuir adsorption isotherm and the maximum adsorption capacity has
obtained 0.65 mg g⁻¹. The R² values between 0 and 1 further indicates a favorable adsorption of cadmium. The linearity of the plots log (qₑ/₂qₑ) versus t confirmed that the sorption process followed by first order kinetics. However, in order to develop its full potential as a commercial sorbent, it is required to investigate uptake of Cd under continuous condition from wastewaters and improve the adsorbent capacity through more experiments.

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REFERENCES


