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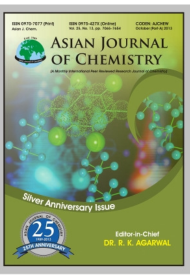

Removal of Heavy Metals from Synthetic Landfill Leachate Using Oyster Shells Adsorbent

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This paper investigated the adsorption capacities of crushed oyster shells- adsorbent for removal of several heavy metal ions from synthetic landfill leachate using batch experiments. Adsorbent characterization, single-constituents metal ion adsorption kinetics, single metal adsorption equilibrium isotherm models were assessed. The results showed that: a 24 h period was considered to provide an adequate contact time between the single-constituent metal ion solutions and the adsorbent to reach equilibrium; the equilibrium adsorption capacities of the adsorbent for single-constituent metal ion solutions was noted to be Cd > Co > Ni > Mn; after a 24 h contact period with crushed oyster shells, the solution pH was generally found to equilibrate at approximately pH of 8. The metal adsorption capacities generally increased with increasing initial metal concentration and decreased when adsorbent masses were increased in solution; the Langmuir model was found to provide a better fit to the experimental equilibrium data of nickel adsorption.

Key Words: Heavy metal, Landfill leachate, Oyster shells adsorbent.

INTRODUCTION

Landfill leachate is a complex wastewater containing various heavy metal ions present in significant concentrations. The heavy metal ions have to be treated before the leachate is discharged to the receiving environment, or they could cause significant environmental problem[1]. Conventional treatment methods being discussed and applied for heavy metal removal are chemical precipitation and ion-exchange. A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it is not economically appealing because of high operational cost. As such, alternative adsorption technologies using natural materials as adsorbents has been shown to be a feasible treatment process for removing heavy metal ions from wastewater. It has been demonstrated to be more economical and to provide a greater heavy metal removal capacity[2]. Oyster shells are noted as naturally occurring, plentiful, inexpensive and effective material. The main structural component of oyster shells is chitin [2-acetamido-2-deoxy-β-dglucose-(*N*-acetylglucan)][3]. The chemical name of chitin is polyacetylglucosamine, the molecular structure looks like the cellulose very much, they are all six-carbon sugars polymers whose molecular weight are all above 1,000,000. The chitin has the massive functional groups, such as acetylamino, primary amino, the hydroxyl group, which have strongly adsorptive capacity. Moreover on the each glucose ring of chitin there are some linear ammonia groups make it easy for the duplet electron pair to combine heavy metals.

The main objective of this paper was to investigate the adsorption capacities of the natural adsorbent media, crushed oyster shells, for several heavy metal ions removal from synthetic landfill leachate using batch experiments. Adsorbent characterization, single-constituents metal ion adsorption kinetics were assessed.

EXPERIMENTAL

In this investigation, the commercially available crushed oyster shells were used as adsorption media. The shells were washed with tap water through and air-dried at room temperature (20-23 ºC) for 48 h. After air drying, the shells were oven-dried in a hotbox oven at 90 ºC to a constant mass and then air-cooled to room temperature. Next, the shells were sorted into mechanical sieve to retain fractions 4.0-4.5 mm.

According the research of VanGulck and Rowe[4], synthetic landfill leachate was prepared, then dissolving corresponding analytical grade soluble heavy metals *e.g.*, salts into synthetic landfill leachate. The initial heavy metal cadmium, nickel, manganese and cobalt concentrations employed in these batch experiments were determined based on a recipe elaborated by VanGulck and Rowe[4] for investigating the treatment of a typical synthetic landfill leachate. The concentration of cadmium, nickel, manganese and cobalt was 200, 100,140 and 40 mg/L respectively.

Bulk density, particle density, porosity and adsorbent pH were determined for crushed oyster shells adsorbent.

Bulk density (ρ_b) values were determined using the method which was used by Loska and Wiechula[5]. Density of the medium was calculated according to eqn. 1.

$$\rho_b = \frac{M_t}{V_t} \quad (1)$$

where ρ_b is the bulk density (g cm^{-3}), M_t is the oven-dried sample mass (g) and V_t is the beaker volume (cm^3).

Particle density was determined using the method described by Laska[5]. Particle density was calculated according to eqn. 2.

$$\rho_s = \frac{\rho_{w M_s}}{M_S - (M_{s+f+w} - M_{f+w})} \quad (2)$$

where ρ_s is the particle density (g cm^{-3}), ρ_w is the density of water (g cm^{-3}), Ms is the mass of oven-dried medium, $M_s + f + w$ is the mass of flask, oven-dried medium and distilled water (g), $M_s + w$ is the mass of flask filled to volume with distilled water.

Porosity values were determined according to eqn. 3.

$$n = [1 - (\frac{\rho_b}{\rho_s})] \times 100\% \quad (3)$$

where *n* is the porosity (unitless).

Adsorbent pH was measured according to the following procedures. About 5 g of adsorbent was placed in a 125 mL volumetric flask with 25 mL of distilled water. The flasks were sealed and shaken at 100 rpm for 0.5 h. After filtration, using filter paper, the pH was measured using a pH meter.

The adsorption kinetic study was conducted in batch experiments to determine the contact time necessary to reach equilibrium concentrations for crushed oyster shells. The adsorbent was tested with each of the four single-constituent metal ion solutions at room temperature (20-23 ºC). Five grams of adsorbent were contacted with 100 mL of each of the metal salt solutions at concentrations of 500 mg/L for cadmium sulfate, nickel sulfate and manganese sulfate and 150 mg/L for cobalt sulfate in 125 mL flasks sealed with parafilm and agitated at 100 rpm for 48 h on a orbital shaker. The pH of the solutions was allowed to equilibrate to the pH of the oyster shells, as this process would take place when the oyster shells were employed in a column environment where pH adjustments or buffering would not be anticipated. The initial and final pH values of the single metal solutions were recorded using a pH meter. Shaking was interrupted for 1-2 min at predetermined time intervals (2h, 4h, 6h, 8h, 12h, 16h…48h), when a small volume (0.25 mL cadmium ion solutions and 0.1 mL other solutions) of supernatant solutions were collected from the flasks. The supernatant solution samples were diluted by a factor of 100 or 400 according to the requirements of the atomic absorption spectrophotometer.

The equilibrium study was undertaken to investigate the effect of initial single metal ion solution concentrations and adsorbent mass on adsorption resulting in the derivation of equilibrium isotherm models. The initial concentrations of single-constituent metal ion solutions are shown in Table-1. In this experiment, 5 g of adsorbent were contacted with each of the 100 mL single-constituent metal ion solutions in 125 mL flasks at four different initial metal concentrations as noted in Table-1. The mixtures were shaken for 24 h at 100 rpm at room temperature (20-23 ºC). The samples were then filtered, collected and diluted and analyzed for metal ion concentration using an atomic absorption spectrophotometer. Similar experiments were carried out to study the effect of adsorbent mass on single-constituent metal ion removal from the aqueous solution. 1, 3, 5 or 7 g of the adsorbent were added to a 125 mL flask containing the 100 mL of single-constituent metal ion solution at concentrations of 500 mg/L for cadmium sulfate, nickel sulfate or manganese sulfate solution, or 150 mg/L of cobalt sulfate solution. The samples were analyzed for metal ion concentrations using an atomic absorption spectrophotometer.

In order to determine the equilibrium time and adsorption kinetics of adsorbent, the metal uptake (mg metal ion/g adsorbent or mmol metal ion/g adsorbent)at different time was computed using eqn. 4:

$$q = \frac{(C_0 - C_t)}{m} \cdot V \quad (4)$$

where q is the adsorbent phase concentration at various time steps (mg adsorbate/g adsorbent or mmol adsorbate/g adsorbent), C_0 is the initial concentration of adsorbate (mg/L or mmol/L), C_t is the concentration of adsorbate at various time steps (mg/L or mmol/L), V is the initial volume of liquid in the reactor (L) and m is the mass of adsorbent added (g). When adsorption reaches equilibrium q is equal to q_e, where q_e is the equilibrium adsorbent phase concentration (mg adsorbate/g adsorbent or mmol adsorbate/g adsorbent), C_t is equal to C_e where C_e is the equilibrium concentration in the solutions (mg/L or mmol/L).

Treatment efficiency, E %, can be determined using eqn. 5:

$$E\% = (1 - \frac{C_e}{C_0}) \times 100\% \quad (5)$$

where C_0 is the initial concentration of adsorbate (mg/L or mmol/L), C_e is the final equilibrium concentration of adsorbate in the solution (mg/L or mmol/L).

The adsorbent characteristics were analyzed and are summarized in Table-1.

TABLE-1
ADSORBENT PROPERTIES

Particle density (g cm^{-3})	Bulk density (g cm^{-3})	Porosity	Media pH
2.57	1.10	0.68	9.2

In batch kinetic and equilibrium adsorption studies examining the removal of metal ions from synthetic landfill leacahte, a period of 24 h is commonly regarded as an adequate contact time to reach equilibrium[6]. A 24-h adsorption kinetic study was conducted contacting single-constituent metal solutions of cadmium (200 mg/L), nickel (100 mg/L), manganese (140 mg/L) and cobalt (40 mg/L) with crushed oyster shells. Experiments were conducted as described earlier using 5 g of adsorbent in 100 mL single-constituent metal ion solutions. Fig. 1 illustrate the change in the adsorption capacity of adsorbent for cadmium, nickel, manganese and cobalt, respectively, as a function of time.

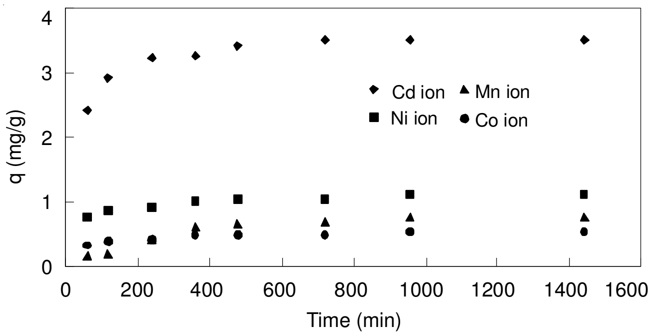

Fig. 1. Metal ions adsorption as a function of time

RESULTS AND DISCUSSION

The adsorption capacities of the crushed oyster shells on Cd ion changed rapidly during the first 8 h. After the first 8 h, the adsorption did not change significantly (< 5 % difference). Hence it was considered to have reached equilibrium. A contact period of 6 to 8 h has also been reported for adsorption of cadmium using crab shells in a study by Benguella and Benaissa[6]. According to Fig. 1, an 6-h contact period would be sufficient for nickel adsorption to reach equilibrium manganese ion adsorption and Co adsorption increased significantly in the first 16 h and the shells reached an equilibrium adsorption capacity within 16 h. From Fig. 1 in most cases, the adsorbents reached equilibrium adsorption capacities within 24 h. Hence, in the equilibrium experiments using various initial metal ion concentrations and adsorbent masses, a 24 h period was considered to provide an adequate contact time between the single-constituent metal ion solutions and the various adsorbents to reach equilibrium.

Adsorption capacities and efficiencies of adsorbent on specific single heavy metals are summarized in Table-2, the equilibrium adsorption capacities for single-constituent metal ion solutions was noted to be Cd > Co > Ni > Mn.

TABLE-2
ADSORPTION CAPACITIES AND ADSORPTION EFFICIENCIES

	Cd	Ni	Mn	Co
q_e (mg/g)	3.42	1.00	0.76	0.48
E (%)	68.4	40.0	27.1	60.0

In utilizing crushed oyster shells, the quantity of counter-ions released is a function of the composition of the crushed oyster shells. Calcium carbonate is the main inorganic constituent of shells[7]. It has been reported that the calcium carbonate in shells starts to dissolve at pH = 11 and most of it could be dissolved at pH = 5[8]. Other carbonate species, HCO_3^- and CO_3^{2-}, species are responsible for the formation of insoluble metal carbonates. Hence, the formation of insoluble metal carbonates would represent the primary contributing mechanism for heavy metal removal in the metal-shell adsorption process and Ca^{2+} would likely be the dominant counter-ion released from the crushed oyster shells. This may explain why oyster shells showed a definite adsorption capacity in this study.

From the kinetic study, the crushed oyster shells adsorbent was noted to be the best adsorbent for C_d ion (E = 68.4 %) and Co ion (E = 60 %).

Typically, landfill leachate pH values are reported between 5.0 and 6.0[4]. When liquid wastewater bearing metal ions is treated in a wastewater treatment plant, the pH of the solution is one of the most important factors to be monitored. As shown in Table-3, when the solutions were treated using the crushed oyster shells as an adsorbent, the final effluent pH was approximately 8. This is due to the natural pH of the adsorbent materials. In this respect, these of crushed oyster shells as an adsorbent would present an advantage because effluents treated through the crushed oyster shells would not require further treatment of the effluent pH in real applications.

TABLE-3
PH VALUES OF SOLUTIONS

Solution	Cadmium sulfate (500 mg/L)	Nickel sulfate (500 mg/L)	Manganese sulfate (500 mg/L)	Cobalt sulfate (500 mg/L)
InitialpH	4.3	5.7	5.6	6.1
Final pH	7.7	8.2	8.2	8.0

The effects of the initial metal ion concentration on the adsorption capacities of crushed oyster shells are presented in Fig. 2 for cadmium, nickel, manganese and cobalt single-constituent metal ion solutions. Fig. 2 shows that the equilibrium adsorption capacities of the crushed oyster shells for different ions increased with increasing initial ion concentrations in solution,which is similar to the results reported in other studies for removal of cadmium[6] and cobalt[8].

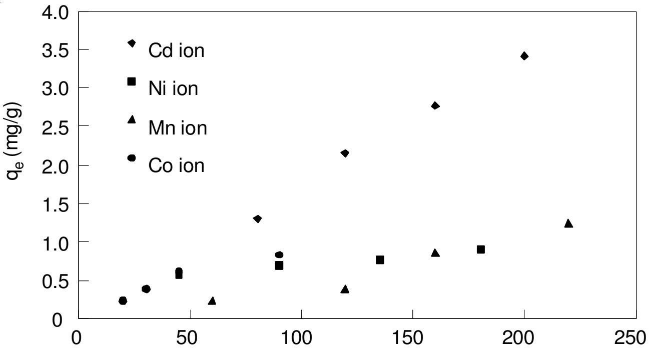

Fig. 2. Initial concentrations of metals and q_e

To examine the effect of adsorbent mass on metal adsorption, equilibrium studies using constant concentrations of initial single-constituent metal ion solutions and a range of adsorbent masses were conducted.

Figs. 3 and 4 illustrate the equilibrium adsorption capacities of the adsorbent, q_e (mg/g), in single-constituent metal ion solutions. The equilibrium adsorption capacities were observed to decrease with increasing adsorbent mass, which might be due to the presence of a higher density of solids that could lead to a decrease in opportunities for contacting all adsorption sites. The removal efficiencies of cadmium, cobalt and nickel ion increased considerably with adsorbent mass addition. The removal efficiency of manganese ion for peat increased considerably with adsorbent mass addition. A number of studies have reported that the use of smaller adsorbent masses provides agreater removal of metal ions[6,8]. These reports state that the decrease in adsorption capacity at higher masses was due to the formation of aggregates with increasing adsorbent mass additions, which decreased the effective adsorption area.

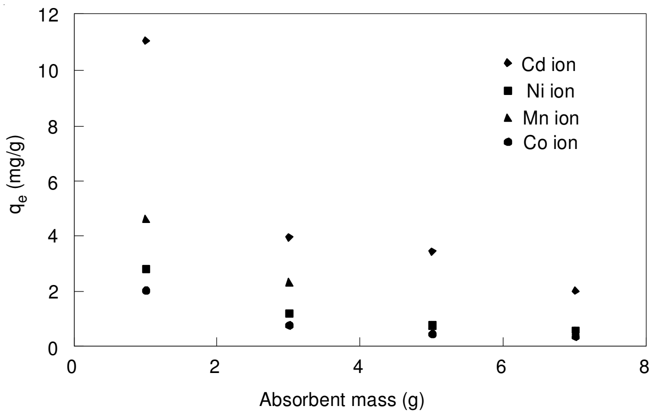

Fig. 3. Effect of adsorbent mass on adsorption

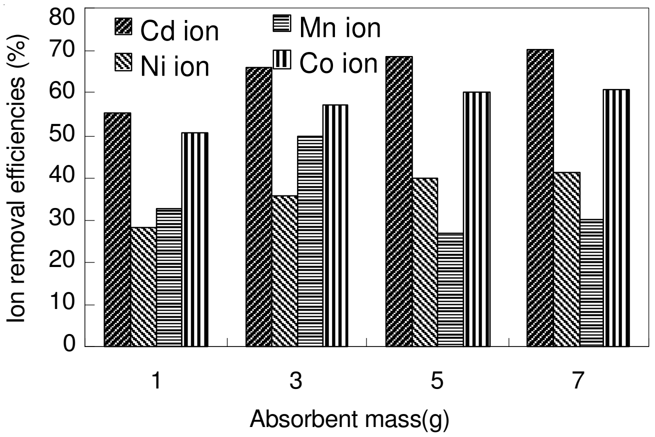

Fig. 4. Removal efficiencies of metal ions

Conclusion

In the equilibrium experiments using various initial metal ion concentrations and adsorbent masses, a 24 h period was considered to provide an adequate contact time between the single-constituent metal ion solutions and the adsorbent to reach equilibrium.

The equilibrium adsorption capacities of the adsorbent for single-constituent metal ion solutions was noted to be Cd > Co> Ni> Mn.

Considering solution pH changes, crushed oyster shells could be a better naturaladsorbent in full-scale applications where final solution pH considerations are required. After a 24 h contact period with crushed oyster shells, the solution pH was generally found to equilibrate at approximately pH of 8.

Parameters such as different initial metal ion concentrations and adsorbent masses were also found to significantly affect the adsorption capacities. The metal adsorption capacities generally increased with increasing initial metal concentration and decreased when adsorbent masses were increased in solution.

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