



## Removal of Cadmium and Cobalt from Heavy Metal Solution Using Oyster Shells Adsorbent

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(Received: 17 November 2012;

Accepted: 26 August 2013)

AJC-13990

This paper investigated the adsorption capacities of crushed oyster shells adsorbent for removal of cadmium and cobalt from aqueous solution of heavy metal using batch experiments and column experiments. 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  $Cd > Co$ . Considering solution pH changes, crushed oyster shells could be a better natural adsorbent in full-scale applications where final solution pH considerations are required. Crushed oyster shells were found to be a better adsorbent for removal of cadmium ion in column testing. When a 10 cm diameter fixed-bed column packed with a 15 cm depth of crushed mollusk shells was hydraulically loaded with a cobalt and cadmium binary aqueous solution at a rate of 1.5 mL/min, the best cadmium treatment efficiency observed was 49.2 %.

**Key Words:** Cadmium and cobalt, Heavy metal solution, Oyster shells adsorbent.

### INTRODUCTION

The heavy metal ions from some kinds of wastewater could cause significant environmental problem because of their toxicity for living beings<sup>1</sup>. The heavy metal ions have to be treated before the wastewater is discharged to the receiving environment. The conventional treatment methods being discussed and applied for removal of heavy metal ions 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 process because of high operational cost. As such, alternative adsorption technologies using low-cost materials as adsorbents has been shown to be a feasible treatment process for removing heavy metal from wastewater. It has been demonstrated that using natural materials as adsorbent was more economical<sup>2</sup>. 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- $\beta$ -D-glucose-(*N*-acetylglucan)]<sup>3</sup>. The chemistry 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 acetyl amino, 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 influencing factor on adsorption such as contact time, pH changes in solution, adsorption capacity, adsorption efficiency, hydraulic loading and bed depth.

### EXPERIMENTAL

In this experiment, the commercially available crushed oyster shells were used as adsorption media. The shells were washed with distilled water and air-dried at room temperature (20-23 °C) for 48 h. After air drying, the shells were oven-dried in a hot box oven at 90 °C 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. The characteristics of oyster shells adsorbent were analyzed and are summarized in Table-1. The binary metal aqueous solution used in this study was prepared by dissolving analytical grade cadmium sulfate and cobalt sulfate into distilled water.

TABLE-1  
ADSORBENT CHARACTERISTICS

Particle density (g cm <sup>-3</sup> )	Bulk density (g cm <sup>-3</sup> )	Porosity	Media pH
2.57	1.10	0.68	9.2

A batch adsorption study was undertaken to investigate the adsorption of cadmium and cobalt in a binary metal ion

solution onto crushed oyster shells adsorbent. The metal ion solution was composed of 500 mg/L cadmium sulfate and 500 mg/L cobalt sulfate. About 5 g of adsorbent was added to a flask containing 100 mL of the binary metal ion solution and shaken on a orbital shaker 100 rpm for 48 h.

Ten diameter and 20 cm deep columns were used as fixed-bed column set-up and the crushed oyster shells were packed into the columns as adsorption media. The column set-up operated in a gravity down-flow manner.

Raised tanks were used to supply influent metal solution to the columns at a certain rate. All experiments were performed at room temperature (19~21 °C). Metal ion concentrations in solution were determined by atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

In batch kinetic and equilibrium adsorption studies examining the removal of cadmium and cobalt from heavy metal solutions, a period of 24 h is commonly regarded as an adequate contact time to reach equilibrium<sup>4</sup>. A 24-h adsorption kinetic study was conducted contacting single-constituent metal solutions of cadmium (200 mg/L) and cobalt (40 mg/L) with crushed oyster shells. Experiments were conducted 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 and cobalt, respectively, as a function of time. 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. Hence it was considered to have reached equilibrium. A contact period of 6 to 8 h has also been reported for cadmium adsorption using crab shells in a study by Benguella and Benaissa<sup>4</sup>. 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.

As shown in Table-2, 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

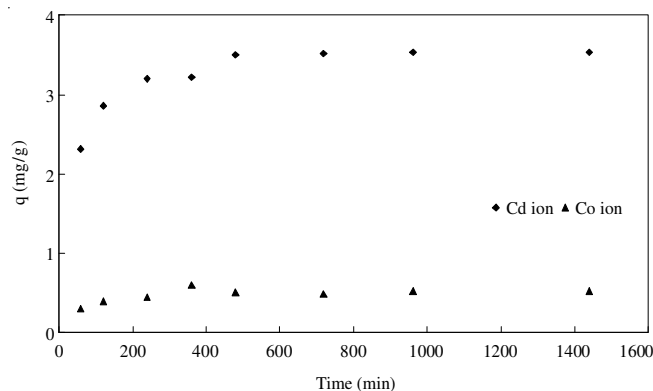


Fig. 1. Metal ions adsorption as a function of time

adsorbent materials. In this respect, the 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-2  
pH VALUES OF SOLUTIONS

Solution	Cadmium sulfate (500 mg/L)	Cobalt sulfate (500 mg/L)
Initial pH	4.3	6.1
Final pH	7.7	8.0

Adsorption capacities of adsorbent on cadmium and cobalt are summarized in Table-3. Based on the results (Table-3), in the single solution adsorption capacities of the adsorbent on cadmium and cobalt was 3.42 mg/g, 0.48 mg/g respectively, the equilibrium adsorption capacities of the adsorbent for single-constituent metal ion solutions was noted to be Cd > Co. 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<sup>5</sup>. 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<sup>6</sup>. Other carbonate species, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, 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<sup>2+</sup> 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.

TABLE-3  
ADSORPTION CAPACITIES ON CADMIUM AND COBALT

	Cadmium	Cobalt
q <sub>e</sub> -single (mg/g)	3.42	0.48
Efficiency (%)	96.2	76.7
q <sub>e</sub> -binary (mg/g)	1.82	0.29
Efficiency (%)	75.1	51.4

In the binary solution adsorption capacities on cadmium was 1.82 mg/g and cobalt was 0.29 mg/g. This indicates that the adsorption capacities of the adsorbents observed in multi-constituent batch experiments were lower than that observed in a single-constituent study, which was attributed to competitive adsorption. Competitive adsorption results from the competition between metals for the limited number of available adsorption sites existing on the surface of the adsorbent when present in a multi-component metal ion aqueous solution.

Column adsorption capacity, treatment efficiency are summarized in Table-4. Table-4 showed that the highest treatment efficiency for cadmium could be achieved in C4 with 15 cm of crushed shells under hydraulic loading conditions of 1.5 mL/min. A removal efficiency of 49.2 % was achieved, which is lower than 96.2 % removal observed during the single-constituent batch study and 75.1 % removal observed in the multi-constituent batch study. This was likely due to the fact that the column configurations and density of the packed material reduced the adsorption capacities of the adsorbents, as a result of a decrease in the contact surface area of the

adsorbent in the packed column configuration. Conversely, the best cobalt ion removal efficiency (11.2 %) was obtained in C3, which was packed with 10 cm of adsorbents and operated at a hydraulic loading of 1.5 mL/min. This was also lower than the 76.7 % removal efficiency reported in the single-constituent batch experiment and 51.4 % removal obtained in multi-constituent batch experiment, which was also likely due to competitive adsorption and column configurations as noted for cobalt removal. These results could also be attributed to the fact that the residence time or empty bed contact time (EBCT) of the metal solution in the columns was not adequately long enough to reach adsorption equilibrium even at the hydraulic loading of 1.5 mL/min.

	C1; 10 cm 3.5 mL/min	C2; 15 cm 3.5 mL/min	C3; 10 cm 1.5 mL/min	C4; 15 cm 1.5 mL/min
$q_m, \text{Cd}$	1.57	1.60	1.91	1.64
$q_v, \text{Cd}$	1.00	1.02	1.05	1.08
Efficiency (%)	13.2	20.2	31.3	49.2
$q_m, \text{Co}$	0.55	0.26	0.33	0.19
$q_v, \text{Co}$	0.31	0.17	0.20	0.13
Efficiency (%)	9.14	6.42	11.2	10.4

Two flow rates, 1.5 mL/min and 3.5 mL/min were applied to columns at 10 cm and 15 cm adsorbent depths and effluent metal concentrations as a function of throughput volume were monitored. The metal breakthrough curves are shown in Figs. 2 and 3.

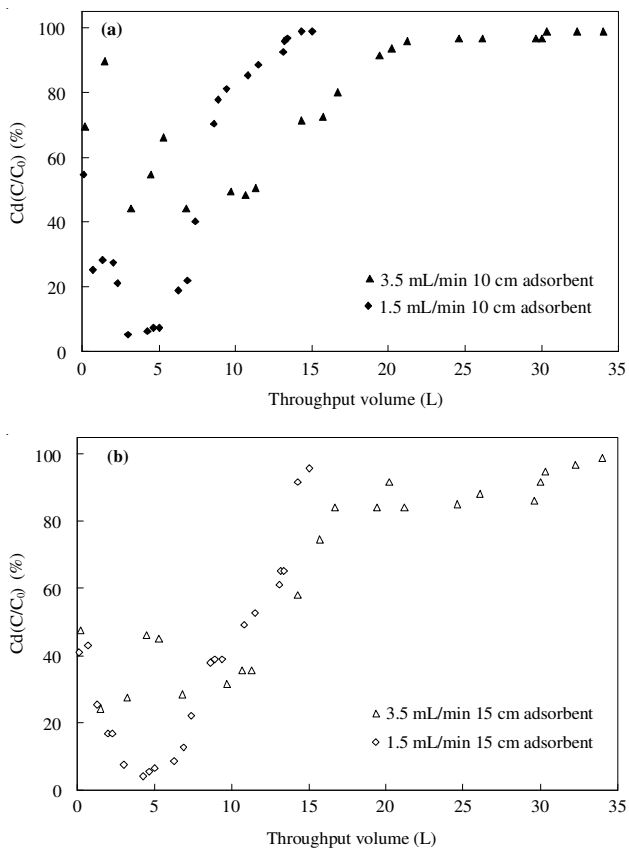


Fig. 2. Breakthrough curves for cadmium ion adsorption in (a) 10 cm and (b) 15 cm bed depths

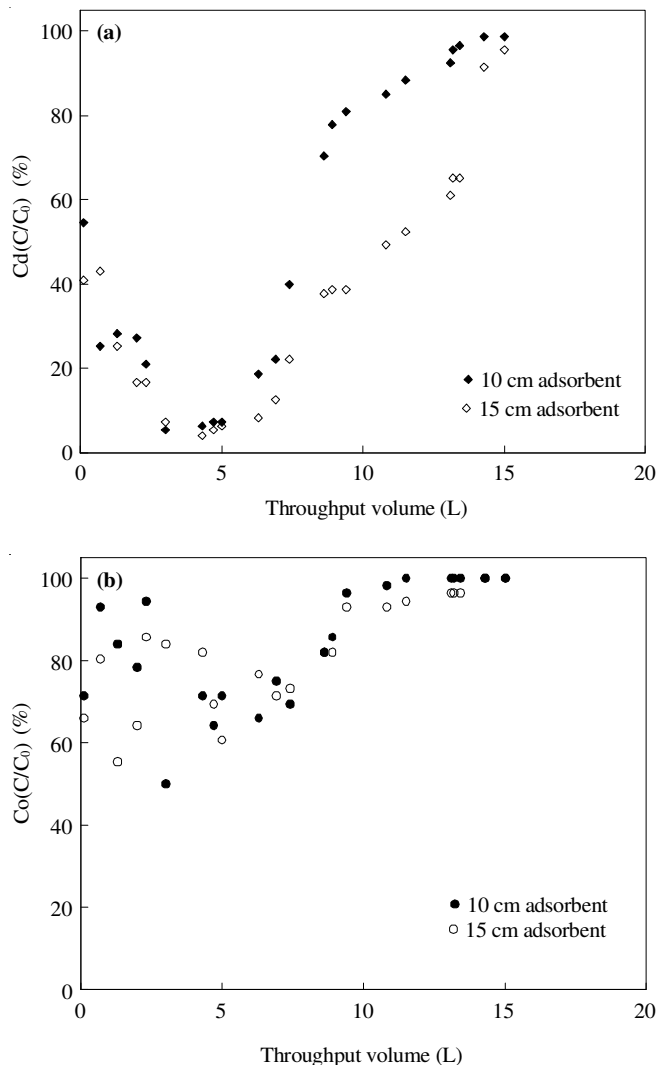


Fig. 3. Breakthrough curves for (a) cadmium ion and (b) cobalt ion

According to Fig. 2(a) and (b), it can be seen that under higher hydraulic loading 3.5 mL/min, cadmium breakthrough was noted immediately. At the lower hydraulic loading of 1.5 mL/min, a typical breakthrough curve was observed which would suggest that lower hydraulic loadings are necessary to ensure that an appropriate contact time is provided for adsorption processes to occur in fixed-bed columns, particularly if a portion of the process involves the dissolution of the calcium carbonate present in the shells and the subsequent formation of insoluble cadmium carbonate.

The effect of hydraulic loading on cobalt adsorption can be seen in Fig. 3(a) and (b). At both the 3.5 mL/min and 1.5 mL/min hydraulic loadings, cobalt breakthrough was found that cobalt adsorption onto crushed oyster shells could not be adequately described using the Freundlich and Langmuir isotherm models and that the effect of the adsorbent on the solution pH may have been a contributing factor. The results also indicated that nickel adsorption using crushed oyster shells as an adsorbent was limited for the range in initial concentrations tested.

**Conclusion**

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  $Cd > Co$ .

Considering solution pH changes, crushed oyster shells could be a better natural adsorbent in full-scale applications where final solution pH considerations are required.

Crushed oyster shells were found to be a better adsorbent for cadmium ion removal in column testing. When a 10 cm diameter fixed-bed column packed with a 15 cm depth of crushed mollusk shells was hydraulically loaded with a cobalt and cadmium binary aqueous solution at a rate of 1.5 mL/min, the best cadmium treatment efficiency observed was 49.2 %.

#### ACKNOWLEDGEMENTS

The Ministry of Construction of China Research and Development Project (2010-k6-28) is gratefully acknowledged for its support of this work.

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