CARBONIZED GREEN MUSSEL SHELL AS HEAVY METAL REMOVAL

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Abstract: Large amount of mollusc shell are usually disposed off and can a create nuisance due to odor and its quantity. Therefore this study aims explored the adsorption capacity of green mussel (*Perna viridis*) shell for cadmium, chromium and lead from aqueous solutions.. The adsorbent has prepared from powdered green mussel shell in the form of carbonized adsorbents shells at 600°C. The carbonization process was conducted for four hours and allowed to cool at room. Characterization of pH, bulk density, moisture content and ash content was also conducted. The effect of various operational parameters such as concentration, pH, temperature and sorption time on the adsorption of heavy metals were investigated using batch process experiments It was found that green mussel shell can be used as a low cost adsorbent for the removal of heavy metals in aqueous solution. The maximum ion adsorption capacities followed the trend lead > chromium > cadmium and the percentage adsorption was found to depend on the concentration of the adsorbent present, the solution pH, temperature and the sorption. This shows that the adsorption of metal ions on the adsorbent is chemisorption. Kinetic treatment of the results gave a pseudo-second order type of mechanism while the adsorption characteristics of the adsorbent followed the Freundlich adsorption isotherm. The results obtained proved that green mussel shells can be alternative resources of adsorbent materials.

Keywords: *Carbonization, green mussel shell, isotherm, kinetic*

1.0   Introduction

Large tonnes of mussel shell are disposed illegally and dumped into public waters and reclaimed lands annually. The shell wastes are generated from fisheries industry. Only very small proportions of the shells are recycled as additives in animal husbandry, poultry farming, soil fertilizers and coating materials and fish fodders. Enormous amounts of these materials are dumped and become environmental burden (Vukovic *et al*., 2010 ; Du *et al*., 2011 and Alidoust *et al*., 2015). Therefore, alternative approaches

for recycling waste mussel shells are needed. The ideal solution would be to convert the waste mussel shells to a product that is both beneficial and economically viable.

It is well known that various types of mollucs's shell have been used as natural adsorbent for nutrient and heavy metal (Odoemelam and Eddy, 2009; Du *et al*, 2012; Peña-Rodríguez *et al*., 2013; Yoshimura and Shiomi, 2014;Seco-Reigosa *et al*., 2014;Hossain *et al*, 2015 and Alidoust *et al*., 2015). It contains a large amount of organic compounds and macromolecules that can form framework for other macromolecular components, strongly implying that it have a potential to be used as adsorbent. It consist of more than 95% of $CaCO_3$ with small amount of SiO_2, protein and polysaccharide (Liu *et al*., 2009 ;Du *et al*., 2012 and Lu *et al*., 2015). Shells are made up of three layers, Oladoja *et al*.,(2013) reported that the hypostracum, is the innermost layer, followed by the ostracum, as the basic shell building layer and the periostracum as the outermost layer. All the layers have different microstructures. The strength and toughness of the shell are determined by the thickness of the individual layers and their microstructure. The periostracum is made of sclerotized proteins. This outermost shell layer, is not made of calcium carbonate, but of an organic material called conchin, a mixture of organic compounds, mostly of proteids. Conchin does not only make the outer shell layer, but is also embedded between the calcium carbonate crystals of deeper layers. The prismatic layer, hypostracum is a form of aragonite, a type of calcium carbonate. It is composed of calcite prisms surrounded by a conchiolin matrix, with the prisms oriented at an angle to the surface.

Metals are an inherent component of the environment that can be a potential hazard to human beings and animals. Heavy metals contamination is one of the vital factors for decline of water quality that has an obvious impact on seafood diversity. Heavy metal consumption from contaminated sites poses a higher health risk to human. It is one of the vital factors for decline in water quality that has an obvious impact on aquatic diversity. Studies have shown that heavy metal toxicity and accumulation not only depends on metal concentrations but on other factors as well. These include the form in which the metal component is present, the type and concentration of other materials and the integration of physicochemical parameters, such as temperature, dissolved oxygen (DO), salinity, sediment grain size, pH and organic carbon. In the aquatic environment, the minute quantities of some metals, such as: copper, zinc, iron, manganese and nickel are essential for biological systems to function but their excessive concentration can be toxic to living organisms. Other metals such as cadmium, mercury, arsenic and lead are non-essential and therefore have toxic effects on living organisms (Heath, 1995 and Sany *et al*., 2013). A possible solution would be to convert the waste shells into calcium-based alkaline adsorbent products. The use of non-living material offers several advantages: it is not necessary to supply nutrients and it is not possible for the system to fail due to a sudden or unexpected surge in metal concentration killing the biomass. Depending on metal ion and concentration, the rate and degree of metal sequestration can vary greatly between shells of different species. This attribute may enable specific

mollusk and certain highly mineralized crustacean shell materials to be used singly or in combination to selectively remove one or several different types of metal ions at different rates. The objective of this study to produce adsorbent from green mussel shell waste for heavy metal removal.

2.0   Materials and Methods

2.1   Sample Collection and Preparation

Green mussel (*Perna virids*) shell waste was collected from Teluk Jawa, Masai, Pasir Gudang. The shells were sorted to commercial size (60-80 mm), cleaned from mud and barnacle, washed thoroughly with tap water and rinsed with deionized water and oven dried at 105°C for 24 hours. Then, the shells were grinded using Wellmax grinder.

2.2   Carbonization

Carbonization of the shell was conducted using a muffle furnace (Carbolite Sheffield England LMF 4) which allows limited supply of air. Carbonization was done at 600°C for four hours and allowed to cool at room temperature for 24 hours then preserved in a sample container for future use.

2.3   Aqueous Solution of Heavy Metal

All reagents used for this study were analytical reagent grade and were procured from Merk, Dermstadt, Germany. 1000 mg/l aqueous solutions of the metals ions from the stock. Working solutions of 10 mg/l were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using Atomic Adsorption Spectrometer (AAS) model PinAAcle 900T (Perkin Elmer).

2.3   Batch Adsorption Studies

Stock solution of cadmium, chromium and lead of 10 mg/L was prepared. Adsorption studies of heavy metal on the green mussel shell-derived adsorbent were carried out in batch mode. Adsorption experiments to study the effect of initial concentration were carried out by contacting 0.1 g of adsorbent with 30 mL of heavy metal solution of 10 mg/L concentrations at constant temperature (30 °C) in 250 mL Erlenmeyer flasks. The effect of initial concentration was then evaluated on various adsorbent for comparison. Removal percentage and adsorption capacity of cadmium, chromium and lead by the mussel shell was calculated using the following equation 1 and 2.

$$\% \ R = (C_o - C_e)/ \ C_o * 100 \qquad (1)$$

where C_o = Initial concentration (mg/L) and C_e= Final concentration(mg/L)

$$q_e = \frac{C_o - C_e \ \times V}{m} \qquad (2)$$

q_e is the equilibrium adsorption capacity (mg/g), C_o and C_e are the initial and equilibrium concentrations of the heavy metal solution (mg/L), respectively, V is the volume of the heavy metal solution (mL/L), and m is the mass of the adsorbent (mg/g).

2.4   Characterization of Adsorbent

The surface morphology of the raw and carbonized was analyzed using scanning electron microscope (Model JEOL JSM-6390LA). The Fourier transform infrared (FTIR) spectroscopy analysis was conducted using FTIR spectrophotometer (Model Shimadzu IRAffinity-1) in the range of 400-4000 cm^{-1} wavelength with 4 cm^{-1} resolution. FTIR characterization was used to determine the functional groups present on the surface of the samples.

2.5   Variation of dosage

In order to determine the removal efficiency with respect to different adsorbent dosage, experiments were performed by varying adsorbent of 10 mg, 30 mg, 50 mg, 100 mg and 200 mg in 30 mL of cadmium, chromium and lead solution at 10 mg/L concentration at ambient temperature. For these experiment, the Erlenmeyer flask were agitated at 120 rpm using orbital shaker (PSU-10i, Grant Bio) for 4 hours to attain equilibrium and keeping others variables constant. Analysis was conducted in replicates.

2.6   Variation of agitation

In order to determine the removal efficiency with respect to different agitation, experiments was performed at 90 rpm, 120 rpm and 150 rpm at 30 mL of cadmium, chromium and lead solution with a concentration of 10 mg/L, 0.1 g adsorbent were used at ambient temperature. This experiment was conducted for 4 hours to attain equilibrium and keeping others variables constant. Analysis was conducted in replicates.

2.7   Variation of contact time

The effect of contact time on the removal of sample was determined by measuring of the adsorbate (cadmium, chromium and lead cadmium, chromium and lead) at 2, 4, 8, 16

and 24 hours and other variables were kept constant. The equilibrium was also determined. Analysis was conducted in replicates.

2.8   *Variation of Initial Metal Ion Concentration*

In order to determine the removal efficiency with respect to different adsorbate (cadmium, chromium and lead) concentration, experiments were performed by varying adsorbate concentration of 0.5 mg/L, 2 mg/L, 6 mg/L, 8 mg/L and 10 mg/L at 8 hours and keeping other variables constant.

2.9   *Variation of pH Value*

To study the effect of pH on adsorbate (cadmium, chromium and lead) removal, the solution was agitated at room temperature using orbital shaker at different pH at 3,5,7,9 and 11. 0.1 M HCl and 0.1 M NaOH buffer was used at 4 hours and keeping other variables constant.

3.0   **Results and Discussion**

3.1   *Characterization of Adsorbent*

FESEM micrographs and FTIR of the raw green mussel and green mussel adsorbent carbonized with 600°C are presented in Figures 1(a) and (b), respectively. From Figure 1(a), the FESEM micrograph shows presence of flaky sheet phase layer structure, rough and disordered surface with low porosity structure and rudimentary pores. Carbonization with 600°C adsorbent resulted presence of wide pores, relatively smooth with spherical particles of porous structure confirming occurrence of thermal decomposition. This activation process is dependent on the raw material which is composed mainly of calcium carbonate.
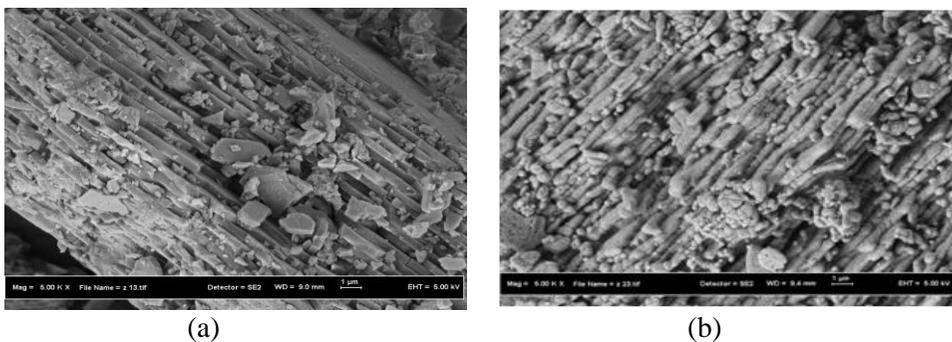

(a)   (b)

Figure 1: FESEM micrographs of (a) Raw green mussel shell, (b) Carbonized with 600°C

From the FTIR spectrum obtained (data not shown), The FTIR patterns of adsorbent (raw and carbonized) and adsorbent with heavy metal were nearly the same. This indicated that green mussel adsorbed heavy metals without changing its surface chemistry (Tan *et al*., 2013). The main functional groups responsible for adsorption process were the hydroxyls, carbonyls, carboxylic and amides (Durve & Chandra, 2014). Clear shifts were observed at wavenumber of 3452.00 cm^{-1} (raw adsorbent) to 3450.94 cm^{-1} (cadmium loaded), 3355.61 cm^{-1} (chromium loaded) and 3453.49 cm $^{-1}$ (lead loaded), which indicated the surface -OH group was one of the functional group responsible for adsorption. The peak in the frequency range of 1000-1200 cm^{-1} is related to the C=O stretch (COOH) in amides, alcohol, carboxylic acids and esters. The peak at 1796.41 cm^{-1} in adsorbent and 1796.15-1796.21 (adsorbent with heavy metal) may be due to the graphite structure (C=C) of carbonized green mussel shell. The intensities of the C–O bands of $CaCO_3$ between 1500 and 500cm^{-1} were the strongest. C–O stretching vibration at 1440 to 1450cm^{-1}. The peaks at 1425.17 cm^{-1} and 1426.75 to 1428.11 cm^{-1} indicate the involvement of the H-C-H asymmetric and symmetric stretches and C-H alkanes stretch. These peaks are attributed to asymmetric stretch; out-of-plane bend and in-plane bend vibration modes for CO_3. The out-of-plane C–O bending vibrations at 710.45 cm^{-1} for carbonized adsorbent and 709.19 – 709.58 cm^{-1} for adsorbent with heavy metal. At 470.48 cm^{-1} for adsorbent without heavy metal the band was assigned to Si-O stretching. Only raw adsorbent shift of these band indicated presence of Si-OH group. Naiya *et, al*. (2011) reported major shift of these band also indicated that Si-OH group is responsible for adsorption.

3.2   Variation of Dosage

Presence of higher dosages of green mussel shell where heavy metal removal efficiency slightly increased from 50 % to 67 % for cadmium, 70 % to 93 % for chromium and 51 % to 97 % for lead (Figure 2). In fact, increasing adsorbent amount provides more chance for the heavy metal ions to adhere to the adsorbent surface due to increase in number of available adsorption sites and surface area. Cd has increase adsorption capacity from 1.5 to 2.0 mg/g, Cr from 1.9 to 2.5 mg/g and Pb from 1.5 to 2.8 mg/g. At dosage above 100 mg, the removal percentage of heavy metal is marginal. Experimental results, with regard to 30 mL of aqueous heavy metal solution, initial heavy metal concentration of 10 mg/L, adsorbent dosage of 100 mg and agitating speed of 120 rpm for 4 hours, produced optimal removal percentage of 60 to 97 % and 1.7 to 2.9 mg/g adsorption capacity. Pb shows good effective adsorption capacity and adsorption percentage. In fact, Pb produce optimal removal at 30 mg adsorbent which it is a good criteria as adsorbent i.e only 30 mg of adsorbent for optimal adsorption than 100 mg for Cd and 200 mg for Cr needed to get optimal removal.
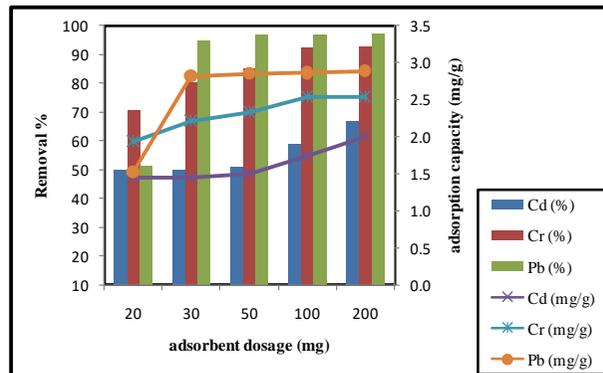
Figure 2 : Effect of adsorbent dosage on cadmium, chromium and lead adsorption

3.3   *Variation of Agitation*

Equilibrium time at suitable agitation speed is another important operational parameter for an economical wastewater treatment process. Figure 3, show that increase in agitation speed will increase removal efficiency until equilibrium adsorption was established. Agitation speed was kept at 90,120 and 200 rpm at 4 hours respectively. At 90 rpm, Cd adsorption percentage was only 57%, increased to 64% at 120 rpm and 65% at 150 rpm. For Cr, adsorption percentage for 90 rpm was 86%, 120 rpm at 89 % and 150 at 90%. Adsorption percentage for Pb was effective but the adsorption capacity was static at 2.8 mg/g. This study shows that equilibrium adsorptions were established within 120 rpm for adsorbent in which Cd, Cr and Pb adsorption capacity and removal percentage from removal efficiencies.
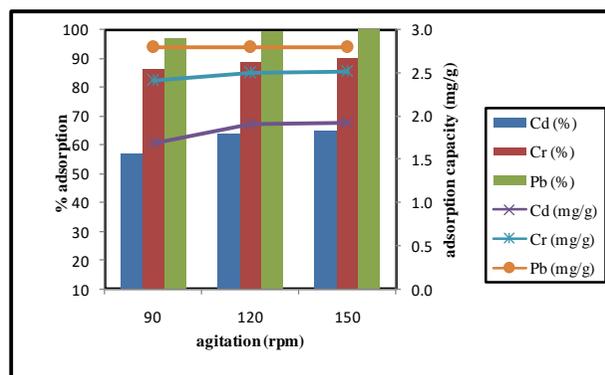

Figure 3 : Agitation at different rpm

3.4 Variation of Contact Time

Cadmium removal efficiency increased from 56% to 78 %, chromium 90% to 94 % and lead 93% to 96 % (Figure 4) respectively, with increasing time. Greater amounts of metal ions were adsorbed by green mussel shell as the agitating time increases. This study shows Cd adsorption using green mussel was not very effective compared to Cr and Pb adsorption. It was observed that the removal percentage increased rapidly at the initial stages because more unsaturated surface and active sites were available on the adsorbent surface area. As the adsorption process proceeds, more surface and active sites are available on the adsorbent surface area. Usually, the metal ions create a monolayer on the adsorbent surface (Abbaszadeh, Wan Alwi, Webb, Ghasemi, & Muhamad, 2016). As the result, the adsorbent surface area becomes gradually exhausted, and the sorption capacity decreased. Based on the results of cadmium, chromium and lead uptake by green mussel shell was obtained after 8 hours, and the uptake trend increased and then become steady after 8 hours indicating Cd, Cr and Pb adsorption capacity were 2.1, 2.6 and 2.7 mg/g at equilibrium.
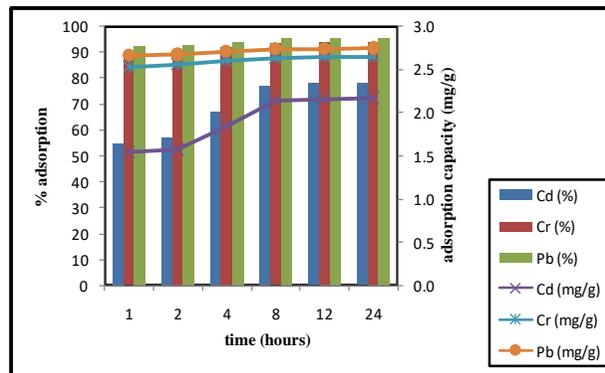

Figure 4 : Effect of contact time on cadmium, chromium and lead

3.5 Variation of Initial Metal Ion Concentration

The removal efficiency of cadmium decreased from 80 to 59 % and increased for chromium and lead at 28 to 92 % and 79 to 95 % (Figure 5) respectively when the initial concentration was increased from 1 to 20 mg/L. The pattern can be predicted because higher initial concentration of metal ions intensifies the adsorption capacity (qe) initially, but as the process proceeds, the higher amount of adsorbate is confronted with a limited (constant) availability of active sites on the adsorbent surface. The adsorption capacity for Cd, Cr and Pb were calculated as 1.7, 2.5 and 2.6 mg/g, respectively. Cd shown decreasing adsorption of heavy metal different from Cr and Pb that increase with adsorption when heavy metal solution increased. More cadmium ions are left

unabsorbed in the solution due to the powerful driving force from initial concentration to overcome the resistance to the mass transfer of ions between the aqueous solution and solid phase and saturation of the binding sites. Consequently, the adsorption efficiency decreases. Correspondingly, at lower concentration, the ratio of metal ions over the adsorption surface is low. Therefore, the metal ions quickly adhere to the available of adsorption sites, resulting in higher adsorption efficiency.
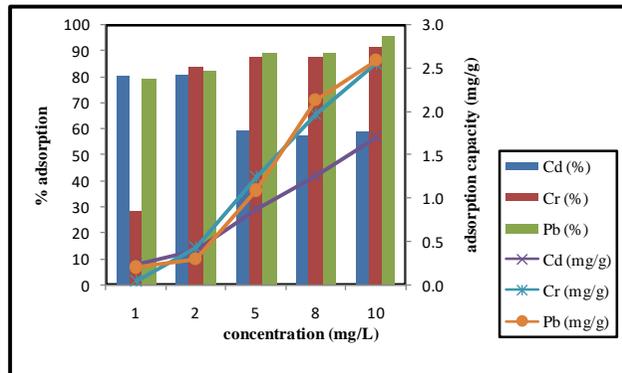

Figure 5 : Initial concentration of Cd, Cr and Pb

3.6   *Variation of pH Value*

Figure 6 shows pH for Cr, Cd and Pb adsorption. Increase in pH shows increase in adsorption. However for Cr adsorption, the adsorption reached equilibrium at pH 9-11. The adsorption percentage was 96% to 99%. For Cd and Pb, the adsorption percentage shows that adsorption was best at both condition either acidic or alkaline. At pH. 7 the adsorption percentage reduced. All metals showed equilibrium was reached at pH 9-11.
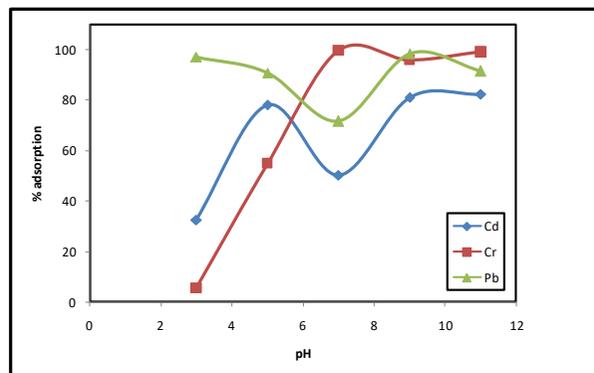

Figure 6 : Effect of pH on cadmium, chromium and lead adsorption

3.7   Adsorption Model Isotherm and Kinetic

From Table 1, it can be seen that the green mussel shell has a maximum adsorption capacity of 2.09 mg/g to form monolayer coverage for Cr. This isotherm is suitable for representing chemisorption on a set of distinct localized adsorption site. However, the negative value of Langmuir constant indicated the inadequacy adsorption of heavy metal using green mussel shell as adsorbent. Freundlich isotherm is usually used for non-ideal adsorption on heterogeneous surfaces. The heterogeneity arises from the presence of different functional groups on the surface, and the various adsorbent-adsorbate interactions. K_F parameter follows the sequence of Pb > Cr > Cd. The n parameter was different from 0.4 to 1.7. K_F values indicate that Pb is the one with the highest adsorption (K_F = 4.18), followed by Cr and Cd. This model assumes that when the adsorbent concentration increases, the concentration of adsorbate (Cd, Cr and Pb) on the adsorbent surface also increased and correspondingly, the sorption energy exponentially decreased over the completion of the sorption centre of the adsorbent. It is proven that the Freundlich model provides a better fit for explaining the adsorption of heavy metal onto all modified adsorbents. For adsorbate, the maximum adsorption capacities follows the order of Cr > Pb >Cd.

Table 1 : Adsorption isotherm parameters for Cd, Cr and Pb using Langmuir and Freundlich Isotherm

Adsorption isotherm model	Parameter value		
Langmuir isotherm			
	Cd	*Cr*	*Pb*
Equation	y = 4.573x - 7.546	y = 0.479x - 0.031	y = 0.513x - 0.020
q_m (mg/g)	0.2187	2.0877	1.9493
K_L (L/mg)	-0.6059	-15.4515	-25.6502
R^2	0.960	0.999	0.999
Freundlich isotherm			
Equation	y = 0.584x - 0.395	y = 2.311x +0.984	y = 1.605x +1.430
K_F (mg/g)(L/mg)$^{1/n}$	0.674	2.675	4.179
1/n	0.584	2.311	1.605
R^2	0.974	0.476	0.797

The linear forms of the pseudo-first-order and second-order equations, rate constants, expected metal uptake and correlation coefficients is described. and represented in Table 2 and 3. For the pseudo first order model the correlation coefficient (R^2 = Cd=0.978,

Cr=0.762, Pb=0.785) and the calculated metal uptake with this model is lower than the expected metal uptake for Cr and Pb. Indicating that the chemisorption process is not a first order reaction. The pseudo second order reaction in chemisorption is based on the sorption capacity on the solid phase. The correlation coefficient in the pseudo second order reaction (R^2 = 0.999) is high for all heavy metal, k is the pseudo-second-order rate constant are in range 6-42 min^{-1} and the calculated metal adsorption is much nearer to the expected value suggesting that the chemisorption process comply to pseudo second order model. The results indicate that the kinetic behaviour of Cr, Cd and Pb on green mussel shell as adsorbent can be satisfactorily explained with the pseudo-second-order sorption equation. Based on the assumption step, chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate.

Table 2 : The pseudo-first–order parameter of heavy metal adsorption at different concentration of Cd, Cr and Pb

Element \ Parameter	Cd	Cr	Pb
Equation	y = -0.410x + 0.110	y = -0.381x - 0.903	y = -0.426x - 1.064
q_e experiment	0.9681	2.3544	2.1465
q_e calculated	1.1163	0.405	0.345
k_1	0.410	0.381	0.426
R^2	0.978	0.762	0.785

Table 3 : The pseudo-second–order parameter of heavy metal adsorption at different concentration Cd, Cr and Pb

Element \ Parameter	Cd	Cr	Pb
Equation	y = 1.028x - 0.025	y = 0.423x - 0.006	y = 0.466x + 0.035
q_e experiment	0.9681	2.3544	2.1465
q_e calculated	0.9728	2.3641	2.1459
k_2	42.2681	29.8206	6.2046
R^2	0.999	0.999	0.999

4.0   Conclusions

Green mussel shell as an aqua cultural solid waste, was successfully utilized as a low-cost alternative adsorbent for the removal of hazardous heavy metal like cadmium, chromium and lead. Since in this work is abundantly and locally available, the resulting expected to be economically viable for removal heavy metal from aqueous solution. FESEM micrographs illustrated that carbonization treatment with 600°C developed porosity on the surface of the adsorbent. The FTIR spectrum obtained for the functional groups responsible for adsorption process like hydroxyls, carbonyls, carboxylic and amides. The relative study of adsorption percentage capacity, shown that can adsorb more than 99% of heavy metal. The equilibrium adsorption data indicated that the equilibrium sorption fitted well with the Freundlich isotherm, displaying higher regression coefficient, R^2 value. The monolayer adsorption capacity of green mussel waste was found to be 2.09 mg/g. The adsorption kinetics can be well described by the pseudo-second-order model equation. Based on the results obtained, mussel shells have the potential to be an alternative and inexpensive adsorbent for heavy metal treatment in aqueous phase, respectively.

5.0   Acknowledgements

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