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Adsorption of Cadmium from Aqueous Solutions by Vermiculite

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ABSTRACT

The present study involves an investigation of a low-cost adsorbent, vermiculite for the removal of cadmium from aqueous solutions. The effects of pH and contact time on the adsorption process were examined. The optimum pH for adsorption was found to be 6. Residual cadmium concentration reached equilibrium in four hours and the rate of cadmium adsorption by vermiculite was rapid in the first hour of the reaction time. Ho's pseudo second order model best described the reaction rate. Batch adsorption experiments conducted at room temperature (22 ± 1°C) showed that the adsorption pattern followed the Freundlich isotherm model. The maximum removal of cadmium obtained from batch studies was 96%. Thomas model was used to describe the adsorption data from column studies. Overall, the results showed that vermiculite could be considered as a potential adsorbent for cadmium removal from aqueous solutions.

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Key Words: Vermiculite; Cadmium; Adsorption; Kinetics; Isotherms.

INTRODUCTION

Heavy metals are defined as those metals and metalloids generally considered to be of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance.[1] These include metals such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn). Cadmium, like other heavy metals, is released into natural waters by industrial and domestic wastewater discharges. In humans, cadmium is accumulated in the kidneys which will begin to malfunction at overdoses, spilling proteins in the urine and disrupting potassium metabolism.[2] It is well known that chronic cadmium toxicity has been the cause of Japanese Itai–Itai disease.[3]

Activated carbon is a commonly used adsorbent for the removal of pollutants present in water and wastewaters. Studies by Sigworth and Smith[4] have shown that the removal of various heavy metal ions from aqueous solutions can be achieved using activated carbon. Inspite of its effectiveness in the removal of heavy metals from wastewaters, the high cost of activated carbon has restricted its more widespread use.[5] Hence, an economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of wastewater containing heavy metals.

Vermiculite is inexpensive and easily available in North American markets; this could make it a strong candidate as an economical adsorbent for removing heavy metals such as cadmium from wastewaters. Vermiculite is defined as a hydrated ferromagnesium–aluminum–silicate mineral,[6] which resembles mica in the crude form. A general formula for natural vermiculite is given by Grim[7]:

$$(OH)_4(Mg{\cdot}Ca)_X(Si_{8-X}{\cdot}Al_X)(Mg{\cdot}Fe)_6O_{20}{\cdot}YH_2O$$

with $X = 1$ to 1.4 and $Y \cong 8$.

The use of vermiculite in wastewater treatment has been studied in recent years and experimental results have shown vermiculite to be a suitable adsorbent for the removal of heavy metals from wastewaters. Keramida and Etzel[8] used an unexpanded (unexfoliated) vermiculite from Enoree, South Carolina, to achieve 58 to 78% removals of copper, zinc, and nickel ions from simulated acid bath plating wastewaters. The experimental conditions were different influent concentrations (20 mg/L, 50 mg/L, 100 mg/L) of metal ions in solutions pumped through an upflow exchange column at pH values ranging from 4.8 to 6.0 at flow rates of 1, 2, and 3 mL/min. They found that column utilization increased significantly with decreasing influent metal concentration. Fushimi and Uchimura[9] showed $Pb^{+2} = Cu^{+2} > Zn^{+2} = Cd^{+2}$ as the adsorption order for vermiculite from Kenya, South Africa. In their studies the adsorbent–solution system reached an equilibrium state in about 10 min and vermiculite adsorbed the metal ions following the Langmuir adsorption isotherm. Das and Bandyopadhyay[10] used unexpanded vermiculite from Bihar, India, to study the removal of lead by vermiculite medium. They found that 95% of the total lead removal took place at 10 g/L of sorbent concentration for an initial lead concentration of 1 to 10 mg/L. The sorption reached equilibrium in 3 to 4 hours following first-order reversible kinetics. The adsorption followed the Freundlich isotherm. Das and Bandyopadhyay[11] also studied Cu(II) removal by vermiculite from Bihar, India, under conditions of constant ionic strength. They reported 80% Cu(II) removal at pH 6 with an equilibrium time of 12 hours, and that the adsorption followed Freundlich isotherm. Bors et al.[12] studied iodide, cesium, and strontium adsorption by untreated and a treated-organophilic vermiculite. They concluded that the cation adsorption was substantially reduced for the organophilic vermiculite.

It has been reported that vermiculite of different origin would have different properties because of the differences in composition.[8] Hence the objectives of this study were to investigate the effectiveness of a commercial exfoliated-horticultural vermiculite mined in the United States for the removal of cadmium by batch and column studies, and to examine the applicability of known kinetic and adsorption isotherm models.

MATERIALS AND METHODS

Cadmium Solutions

Cadmium stock solutions were prepared from atomic absorption spectroscopy reference solutions for cadmium which contained cadmium metal as solute dissolved in 2–5% nitric acid solvent. Cadmium concentration in solutions were determined by a Varian AA10 atomic absorption spectrometer.

Vermiculite

Vermiculite used in this study was supplied by Green Harvest Ltd., Calgary, Alberta, Canada, in the form of exfoliated-horticultural vermiculite. Vermiculite was initially washed with deionized water several times and then dried in an oven at 70°C until dry. The dried vermiculite samples were screened through ASTM: 11 sieves. Vermiculite particles passing through #10 sieve (aperture: 2 mm) and retained in #12 sieve (aperture: 1.70 mm) were used throughout the experiments. The specific surface area of vermiculite particles was 5.04 m^2/g and total porosity was 55%.

Batch pH Studies

Batch pH studies were conducted by shaking 100 mL of metal solution containing 1 mg/L of cadmium with 0.2 g of vermiculite for 12 hours, over a range of initial pH values from 3 to 10 in increments of 1. The samples were shaken in 250 mL conical flasks sealed with Parafilm "M," on a New Brunswick Scientific Shaker manufactured by Fisher Scientific Ltd. The final pH of the reaction mixture was recorded and samples were vacuum-filtered through 0.45 μm polycarbonate filters (Micron Separations Inc.). Filtered samples were used for analyzing the cadmium ion concentrations. The experiments were conducted in duplicate, and mean values were used in the analysis of the data.

Batch Kinetic Studies

Batch kinetic experiments were conducted at pH 3, 4, 5, 6, and 7 to study the effects of pH on the equilibrium time required for the adsorption of cadmium on vermiculite. The initial cadmium concentration of metal ion was adjusted to approximately 1 mg/L. The pH of the solutions was adjusted using 1M NaOH or HNO_3 solution. After adjusting the pH of the solution, 0.2 g of vermiculite was added to metal solutions in 250 mL conical flasks and the reaction mixture pH was not controlled after initiation of the batch experiments. A blank, containing 100 mL of only the cadmium solution without any adsorbent was shaken simultaneously to determine any adsorption of cadmium ions onto the walls of the conical flasks. A control, with 100 mL of deionized water (no metal ion added) and 0.2 g of vermiculite was also shaken simultaneously to determine any leaching of cadmium ion from vermiculite. Seven samples were placed on a shaker and shaken at 170 rpm. Samples were collected at 0.5, 1, 2, 4, 6, 8, and 12 hours for each pH value. Upon collection, samples were vacuum-filtered through 0.45 μm polycarbonate filters and cadmium ion concentrations in the filtrate were determined. The experiment was replicated.

Upon determining the equilibrium time, an optimum pH was selected and the removal of cadmium ion by vermiculite was studied at much closer intervals of time. For this, a separate set of experiments were run at pH 6 (optimum pH) and the samples were collected at 5 min, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 5, and 6 hours. Upon collection, samples were filtered and analyzed for cadmium.

Batch Isotherm Studies

After determining the optimum pH and equilibrium time, isotherm studies were conducted at room temperature (22 ± 1°C) by varying the mass of vermiculite. Representative masses (0.03 g, 0.06 g, 0.09 g, 0.12 g, 0.15 g, 0.18 g, 0.2 g, 0.23 g, and 0.26 g) of vermiculite were mixed with 100 mL of the solution containing approximately 1 mg/L of cadmium ion for four hours, which is the equilibrium time for the vermiculite and cadmium ion reaction mixture. The initial pH of the metal solutions was adjusted to an optimum value of 6 with either 1M NaOH or HNO_3. The cadmium concentration at the end of the study period was determined after filtering the samples. The experiment was repeated for duplicate values.

Column Studies

Column studies were conducted using an acrylic column with an inner diameter of 3.18 cm (1.5 in) and a length of 60.96 cm (24 in). The column was packed with 65 g of vermiculite and a bed height of 38 cm was obtained. The influent concentration and flow rate of the cadmium solution were 1 mg/L and 13 mL/min, respectively. Samples were collected at regular intervals of time and acidified with trace metal grade nitric acid to a pH below 2 for storage in polyethylene bottles before analysis. Column studies were terminated when the column reached exhaustion.

RESULTS AND DISCUSSION

The chemical composition of vermiculite (Table 1) shows that it is composed mainly of silica as SiO_2 (39.37%), magnesium as MgO (23.37%), aluminum as Al_2O_3 (12.08%), and iron as Fe_2O_3 (5.45%) and FeO (1.17%). Varying amounts of other minor oxides and a few elements make up the remaining composition. The properties that make vermiculite a good adsorbent are surface properties like broken edges of the alumino silicate units, high specific surface area, high void content, and negative surface charge. It was found from blank and control studies that adsorption of

Table 1. Typical analysis of exfoliated-horticultural vermiculite.

Parameter	Value
pH value (in water)	7.0 to slightly alkaline
Specific gravity	2.6
% moisture (105°C for 1 hour)	0–2.0
Compounds	% by weight
SiO_2	39.37
TiO_2	1.26
Al_2O_3	12.08
Fe_2O_3	5.45
FeO	1.17
MnO	0.30
MgO	23.37
CaO	1.46
Na_2O	0.80
K_2O	2.46
P_2O_5	0.15
Li_2O	0.03
ZrO_2, Cr_2O_3, V_2O_3, NiO, CaO, F	Nil
BaO	0.03
Cl, SO_3	0.02
S	0.18
Free silica content	<1.0
CO_2	0.60

Source: Therm-o-Rock, USA.

cadmium ions onto the walls of the conical flasks was negligible and that vermiculite did not leach any cadmium into aqueous solutions.

Vermiculite was not pre-equilibrated before the experiments. Since vermiculite offered the only buffering in the system, a general increase in initial pH values to a more or less constant range of pH, almost immediately, was observed.

Batch pH Studies

Since the surface charge of an adsorbent can be modified by changing the pH of the solution, the pH is one of the most important parameters affecting the adsorption process of metal ions.[13] The pH dependence of adsorption of

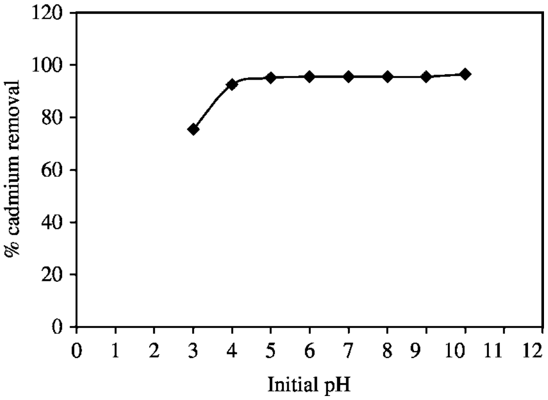

Figure 1. The effect of pH on adsorption of cadmium on vermiculite.

cadmium can be observed for vermiculite from Fig. 1. At a pH of 3, only 76% of the cadmium was adsorbed but at pH 4 the cadmium adsorption increased to 93%. From pH 5 to pH 9 the cadmium adsorption approximately remained constant, ranging from 95 to 96%. At pH 10, the cadmium removal was approximately 97%, which was a slight increase from the previous values. It could be noted that between pH 4 and pH 10, cadmium adsorption increased only marginally.

The cadmium adsorption on vermiculite could be a cation exchange mechanism. Where ion exchange is the mechanism for adsorption, it has been suggested that an increase in cation exchange capacity with increasing solution pH is the result of two mechanisms.[14,15] As the pH of the solution increases, the following phenomena occur:

1. H^+ ions compete to a lesser degree with other cations for exchange on the exchange material.
2. The OH^- activity increases, which neutralizes weakly acidic groups within the mineral structure. This results in adsorption of cations for saturation.

The first mechanism is the controlling factor at pH values below 7, whereas the second mechanism is important mainly at pH values of 9 and higher.[15]

The causes of cation exchange in vermiculite can be considered under two headings[7]:

1. Broken bonds: Broken bonds around the edges of the silica–alumina units would give rise to unsatisfied charges, which would

be balanced by adsorbed cations. The number of broken bonds and hence the exchange capacity due to this cause would increase as the particle size decreased. In vermiculite, broken bonds are responsible for a relatively small portion (approximately 20%) of the cation exchange capacity.

2. Substitutions within the lattice structure: The structure is unbalanced chiefly by substitutions of Al^{+3} for Si^{+4}. These substitutions may be partially balanced by other substitutions within the mica lattice, but there is always a residual net-charge deficiency of 1 to 1.4 per unit cell. The charge deficiency is satisfied by cations which occur chiefly between the mica layers and are largely exchangeable. In vermiculite, substitutions within the lattice account for approximately 80% of total cation exchange capacity.

The reason for only a marginal increase in cadmium adsorption beyond pH 4 was probably due to the ample time (12 hours) given for the metal solution and vermiculite to react, during which stabilization of different initial pH values into more or less a constant range of final pH took place leading to the adsorption of most of the cadmium ions. This was also noted by Das and Bandyopadhyay[11] for the adsorption of Cu(II) on vermiculite. A slight enhancement in removal at pH 10 might be due to the formation of the $Cd(OH)_{2(s)}$ precipitate, which could have been removed by filtration through 0.45 μm polycarbonate membrane. This should not be confused with the process of adsorption because precipitation masks adsorption of metal ions. Different researchers have observed different pH values at which cadmium precipitates as $Cd(OH)_{2(s)}$. Bhattacharya and Venkobachar[16] observed in their studies that cadmium precipitates at pH values greater than 10 and Gosset et al.[17] observed cadmium precipitation beyond pH 6.5. Ozer et al.[13] reported that the optimum pH for cadmium adsorption was 6.3. This may be due to the difference in the aqueous medium employed in their experiments. In the present study, an optimum pH of 6 was selected for cadmium–vermiculite system.

Batch Kinetic Studies

Figure 2 shows the plots of concentration of cadmium remaining in solution with time for pH values of 3, 4, 5, 6, and 7, respectively. At pH 3, though the adsorption was significant, it took 10 hours for the system to reach equilibrium. At pH 4, the system reached equilibrium in 8 hours. Adsorption of cadmium reached equilibrium in 4 hours at pH 5, 6, and 7. As the precipitation

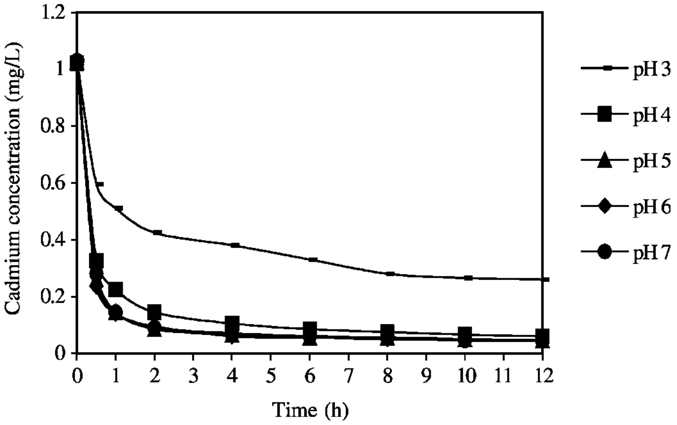

Figure 2. Cadmium concentration versus time at various pH values for vermiculite.

of metal ions as hydroxides are likely at pH values above 7, kinetic studies above pH 7 were not attempted. The final pH values for experiments of initial pH 3, 4, 5, 6, and 7 were 3.4, 6.2, 6.3, 6.5, and 7.0, respectively. Fushimi and Uchimura[9] observed in their studies that sorption rate of metal ions (Pb, Cu, Zn, and Cd) on vermiculite was relatively high, and the adsorbent–solution system reached an equilibrium state in about 10 minutes. Das and Bandyopadhyay[11] reported 12 hours as contact time needed for copper–vermiculite systems to achieve equilibrium conditions. It could be noted that reaction kinetics of vermiculite is much slower in their case due to pre-equilibrated conditions under which their study was conducted, leading to isolation of adsorption under steady-state conditions. By this way, many different chemical reactions, other than metal sorption, could be avoided thereby preventing uncontrolled reactions. Several workers[11,18,19,20] have mentioned that when the adsorbent materials are in suspension the adsorption of metals seems to be rapid, taking place within a few minutes or hours.

It was interesting to note that the kinetics of cadmium adsorption on vermiculite behaved more or less similarly at pH 5, 6, and 7. A closer look at the figures shows that there are two phases in the adsorption of cadmium on vermiculite. There was an initial rapid phase where adsorption was fast and significant, and a second phase where adsorption was slower and less significant. At pH 3 and pH 4, the first-rapid phase lasted for 2 hours and the second-slow phase contributed to the rest. The first phase of adsorption kinetics lasted for 1 hour for pH 5, 6, and 7 where metal adsorption was quick and significant. The second-slow phase had a relatively small contribution toward the metal adsorption.

The kinetics of cadmium adsorption for vermiculite at its optimum pH of 6 was studied at much closer intervals of time for a period later than 4 hours. This helped in evaluating which reaction models were suitable for the cadmium adsorption on vermiculite. Figure 3 shows the kinetics of cadmium adsorption on vermiculite at closer intervals of time at the optimum pH of 6.

Lagergren first order model (Eq. (2)) and Ho's et al. pseudo order model (Eq. (4)) were used to describe the kinetics of cadmium adsorption on vermiculite. The first order Lagergren rate equation used by researchers[21,22] to study the kinetics of heavy metal adsorption is as follows:

$$\ln(q_e - q_t) = \ln(q_e) - K_L t \qquad (1)$$

By rearranging it we can get:

$$q_t = q_e(1 - e^{-K_L t}) \qquad (2)$$

where,

K_L = Lagergren rate constant for adsorption (h^{-1})

q_e = amount of metal ion adsorbed at equilibrium (mg/g)

q_t = amount of metal ion adsorbed at any given time t (mg/g)

Ho et al.[23] used a pseudo second order rate equation to study the kinetics of adsorption of heavy metals on peat:

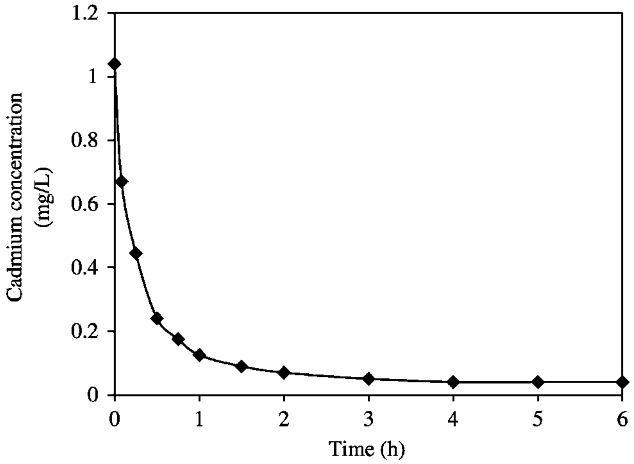

Figure 3. Plot of cadmium concentration versus time at pH 6 for vermiculite.

The Ho et al. pseudo second order equation is:

$$t/q_t = 1/(2Kq_e^2) + t/q_e \quad (3)$$

By rearranging it we can get:

$$q_t = (2Kq_e^2 t)/(1 + 2Kq_e t) \quad (4)$$

where,

K = pseudo second order rate constant for adsorption (g/mg h)
q_e = amount of metal ion adsorbed at equilibrium (mg/g)
q_t = amount of metal ion adsorbed at any given time t

The batch kinetic data for optimum pH 6 was fitted to both the models by nonlinear regression analysis using software package STATISTICA (Release 5.0) for WINDOWS. Though both models adequately described the kinetic data at 95% confidence level, Ho's pseudo second order model described the kinetic data quite well with higher R values compared to the Lagergren first order model. Figures 4 and 5 show the Lagergren's first order and Ho's pseudo second order model plots for the kinetics of cadmium adsorption on vermiculite. Table 2 shows the Lagergren's first order model equations and Ho's pseudo second order model equations for cadmium adsorption on vermiculite. The first order and pseudo second order kinetic rate constants for cadmium adsorption on vermiculite were $K_L = 3.54\,h^{-1}$ and $K = 0.74\,g/mg\text{-}h$. The first order kinetic rate constants reported by other

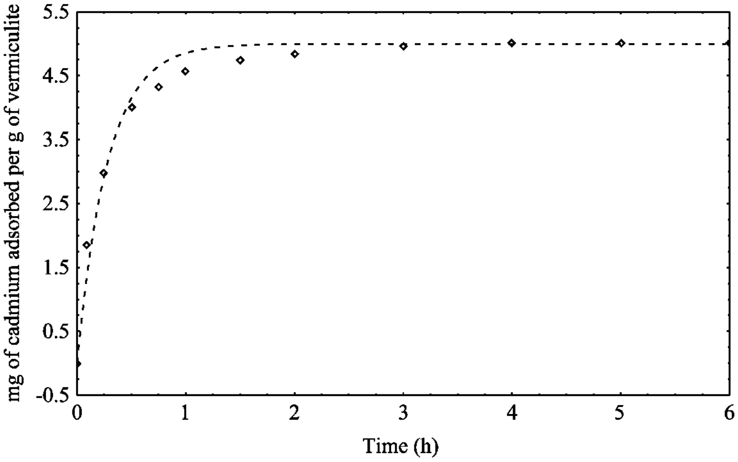

Figure 4. The Lagergren first order model plot for adsorption of cadmium on vermiculite.

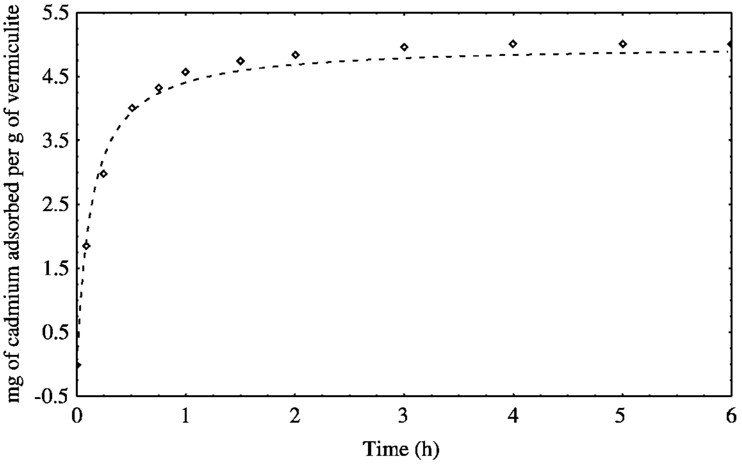

Figure 5. The Ho's pseudo second order model plot for adsorption of cadmium on vermiculite.

researchers are $0.0134\,h^{-1}$ for cadmium adsorption on peat,[24] $1.398\,h^{-1}$ for cadmium adsorption on fly ash,[25] $0.44\,h^{-1}$ for cadmium adsorption on *Aspergillus niger* biomass,[26] and $0.2218\,h^{-1}$ for lead adsorption on vermiculite.[10] Comparing the value of first order rate constant from this study with other studies reported above shows that the rate of cadmium adsorption on vermiculite was quite rapid.

Batch Isotherm Studies

The final pH of batch isotherm studies which were set at an initial pH of 6 were in the range 6.4–6.5. The adsorption data was fitted to the Freundlich

Table 2. First order and pseudo second order rate equations for cadmium adsorption on vermiculite.

Model type	Model equation	R
First order	$q_t = 5(1 - e^{-3.54t})$	0.99[a]
Pseudo second order	$t/q_t = 1/[2(0.74)(5^2)] + t/5$	0.99[a]

[a] Indicates that model parameters are statistically significant (t-test) at 95% confidence level.

(Eq. (5)), and the Langmuir (Eq. (6)) models using the nonlinear regression analysis.

The Freundlich equation is[27]:

$$q = K_f C_e^{1/n} \tag{5}$$

where,

q = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

K_f = equilibrium constant indicative of adsorption capacity

n = adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity

C_e = concentration of adsorbate in solution at equilibrium (mg/L)

The Langmuir equation can be expressed as:

$$q = (q^o b C_e)/(1 + bC_e) \tag{6}$$

where,

q^o = amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g)

b = constant related to the energy or net enthalpy of adsorption

C_e = concentration of adsorbate in solution at equilibrium (mg/L)

The nonlinear regression analysis was conducted using the software package STATISTICA. It was found that the adsorption data obtained was best described by the Freundlich isotherm model. The constants estimated by the Freundlich model were statistically significant at 95% confidence level. Although adsorption data provided good fits with high R values for the Langmuir isotherm model, the Langmuir constants evaluated were not significant at 95% confidence level. Figure 6 shows the Freundlich model plots for cadmium adsorption on vermiculite. Table 3 shows the isotherm model equations along with R values.

The Freundlich constants obtained can be used to calculate the theoretical adsorption capacity of vermiculite for cadmium. A value of 5.5 mg/g had been obtained as the adsorption capacity of vermiculite for cadmium from batch studies. This means 1 g of vermiculite could sorb 5.5 mg of cadmium ions from aqueous solutions, under present experimental conditions. The adsorption capacity of vermiculite obtained by few other researchers are: 1.65 mg of lead per gram of vermiculite[10] and 1.25 mg of Cu(II) per gram of vermiculite.[11] Comparing these values with the one obtained in this study (5.5 mg/g) shows that vermiculite used in this research exhibited a very high capacity for cadmium adsorption from aqueous solutions.

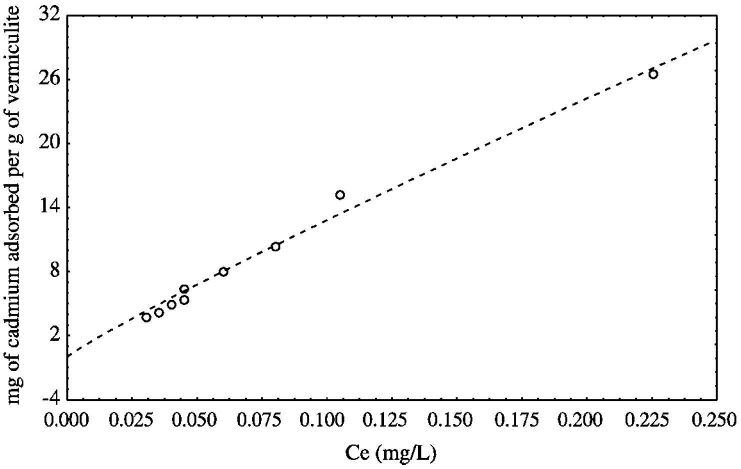

Figure 6. The Freundlich model plot for adsorption of cadmium on vermiculite.

Column Studies

In the case of column studies, the pH of the feed solution was 6.0 and the pH of the effluent from the column was in the range 6.4–6.5. The adsorption data from column studies was analyzed using the Thomas model (Eq. (7)). The Thomas model utilizes a kinetic equation based on the derivation by Thomas. The principal experimental information required is a breakthrough curve from a test column, either laboratory or pilot scale. The Thomas model has the following form[28]:

$$C_e/C_o = 1/(1 + \exp[(K_T(q_o m - C_o V))/Q]) \tag{7}$$

Table 3. Freundlich and Langmuir model equations for cadmium adsorption on vermiculite.

Model type	Model equation	R
Freundlich	$q = (106)Ce^{1/1.09}$	0.99[a]
Langmuir	$q = [(153)(0.94)Ce]/[1 + (0.94)Ce]$	0.99[b]

[a] Indicates that model parameters are statistically significant (t-test) at 95% confidence level.

[b] Indicates that model parameters are not statistically significant (t-test) at 95% confidence level.

where,

C_e = effluent adsorbate concentration (mg/L)
C_o = influent adsorbate concentration (mg/L)
K_T = Thomas rate constant (L/min.mg)
q_o = maximum solid phase concentration of the solute (mg/g)
m = mass of the adsorbent (g)
V = throughput volume (L)
Q = volumetric flow rate (L/min)

The constants K_T and q_o are calculated using breakthrough data for use in the design of a full-scale adsorption bed.

Figure 7 shows the Thomas model plot. From the graph it can be seen that the column did not achieve breakthrough until 110 L and reached exhaustion after 175 L of throughput volume. The Thomas equation coefficients for cadmium adsorption by vermiculite are $K_T = 1.37\,\text{mL/min.mg}$ and $q_o = 2.07\,\text{mg/g}$. The value of q_o is a measure of the adsorptive capacity of the vermiculite for cadmium. In the present case, $q_o = 2.07\,\text{mg/g}$; this means that every gram of vermiculite could sorb 2.07 mg of cadmium under the present column experimental conditions. Based on batch studies, a value of 5.5 mg/g was obtained as the adsorption capacity of vermiculite for cadmium. The reason for the lower adsorption capacity of vermiculite in column experiments than in batch experiments may be due to non pre-equilibration of column chemically or hydrologically. For chemical pre-equilibration, the appropriate background solution without the spike should be passed through the column

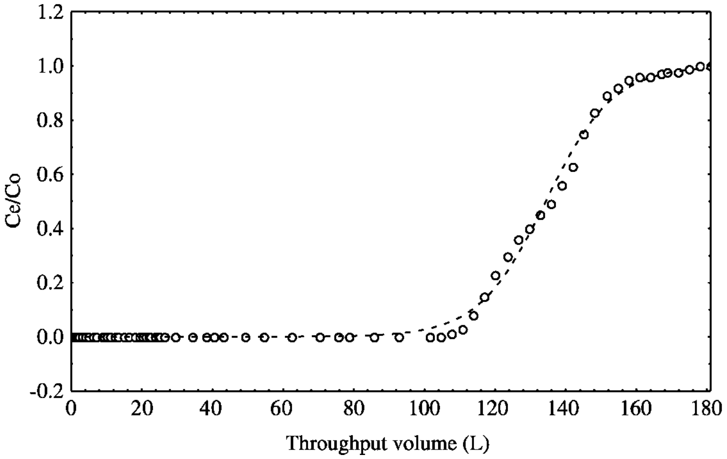

Figure 7. Thomas equation plot for adsorption of cadmium on vermiculite.

until saturation. Bringing a column to hydraulic steady state generally requires running the solution from the bottom up through the column overnight. A high flow rate (13 mL/min) employed in the column studies might be one of the reasons for lower adsorption capacity observed for vermiculite.

General Discussion

Based on the experimental results, it can be concluded that vermiculite exhibited quite a high capacity for removing cadmium from aqueous solutions. The maximum cadmium removal at a pH of 6 was 96%. The rate of cadmium adsorption was fast and the cadmium–vermiculite system attained equilibrium in four hours. The reaction was best described by Ho's pseudo second order model and the adsorption followed the Freundlich isotherm. Table 4 shows adsorption of cadmium by vermiculite in comparison with a few other adsorbents used by other researchers.

From the Table 4 it can be seen that activated carbon (Nuchar-190-N) exhibits the maximum cadmium removal (98%) followed by vermiculite (96%). It must be noted that the mass of vermiculite used (2 g/L) was less than the mass of activated carbon (Nuchar-190-N) used (10 g/L) in the adsorption experiments. But the initial cadmium concentration for vermiculite system was low, 1 mg/L, when compared with the initial cadmium concentration for activated carbon system, 56.2 mg/L, and that the equilibrium time for activated carbon system was 30 min to 1 h, which was much lower than the 4-h equilibrium time for the vermiculite system. Vermiculite was equally good for cadmium removal when compared with other promising adsorbents such as peat, fly ash, dried leaves, and Giridih coal.

Vermiculite used by Das and Bandyopadhyay[10,11] showed 95% and 80% removal for Pb and Cu(II) from aqueous solutions. Keramida and Etzel[8] reported 58 to 78% removal of copper, zinc, and nickel ions from simulated acid bath plating wastewaters. Exfoliated-horticultural vermiculite used in this study was very much comparable with other vermiculites in terms of maximum percentage removal (96%) and overall performance in removing cadmium from aqueous solutions.

The cost of the adsorbent is also one important issue that must be considered when selecting an adsorbent. The cost of commercial activated carbon is \$5–\$6/kg (approximately), whereas the cost of vermiculite is less than \$2/kg. The cost of regeneration/disposal of the spent adsorbent would also have to be considered. A detailed economic analysis is required to determine the most economical adsorbent.

Table 4. Adsorption of cadmium by vermiculite in comparison with a few other adsorbents used by other researchers.

Adsorbent used	Initial Cd concentration	Equilibrium time	Maximum removals	Type of wastewater	Reference
Vermiculite (2 g/L)	1 mg/L	4 h	96%	sw	This study
Activated carbon (10 g/L)	56.2 mg/L	30 min to 1 h	98%	sw	Huang and Ostovic[29]
Activated carbon (sugar beet pulp)	500 mg/L	2 h	57%	sw	Ozer et al.[13]
Giridih Coal (1 g/L)	1 mg/L	24 h	85%	sw	Bhattacharya and Venkobachar[16]
Crushed coconut shell (1 g/L)	1 mg/L	24 h	75%	sw	Bhattacharya and Venkobachar[16]
Peat (5 g/L)	1 mg/L	2 h	95%	aw	Viraraghavan and Rao[24]
Flyash (20 g/L)	1 mg/L	3 h	93%	aw	Viraraghavan and Rao[5]
Reed leaves (20 g/L)	1 mg/L	4 h	92%	sw	Sayrafi et al.[30]

sw—synthetic wastewater, aw—actual wastewater.

CONCLUSIONS

The following conclusions were drawn from this study.

1. The batch pH studies indicated that the cadmium adsorption on vermiculite increased from 76% to 96% when the pH was varied between 3 and 9. Beyond pH 9, precipitation of cadmium as cadmium hydroxide was observed. The optimum pH was 6 and the cadmium removal at this pH was 96%.

2. The kinetic studies at pH 6 indicated that equilibrium time for cadmium adsorption on vermiculite was 4 hours.
3. The Ho's et al. pseudo second order reaction rate model explained the kinetic data quite well. The pseudo second order rate constants for the adsorption of cadmium on vermiculite was found to be 0.74 g/mg-h.
4. Isotherm analysis of the data showed that the adsorption pattern for cadmium on vermiculite followed the Freundlich isotherm.
5. The adsorptive capacity of vermiculite for cadmium in column experiments was 2.07 mg of Cd/g of vermiculite.

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REFERENCES

1. Lester, J.N. *Heavy Metals in Wastewater and Sludge Treatment Processes*; CRC Press Inc.: Boca Raton, FL, 1987.
2. Patterson, J.W.; Passino, R. *Metals Speciation Separation and Recovery*; Lewis Publishers, Inc: Chelsea, MI, 1987; 175–200.
3. Friberg, L.; Piscato, M.; Nordbert, C.G.; Kjellstrom, T. *Cadmium in the Environment*; Springer-Verlag: Berlin, Germany, 1979.
4. Sigworth, E.A.; Smith, S.B. Adsorption of inorganic compounds by activated carbon. J. Am. Water Works Assoc. **1972**, *64* (6), 386–391.
5. Viraraghavan, T.; Rao, A.K. Adsorption of cadmium and chromium from wastewater by fly ash. J. Environ. Sci. Health Part A **1991**, *A26* (5), 721–753.
6. Lin, I. Perlite and vermiculite: crudely speaking the potential is good. Ind. Miner. **1998**, *368*, 55–59.
7. Grim, R. *Clay Mineralogy*; McGraw-Hill Book Company: New York, 1968.
8. Keramida, V.; Etzel, J. *Treatment of Metal Plating Wastewater with a Disposable Ion Exchange Material*, Proceedings of the 37th Industrial Waste Conference, Ann Arbor Publishers: Ann Arbor, MI, 1983.
9. Fushimi, H.; Uchimura, T. Adsorption, desorption, and recovery of heavy metal ions by vermiculite. J. Min. Metall. Inst. Jap. **1984**, *100* (1155), 417–422.

10. Das, N.C.; Bandyopadhyay, M. Removal of lead by vermiculite medium. Appl. Clay Sci. **1991**, *6*, 221–231.
11. Das, N.C.; Bandyopadhyay, M. Removal of copper(II) using vermiculite. Water Environ. Res. **1992**, *64* (7), 852–857.
12. Bors, J.; Gorny, A.; Dultz, S. Caesium and strontium adsorption by organophilic vermiculite. Clay Miner. **1997**, *32*, 21–28.
13. Ozer, A.; Tanyildizi, M.S.; Tumen, F. Study of cadmium adsorption from aqueous solution on activated carbon from sugar beet pulp. Environ. Technol. **1998**, *19*, 1119–1125.
14. Bower, C.; Reitemeier, R.; Fireman, M. Exchangeable cation analysis of saline and alkali soils. Soil Sci. **1952**, *73* (4), 251.
15. Mitra, R.; Rajagopalan, K. Origin of the base-exchange capacity of clays and significance of its upper limiting value. Soil Sci. **1952**, *73* (5), 349.
16. Bhattacharya, A.K.; Venkobachar, C. Removal of cadmium(II) by low cost adsorbents. J. Environ. Eng. **1984**, *110* (1), 110–122.
17. Gosset, T.; Trancart, J.; Thevenot, D.R. Batch metal removal by peat, kinetics and thermodynamics. Water Res. **1986**, *20* (1), 21–26.
18. Inskeep, W.P.; Baham, J. Adsorption of Cd(II) and Cu(II) by Na-montmorillonite at low surface coverage. Soil Sci. Soc. Am. J. **1983**, *47*, 660–665.
19. Aringhieri, R. Kinetics of Cu^{2+} and Cd^{2+} adsorption by an Italian soil. Soil Sci. **1985**, *139*, 197.
20. Ghanem, S.A.; Mikkelsen, D.S. Sorption of zinc on iron hydrous oxide. Soil Sci. **1988**, *146*, 15.
21. Kapoor, A.; Viraraghavan, T.; Roy Cullimore, D. Removal of heavy metals using the fungus *Aspergillus niger*. Bioresource Technol. **1999**, *70*, 99–104.
22. Lagergren, S. Zur Theorie der sogenannten adsorption geloster Stoffe. Stockholm. Bihang till. K.Sv.Vet.akad.handl. **1898**, *24* (Afd.2n:o4), 39.
23. Ho, Y.S.; Wase, D.A.J.; Forster, C.F. Kinetic studies of competitive heavy metal adsorption by sphagnum peat. Environ. Technol. **1996**, *17*, 71–77.
24. Viraraghavan, T.; Rao, A.K. Adsorption of cadmium and chromium from wastewater by peat. Int. J. Environ. Stud. **1993**, *44*, 9–27.
25. Yadava, K.P.; Tyagi, B.S.; Panday, K.K.; Singh, V.N. Fly ash for the treatment of Cd(II) rich effluents. Environ. Technol. Lett. **1987**, *8*, 225–234.
26. Kapoor, A. Removal of heavy metals from aqueous solution by *Aspergillus niger*. Ph.D. Thesis, University of Regina, Saskatchewan, Canada, 1998.

27. Weber, W.J., Jr. *Physicochemical Process for Water Quality Control*; John Wiley and Sons, Inc.: New York, 1972; 199–260.
28. Reynolds, T.D.; Richards, P.A. *Unit Operations and Processes in Environmental Engineering*; PWS Publishing Company: New York, 1996; 350–375.
29. Huang, C.P.; Ostovic, F.B. Removal of cadmium(II) by activated carbon adsorption. J. Environ. Eng. **1978**, *104* (1), 110–122.
30. Sayrafi, O.; Salim, R.; Sayrafi, S.A. Removal of cadmium from polluted water using decaying leaves—effects of type of leaves and concentration of cadmium. J. Environ. Sci. Health Part A **1996**, *A31* (10), 2503–2513.

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