Mussel Shell and Waterworks Sludge as Sorbent Materials for the Removal of Cu(II) from Aqueous Solution

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ABSTRACT

Waterworks sludge generated from water treatment plants and mussel shells generated from the mussel cultivation industry contribute to the problem of solid waste in the environment. Reusing them as sorbent materials for the removal of heavy metals from water systems not only reduces the problem of solid waste management but also solves the problem of heavy metal pollution. In this study, the properties and capability of mussel shells (MS), waterworks sludge (AS), mussel shell-bentonite clay mixture (MSBC) and mussel shell-alum sludge mixture (MSAS) to remove copper from aqueous solutions were investigated. The bulk density, particle density, porosity and pH were determined to discern the physical properties of the sorbents. The addition of MS into BC and AS increased the sorption capability for Cu(II). The order of removal of copper ions by each sorbent was MSBC > MSAS > AS > BC which was established in 300-360 minutes. The maximum sorption capacities were in the range of 9.0-11.8 mg/g, with mixed sorbents exhibiting higher capacity. Kinetic studies showed that the pseudo second-order kinetics correlated well with experimental data. In addition, the removal of Cu(II) were well described by the Langmuir isotherm.

| Waterworks sludge | Mussel shell | Bentonite clay | Copper | Sorbent |

1. INTRODUCTION

In many parts of the world, including Malaysia, alum-derived waterworks sludge (AS) is produced by municipal waterworks operators that provide household clean water. Large quantities of the AS is either left idle in dewatering lagoons or transferred to waste disposal areas after dewatering [1]. The AS is a scheduled waste governed by stringent regulations on waste management by the Department of Environment (DOE) [2], and must be disposed of accordingly. The disposal of AS is costly for waterworks operators in terms of sludge transportation. In addition, there are concerns over the issue of overfilled landfills in the future. Generally, AS has been reused as construction material and remediation media for constructed wetlands [3-5]. AS is amorphous in nature and provides large surface areas that are reactive for sorption reactions. Previous studies have shown that spent AS was effective in removing phosphate, lead, mercury, arsenic, selenium, and chromium from solutions [1, 6-9]. AS tend to be similar in mineral form to clay. Bentonite Clay (BC) is a soft and porous clay material. Montmorillonite is the dominant component in Bentonite, while the remaining components (~10%) are quartz, feldspar, illite and organic substances. Studies have shown that clay materials have high affinity for Cu^{2+} [10], hence AS is compared to BC in this study

Green mussel is widely cultivated in Malaysia, where there are at least 360 mussel cultivation areas producing at least 10 thousand tons of mussels per year, in the State of Johore alone [11]. Mussel Shells (MS) generated by these mussel cultivation industries have some applications in the construction industry. However, when the generation of shell volume exceeds the demand, disposal of the shells becomes an environmental issue. MS is rich in calcium carbonate. The middle prismatic layer of the shell is composed of crystalline calcium carbonate and the innermost nacreous layer consists of thin layers of calcium carbonate [12].

Heavy metal bearing wastewaters containing Copper (Cu) are generated by mining activities, petroleum refining, as well as industries engaging in metal plating, battery manufacturing, printing, pesticides production, paint/pigment production, and so on [13]. Cu does not degrade in the environment, and accumulates in plant and animal tissues causing serious health threats to humans. Cu has also been identified as a culprit in Alzheimer's disease [14]. Reviews on the adsorption mechanism, factors that influence adsorption, favorable conditions, and competitive ions for the removal of heavy metals from wastewater using adsorbents from various chemically modified plant and industrial wastes have been documented [15, 16], but no studies had been done on sorption of high copper concentrations using waste shell and sludge mixtures.

The aim of this study is to investigate the feasibility of reusing and incorporating mussel shells into waste

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waterworks sludge as sorbents to remove copper ions at high dosages from water. The removal of copper in aqueous system was evaluated without prior treatment or pH adjustments. Since the chemical composition of waterworks sludge has been shown to be similar to clay, rich with silicon and aluminum oxides, thus we used Bentonite clay as comparison. The Langmuir and Freundlich isotherms were employed to ascertain the adsorption equilibrium, and the pseudo-first-order equation and the pseudo-second-order equation were applied to investigate the adsorption mechanisms. The results could provide an alternative material for removing copper from wastewater, help solve the cost of AS management by waterworks operators, as well as provide added value to the mussel cultivation industry.

2. EXPERIMENTAL

2.1 Materials, method and instruments

Mussel shells obtained from mussel cultivation areas of Danga River, Johore, Malaysia, were cleaned, oven-dried at 100 ^{o}C to a constant mass, ground to powder and sieved (1-2 mm). Bentonite clay was purchased commercially and waterworks sludge was collected from the Semanggar Waterworks Plant, Kota Tinggi, Johore, Malaysia. Samples were oven-dried, ground and sieved (particle size: 1-2 mm). The waterworks sludge (AS) and Bentonite clay (BC) were studied as single sorbents, while mixtures of mussel shell-Bentonite clay (MSBC) and mussel shell-waterworks sludge (MSAS) were studied as mixed sorbents.

Synthetic copper-bearing wastewater was prepared by dissolving $CuSO_4.5H_2O$ in deionized distilled water at 1000 g/L, and Cu(II) adsorbates were appropriately diluted from the stock solution. Samples (100 mL working volumes) were shaken in 250 mL Erlenmeyer flasks at 100 rpm on an orbital shaker (Hotech, Model 722) for designated time periods at room temperature (25-27°C). The concentration of Cu(II) in solution was analyzed using an atomic absorption spectrophotometer (AAS, Perkin-Elmer AAnalyst 400). Solution pH was measured using a pH meter (CyberScan, Model 500).

2.2 Analysis of Adsorptive and Physical Characteristics of Sorbent

Preliminary tests were conducted to determine the optimum ratio of MS to BC and AS that was able to effectively remove Cu(II) from solution. A series of 0.3-g samples, each containing 5, 10, 15, 30 and 60% MS in BC, were added to 250 mL Erlenmeyer flasks containing 100 mL of 300 ppm Cu(II) solution. The flasks were shaken at room temperature and 100 rpm for 12 h. The samples were then filtered using Whatman filter paper, and the concentration of Cu(II) in solution was analyzed using AAS. The experiment was repeated using a series of samples containing the same percentage of MS in AS, and other additional samples containing 0.3 g MS, BC and AS.

The pH was determined by mixing 0.3 g of sorbent with 100 mL distilled water and shaking at 100 rpm for 3 h. Each sample was filtered and the solution pH was measured using a pH meter. Bulk density, particle density and porosity of the sorbents were determined using physical methods described by Blake and Hartge [17].

2.3 Batch Adsorption Studies

Batch studies were conducted to investigate the effects of sorbent dose, initial Cu(II) concentration and agitation time. The sorption characteristic was investigated by contacting a constant dose of sorbent with a series of 100 mL Cu(II) solutions (50-500 ppm) in 250 mL Erlenmeyer flasks at room temperature (25-27°C). The samples were shaken at 100 rpm for 3 h, filtered and the solutions analysed for Cu(II) using AAS. To study the effect of sorbent dose, a series of 100 mL Cu(II) solutions (50-500 mg/L) were contacted with a series of each sorbent (0.5-5.0 g/L) in 250 mL flasks. The mixtures were shaken for 3 h at 100 rpm and room temperature (25-27°C). The samples were then filtered and analyzed for Cu(II) using AAS. Kinetic studies were conducted on mixed sorbents (MSBC and MSAS). The optimum dose of each sorbent was contacted with a series of 100 mL Cu(II) solutions and shaken at 100 rpm and room temperature. At the end of 15, 30, 45, 60, 90, 120, 180, 240, 300, 360, 480 and 720 min a sample mixture was filtered through Whatman filter paper and the Cu(II) in the filtrate was determined using AAS. All experiments were done in triplicates.

2.4 Data Analysis

Data from the equilibrium and kinetic studies were calculated and analyzed using a number of equations defined for adsorption studies. The amount of copper adsorbed at time t, q_t was calculated from Eq. (1).

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q_t is the amount of metal adsorbed (mg/g) at time t (min), C_0 and C_t are the initial and final metal concentration in solution (mg/L), V is the working volume (L). When time t is equal to the equilibrium time, $C_t = C_e$ and $q_t = q_e$, where q_e is the amount of Cu(II) adsorbed at equilibrium, and C_e is the equilibrium metal concentration in solution (mg/L).

The metal removal efficiency (% Removal) is calculated using Eq. 2:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

The Langmuir and Freundlich isotherm models were applied to determine the sorption equilibrium. The Langmuir sorption isotherm describes that removal of adsorbate occurs on a homogeneous surface by monolayer sorption, without interaction between adsorbed molecules.

The linear form of the Langmuir isotherm is expressed as Eq. 3 [18].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (3)$$

where q_e (mg/g) and C_e (mg/L) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, q_m (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the adsorption equilibrium constant. K_L and q_m are determined from the slope and intercept of the plot of C_e/q_e against C_e. The equilibrium parameter R_L expressed by Eq. 4, indicate the shape of the isotherm.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (4)$$

where C_0 is the initial metal concentration (mg/L) and K_L is the Langmuir constant (L/mg). The isotherm is unfavorable if $R_L>1$, linear if $R_L=1$, favorable if $0<R_L<1$, and irreversible if $R_L=0$.

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces. The linear form of the isotherm is represented as Eq. 5 [19].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

where q_e is the equilibrium metal adsorbed (mg/g), C_e is the equilibrium metal concentration in solution (mg/L), K_F (mg/g)(L/g)$^{1/n}$ is the Freundlich constant related to sorption capacity and n is the heterogeneity factor. K_F and $1/n$ are determined from the intercept and slope of the plot of $\log q_e$ against $\log C_e$.

The extent of Cu(II) uptake by the sorbents was quantified using the Lagergren's pseudo-first-order and pseudo-second-order kinetic models. The linear pseudo-first-order equation is given as Eq. 6 [20].

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

where k_1 (min^{-1}) is the adsorption rate constant calculated from the slope of the linear plot of $\log(q_e - q_t)$ *versus* t; and q_t and q_e are the amount of metal adsorbed at time t and at equilibrium (mg/g). The pseudo-second-order kinetic model is given by Eq. 7 [21].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where k_2 (gm/g.min) is the adsorption rate constant determined from the intercept, and $1/q_e$ is the slope of the linear plot of t/q_t versus t.

3.   RESULTS & DISCUSSION

3.1   Adsorptive and Physical Characteristics of Sorbents

The effect of mixing MS into AS and BC for the removal of Cu(II) from solution is shown in Figure 1. The incorporation of up to 10% MS into AS and BC showed an increase in Cu(II) removal. The maximum Cu(II) removal for MSAS and MSBC was 90% and 93%, respectively. Samples containing >10% MS, showed lower but constant Cu(II) removal (~73-88%) and the sorbent particles were not well dispersed in solution. Thus, mixed sorbents containing 10% MS were considered optimal.
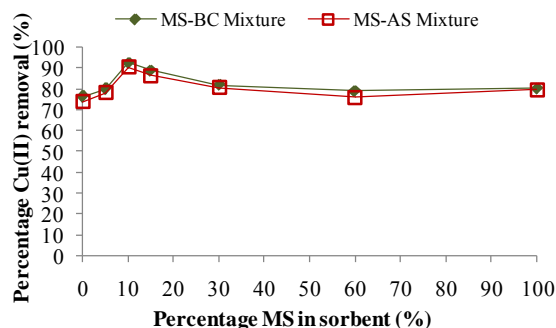

Fig. 1   Effect of MS in BC and MS on Cu(II) removal [sorbent dose: 3.0 g/L, Cu(II) conc: 300 mg/L, agitation: 100 rpm/ 12 h, room temp].

The physical properties of the MSBC and MSAS (at 10% MS ratio), MS, AS and BC are shown in Table 1. Lower than 1.2 g/cm^3 bulk densities and particle density values of less than 2.2 indicate fine particles that should provide high metal sorption. The addition of MS has the effect of lowering the porosity of AS and BC, thus providing larger surface area for inter particle bonding [17]. The addition of MS also increased the pH of AS and BC, indicating some form of carbonate enrichment provided by the presence of $CaCO_3$ in MS. The pH of a solution and a sorbent material has been shown to influence copper species in solution. At mid acidic conditions of ~pH 3-5, functional groups on a sorbent material are deprotonated and are negatively charged, enhancing the attraction of positively charged Cu(II) ions [22]. Free Cu ions are dominant at pH below 6.0, whereas precipitation or complexation of Cu^{2+} with OH^- forming $Cu(OH)_2$ is expected to occur at higher pH [23].

In this study, Cu(II) ions are expected to be removed by either adsorption or precipitation or both mechanisms. The mechanisms of copper (II) adsorption on the sorbents include formation of surface complexation and surface precipitation.

Table 1 Proximate physical characteristics of MS, AS, BC, MSAS and MSBC

Characteristic	AS	BC	MS	MSAS	MSBC
Bulk Density (g/cm^3)	0.83±0.06	0.89±0.05	1.12±0.04	0.59±0.04	0.57±0.03
Particle Density (g/cm^3)	2.16±0.06	2.07±0.04	2.15±0.03	1.69±0.01	1.53±0.01
Porosity (%)	11.48±0.02	9.05±0.01	0.70±0.02	0.86±0.02	1.09±0.01
pH of sorbent	4.28±0.01	7.01±0.02	8.25±0.02	8.19±0.01	8.90±0.01

At the alkaline natural pH of the sorbents, removal of Cu(II) was high, indicating that surface complexes reaction was more important than ion-exchange [24]. At the pH of 8.19 and 8.25, the MS and MSAS samples were equally effective and would be desirable for removing Cu(II) from contaminated water.

3.2   Effect of Contact Time

The effect of contact time on Cu(II) solution is presented in Figure 2. The highest amount of Cu(II) adsorbed per unit sorbent at time t (q_t) was achieved in 300-360 min depending on the sorbent (10.7, 10.1, 8.9 and 7.9 for MSBC, MSAS, BC and AS, respectively). The rate of adsorption was high in the first 200 min and became constant after 360 min. Since the equilibrium concentration of Cu(II) did not show obvious variation from 300 to 360 min, the equilibrium time of later adsorption experiments was therefore determined at the 360 min mark. A short contact time is generally advantageous for an adsorption system.
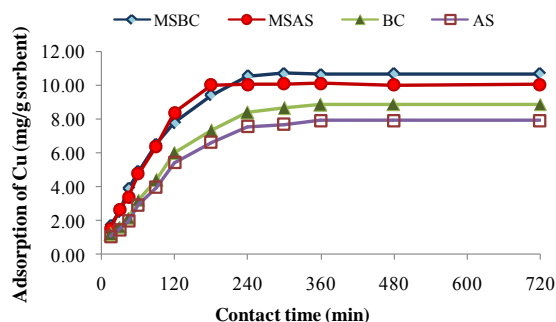

Fig. 2 Effect of contact time on Cu(II) adsorption [sorbent dose: 3.0 g/L, Cu(II) conc: 300 mg/L, agitation: 100 rpm, contact time: 15, 30, 45, 60, 90, 120, 180, 240, 300, 360, 480, 720 min, room temp.]

The uptake vs time curves for MSBC, MSAS, BC and AS were single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of the Cu(II) on the surface of each sorbent. However, equilibrium time varied due to the difference in initial Cu(II) concentration and also the affinity of the sorbent for the copper ions. Experiments conducted on Cu(II) at concentrations higher than 300 mg/L (results not shown)

indicated a longer time to attain equilibrium. This is due to the presence of proportionally high amount of metal ions and that the available adsorption sites on the sorbents were the limiting factor for metal uptake.

3.3   Effect of Initial Cu(II) Concentration and Sorbent Dosage

The effect of initial Cu(II) concentration on adsorption characteristics is shown in Figure 3. Increasing initial Cu(II) concentration resulted in decreased Cu(II) removal (%) and increased sorption capacity (mg/g).
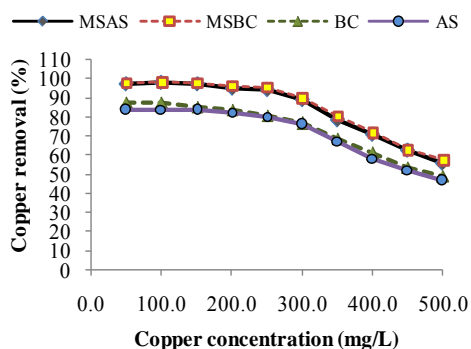
(a)
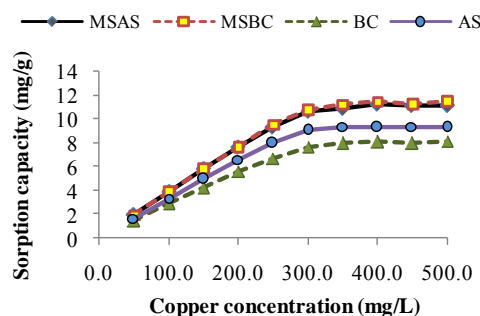
(b)

Fig. 3 Effect of initial Cu(II) concentrations on Cu(II) sorption: (a) percentage removal (%) and (b) sorption capacity (mg/g) [sorbent dose: 3.0 g/L, Cu(II) conc: 50-500 mg/L, agitation: 100 rpm/3 h, room temp.]

Although the percentage of Cu(II) uptake was smaller at high initial concentrations, the actual amount of the metals adsorbed (q) increased with increase in the initial concentration in the solution. There were differences in the

Cu(II) sorption due to the difference in the chemical compositions and physical properties of each sorbent.

The effects of sorbent dose on removal of Cu(II) is presented in Figure 4. The percentage of Cu(II) removed increased with increasing sorbent dose because the surface area and number of adsorption sites were increased with increasing sorbent dose. However, the removal tended to reach a saturation level at high doses, which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces [25].
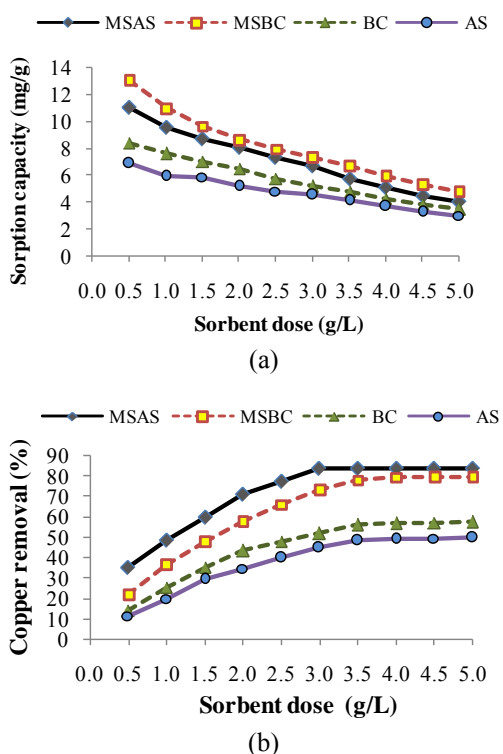

(a)

(b)

Fig. 4 Effect of sorbent dose on Cu(II) sorption at different initial concentrations: (a) percentage removal (%) and (b) sorption capacity (mg/g) [sorbent dose: 0.5-5.0 g/L, Cu(II) concentration: 50-500 mg/L, agitation: 100 rpm/3 h, room temp.]

In addition, the adsorption capacity decreased with increasing dose due to a decrease in available sorbent surface area per unit mass which is caused by overlapping and aggregation of adsorption sites. Inter-particle interaction, such as aggregation, resulting from high adsorbent concentration could also lead to a decrease in the total surface area of the adsorbent and an increase in the diffusion path length [26].

Generally, 3.0-4.0 g/L of MSBC and MSAS were sufficient to remove more than 80% Cu(II) from solution in this study. However, BC and AS were less efficient in removing the Cu(II) ions. The extent of sorption was limited at high sorbent concentrations. At constant initial Cu(II) concentrations the sorbent dose should be low in order to maximize the solid phase Cu(II) ion concentration at equilibrium.

3.4 Adsorption Isotherms

The Langmuir and Freundlich constants for Cu(II) adsorption by AS, BC, MSBC and MSAS are presented in Table 2. Freundlich isotherms were obtained by agitating a fixed concentration of Cu(II) solution with different doses of sorbent at a contact time greater than the equilibrium time. A linearized equation was derived for the log q_e *vs* log C_e plot, and the equation was used to calculate the Freundlich constants. K_F and $1/n$ were calculated from the slopes of the Freundlich plots. The magnitude of $1/n$ indicates the intensity of the adsorption and K_F gives the indication of favourability and the capacity of the sorbent/adsorbate system. The Freundlich isotherm indicates the ease or difficulty of an adsorption process. The Langmuir isotherms were obtained by agitating a fixed sorbent dose against Cu(II) of different concentrations for a contact time greater than equilibrium time. A linearized equation derived for the (C_e/q_e) vs C_e plot was used to compute the Langmuir constants. The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the sorbent surface.

The maximum specific uptake corresponding to the site saturation is given by q_{max}, and K_L is the ratio of the adsorption and desorption rates. When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The R^2 values in this study indicated that adsorption of Cu(I) on all the sorbents tend to obey the Langmuir isotherm.

Table 2 Isotherm parameters for adsorption of Cu(II) onto BC, AS, MSBC and MSAS

Sorbent	Langmuir isotherm parameters				Freundlich isotherm parameters		
	R^2	K_L (L mg^{-1})	q_m (mg g^{-1})	R_L	R^2	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	$1/n$
MSBC	0.999	0.306	11.765	0.9217	0.931	1.398	0.608
MSAS	0.997	0.209	11.628	0.9208	0.931	2.646	0.852
BC	0.994	0.046	9.009	0.9001	0.861	5.726	1.123
AS	0.986	0.039	10.638	0.9141	0.880	8.134	1.210

The separation factor values obtained in this study, in the range of 0.9001-0.9217 ($0<R_L<1$), indicated favorable (almost linear) adsorption for all the sorbents. The maximum adsorption capacity (q_{max}) for the study was in the order of MSBC>MSAS>AS>BC at 11.765, 11.628, 10.638 and 9.009, respectively. Sorption capacities of 3.2-4.1, 2.4-4.2 and 12 mg/g on sewage sludge ash, fly ash and Ca-bentonite, respectively had been reported in previous Cu(II) adsorption studies, and all followed the Langmuir isotherm model [27]. In this study, the expected primary mechanism for Cu(II) removal by mussel shell is the formation of insoluble metal carbonates, and Ca^{2+} is the likely dominant counter-ion released from the shells due to the fact that most of the $CaCO_3$ in shells dissolve between pH 5-11 [28].

The expected primary adsorption mechanism for Cu(II) removal by the waterworks sludge is surface complexation and precipitation on the sludge. In surface complexes reactions positively charged ions are attracted to negatively charged surface without the exchange of ions or electrons. Mononuclear and multinuclear surface complex reactions of copper with the ionized surfaces are possible at high pH. Copper ions were precipitated, and the precipitate that was coated onto the sludge was more predominate than it was in the water phase [29, 30].

3.5 Sorption kinetics

The Lagergren constants for the sorption of Cu(II) on MSBC and MSAS are presented in Table 3. The pseudo-first-order kinetic constants were computed from linear equations of the log (q_e-q) vs t plot. The sorption rate constant, k_1 (min^{-1}) and q_{cal} were calculated from slope and 1/slope. The sorption rate constant, k_2 (g $mg^{-1}min^{-1}$) was calculated from the intercept of the linear t/qt vs t plot. The R^2 values indicated that the adsorption was better fitted to the pseudo-second-order kinetics. The calculated sorption capacity, $q_{calculated}$ agreed with the experimental sorption capacity, $q_{experiment}$.

4.0 CONCLUSIONS

The study shows that waterworks sludge and mussel shells can be affectively used as sorbents for removing Cu(II) at high concentrations from aqueous solutions. The removal efficiency was increased when the sludge and shells were mixed together in a 1:9 ratio of shell to sludge. The physical properties of the sorbents indicated good adsorption capabilities based on surface area and their natural pH. The waterworks sludge was considered equally effective as bentonite clay in removing Cu(II) from solution.

The effect of contact time showed that the uptake of copper increased with increase in contact time until equilibrium was reached. Depending on the sorbent, a time of 300-360 minutes was adequate for removing most of the Cu(II) from solution. The effect of initial adsorbate concentration indicated that as the initial Cu(II) concentration was increased the percent removal was decreased, but the amount of Cu(II) uptake (q) per unit weight of the sorbent was increased. The effect of sorbent dosage on the adsorption of metals showed that the percentage of metal removed increased with increase in sorbent dosage. Sorbent dosage of 3.0-4.0 g/L of the mixed sorbents MSBC and MSAS was sufficient to remove more than 90% of Cu(II) solution at 300mg/L, although AS and BC were able to remove only ~70-80% copper.

Adsorption data for a wide range of Cu(II) concentrations and sorbent doses treated by Langmuir and Freundlich isotherms showed that the Langmuir isotherm was obeyed. The values of equilibrium parameter, R_L from Langmuir isotherm indicate that the adsorption process is favorable and almost linear for Cu(II). Kinetic studies on the adsorption of Cu(II) on MSBC and MSAS revealed that the pseudo-second-order kinetic model was followed and that the experimental sorption capacity agreed with the calculated.

Table 3 Kinetic parameters for adsorption of Cu(II) onto MSBC and MSAS

Sorbent	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			q_{cal} (mg/g)	q_{exp} (mg/g)
	Linear equation	R^2	k_1 (min^{-1})	Linear equation	R^2	k_2 (g mg^{-1} min^{-1})		
MSBC	y = -0.0001x + 0.767	0.520	0.0002	y = 0.090x + 7.725	0.991	0.001	11.11	11.70
MSAS	y = -0.0001x + 0.646	0.448	0.0002	y = 0.096x + 6.042	0.992	0.002	10.42	10.12

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