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Adsorption of heavy metal ions onto chitosan grafted cocoa husk char

Aderonke A. Okoya[1]*, Abimbola B. Akinyele[1], Ifeanyi E. Ofoezie[1], Omotayo S. Amuda[2], Oluwagbemiga S. Alayande[3] and Oladotun W. Makinde[3]

[1]Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile – Ife, Nigeria.
[2]Ladoke Akintola University of Technology, Ogbomoso, Nigeria.
[3]Center for Energy and Research Development, Obafemi Awolowo University, Ile – Ife, Nigeria.

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The use of chitosan-grafted cocoa husk char (CCH) and unmodified cocoa husk char (CH) as adsorbents for the removal of Cr^{6+} and Pb^{2+} were studied. The adsorption efficiencies were compared with that of the commercial activated carbon (GAC F-300). Energy Dispersive X-ray spectroscopy (EDS) was used to determine the elemental compositions of the adsorbents while Scanning Electron Microscope (SEM) was used for the surface texture and morphological characteristics of the cocoa husk. The study optimised metal ion concentration, adsorbent dosage, agitation time and adsorbent particle size for the removal of the metals from simulated wastewater using Atomic Absorption spectroscopy (AAS) and removal efficiencies were calculated. Langmuir and Freundlich models were employed to study the adsorption pattern. The equilibrium experimental data results of Pb^{2+} fitted well to Langmuir and Freundlich the two adsorption isotherms. The coefficient of correlation (R^2) for both models falls within $0<R^2<1$. The experimental data obtained from the sorption of Cr^{6+} by the adsorbents, except CH, fitted Langmuir model than Freundlich model. The Langmuir isotherm fits the experimental data than Freundlich isotherm for Cr^{6+} sorption by the CCH modified cocoa husk and the activated carbon except the unmodified cocoa husk. The study concluded that cocoa husk, an agricultural waste material, have potential as an adsorbent to remove toxic heavy metal like chromium and lead from industrial waste water. Modification of this waste with chitosan also enhances its performance in the removal of the metals.

Key words: Adsorption, cocoa husk, chitosan, heavy metal, atomic absorption spectroscopy, isotherm.

INTRODUCTION

Heavy metals contamination has been a serious environmental concern due to its toxicity, persistency and accumulation. This contamination has increased over decades due to increase in population which has increased the consumption rate and has led to rapid industrialization. The metals through industrial processes are released into the air, soil, and water (Deniz et al., 2012). It has been consistently desired that their concentrations be lowered in industrial and municipal effluents before ultimate disposal into the environment

*Corresponding author. E-mail: ronkeokoya@yahoo.com

(Muthusamy et al., 2012).

Researchers have developed various methods such as chemical precipitation, coagulation, adsorption, ion exchange and membrane filtration for the removal of heavy metals from waters and wastewaters (Deniz et al., 2012; Onundi et al., 2010; Georg Steinhauser, 2008). The limitations associated with these methods are high operational cost, sludge production and they differ in their effectiveness, especially when metals are present in solution at very low concentrations. Of all the treatment methods mentioned above, adsorption had been reported as an efficient method for the removal of heavy metals from aqueous solution because of their effectiveness even at low concentration (Liang et al., 2009; Amuda and Edewor, 2013).

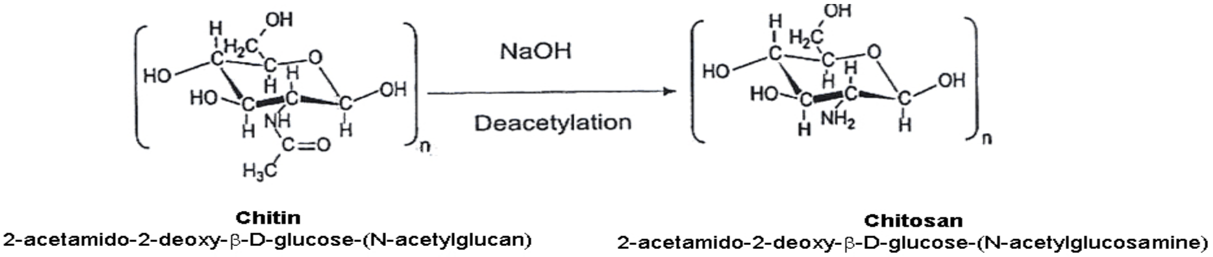
The commercial activated carbon most widely used as an adsorbent has become economically less feasible owing to its relatively high cost. Recently, different low cost biosorbent sourced from natural materials and biological wastes from industrial processes has been studied for the development of cheap and effective metal sorbents (Onwu and Ogah, 2010; Sethu et al., 2010). Also, the development of surface modified activated carbon has produced a variety of activated carbon with far surpassing adsorption capacity (Amuda et al., 2007; Lwin et al., 2008). Surface modification of natural adsorbent derived from agricultural waste improves their metal uptake performance which would add to economic value (Amuda and Edewor, 2013; Lwin et al., 2008). Biochar is a charcoal made from carbon rich material (biomass). Latest developments in renewable bioenergy technologies make it possible to convert waste biomass, for instance agricultural waste, into value-added biochar and at the same time produce bioenergy (Dong et al., 2011). In any agricultural country such as Nigeria, accumulation of waste material is always one of the by-products of farming activities. The uses of such agricultural by-products have been in their conversion into usable forms. It is the policy of the Nigerian government to encourage and promote the utilization of the country's raw material and waste such as cocoa husk, for other industrial processes. Caustic soda is a widely used industrial alkali, and it serves at least 61 major industries in the country (Essien et al., 1986; Okoya and Ogunkoya, 2009). It has numerous applications in rayon and other textile manufacture, pulp and paper production, reclaiming of rubber, food production, detergents and soap production. Despite all these reports, cocoa husk, the major raw material in the production of caustic alkali, still constitute an environmental problem in the light of the way it is being disposed in Nigeria, just as in many other tropical countries in which the disposal problem of agricultural wastes is widely recognized, efforts to find solutions are not equal for different sectors (Ulloa et al., 2003). Mosquitoes breed inside them wherever they are heaped up due to under utilization for the production of caustic alkali (Okoya and Ogunkoya, 2009), local black soap, medicinal and other purposes by the indigenous people. Hence there is need to exploit the possibility of utilizing this underutilized material as an adsorbent for the removal of metals from waste water.

Biochar shows a great affinity for heavy metals and their sorption capacity is comparable with other biosorbents. For instance, the ranges of Pd sorption capacity of different biochar are from 2.4 (rice husk) to 20.5 mg/g (sugarcane bagasse) (Mohan et al., 2007; Liu and Zhang, 2009; Ding et al., 2010; Cao et al., 2009). Even though little Cr removal by biochar information is available, the effectiveness of its removal by various biomaterials has been investigated (Park et al., 2008; Abdullah and Prasad, 2009). The production of biochar of different waste biomass has help reduce the cost involved in waste disposal and provides potentially inexpensive alternatives for commercial activated carbon (Amuda and Edewor 2013; Lwin et al., 2008).

In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. Among these low cost adsorbents, chitosan has the highest sorption capacity for several metal ions (Amuda et al., 2007; Amuda et al., 2009). Chitin (2-acetamido-2deoxy- -d-glucose-(N-accetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps. Chitosan (2-acetamido-2-deoxy-B-d-glucose-(N-acetyl glucosamine) is a partially deacetylated polymer of chitin and is usually prepared by deacetylation of chitin with a strong alkaline solution as shown in Scheme 1 (Amuda et al., 2009).

Yang and Zall (1984) reported that chitosan can chelate five to six times greater concentrations of metals than chitin. They further reported this property to be related to the free amino groups exposed in chitosan because of deacetylation of chitin. Chitosan is slightly soluble at low pHs and posesses problems for developing commercial applications. Also, the active binding sites of chitosan are not readily available for sorption. The sites are reported to be soft and have a tendency to agglomerate or form gel in aqueous solutions. Transport of metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications.

However, minimal work has been done on modifying cocoa husk biochar, comparing the removal efficiency of chitosan modified biochar with commercial activated carbon and comparing their effectiveness in removing different toxic metal. The purpose of this study is to evaluate the efficiency of cocoa husk char as adsorbent for Lead and Chromium, to study the effect of surface modification of cocoa husk char with chitosan on the removal of the metals from wastewater; and also to compare the efficiency of CCH and CH with that of GAC F – 300.



Scheme 1. Conversion of chitin to chitosan by deacetylation. Source: (Amuda et al., 2007; Souundarrajan et al.,2012)

MATERIALS AND METHODS

The cocoa husks used for this research were collected from Obafemi Awolowo University Teaching and Research Farm while the snail shell used for the extraction of chitosan was collected from a household in Idanre, Ondo State. Activated carbon (GAC F-300) by Boncaki Nig. Ltd was purchased commercially. Synthetic wastewater was employed for the adsorption studies. 500 mg/L each of stock solution of analytical graded $K_2Cr_2O_7$ and $Pb(NO_3)_2$ was prepared by dissolving exact quantity of the salts in deionized water. The range (5 to 25 mg/L) of concentrations of Cr^{+6} and Pb^{+2} was prepared from the stock solution.

Preparation of cocoa husk char

The cocoa husks collected were sun dried, cut, ground and sieved to three particle sizes of 150, 212 and 300 µm. The char of the cocoa husk was prepared using the modified methods of Lwin et al. (2008) and Amuda and Edewor (2013). About 15 g of each of the raw material was placed in a crucible, and put into a furnace. The furnace temperature was increased at a rate of 10°C/min from room temperature to 500°C in a nitrogen environment to ensure nitrogen free environment and the temperature was held at this temperature for 2 h after which they were washed with distilled water to remove any leachable impurities due to free acid and adherent powder.

Adsorbent characterization

The elemental composition of the prepared husk was determined using Energy Dispersive X-ray Micro Analysis (EDX) while Scanning Electron Microscope (SEM) (High resolution SEM EVO MA 10 carl Zeiss) was used to study the surface morphological characteristics.

Activation of cocoa husk char

The char samples were treated with 2% H_2SO_4 (v/v) in an incubator for 24 h at a temperature of 110°C. The treated char sample was then soaked in deionized water until the pH was stabilized. It was then soaked in 2% $NaHCO_3$ to remove the residual acid. The acid-treated cocoa husk carbon was then dried overnight in an oven at 110°C, and stored in desiccators until use (Kadirvelu et al., 2001).

Preparation of chitosan

The snail shells were powdered and sieved with 2 mm sieve. 50 g of the less than 2 mm size powdered snail shell was weighed into a 500 ml beaker and 200 ml of 4% (w/v) KOH was added with constant stirring for 6 h at 80°C and filtered. The residue was washed with distilled water until it is free of base and then dried at 100°C for 2 h. The deproteinized snail shell residue was then poured into a 250 ml conical flask and 100 ml of 3 % (v/v) 1 M HCl was added and placed on a magnetic stirrer for 3 h at 30°C to demineralise it. The content was later filtered and the residue was washed until it is free of acid. The acid free residue was then dried at 90°C for 1 h after which it was decolourized by refluxing in acetone for 3 h at 60°C. The content was filtered and the residue dried. A snow white residue called chitin was obtained.The chitin was poured into a 250 ml conical flask for deacetylation, 50% (w/v) NaOH solution was added, stirred at 30°C for 4 h and filtered. After filtration, the residue, which is chitosan (2-acetamido-2-deoxy-β-D-glucose-N-(acetylglucosamine), was then washed and dried at 90°C for 1 h.

Preparation of chitosan gel

About 5 g of chitosan was slowly added to 100 ml of 10% (w/v) oxalic acid with constant stirring in a beaker. The mixture was also heated to about 50°C to facilitate mixing. A chitosan-oxalic acid mixture was formed (a whitish viscous gel).

Modification of adsorbent

The chitosan gel (100 ml) was diluted with water (~500 ml) and heated to about 50°C. 50 g of cocoa husk char was slowly added to the diluted gel in separate container, and mechanically agitated using a shaker at 200 osc/min for 24 h. The chitosan-coated cocoa husk char were then washed with distilled water and dried after which it was soaked in 0.5 % (w/v) NaOH solution for 3 h. It was then extensively rinsed with deionized water and dried in an oven at 102°C for 2 h, cooled at room temperature and stored in a desiccator.

Batch adsorption studies

Experiments were conducted in 5 different 250 ml Erlenmeyer flasks containing 100 ml varied concentration (5, 10, 15, 20 and 25 mg/L) of Cr^{+6} solutions and CH (150 µm cocoa husk) dosage of 1.5 g was added to the different flasks. Flasks were agitated on a shaker at 400 osc/m constant shaking. The mixture was filtered using Whatman no.1. after 30 min, and the filterate analysed spectrophotometrically using Atomic Absorption Spectroscopy (AAS). The adsorption procedure was repeated using different adsorbents (150, 212 and 300 µm) sizes of unmodified cocoa husk, modified cocoa husk and activated carbon), dosages (0.5, 1.0, 1.5, 2.0 and 2.5 g) and different adsorbent, contact period (30, 60, 90, 120 and 150 min) in turns. Triplicate analyses were carried out for each adsorption. Batch adsorption studies for varied concentration of Pb^{2+} were also carried out. The removal efficiency (E) of adsorbent on Cr^{+6} and Pb^{+2} were calculated as follows:

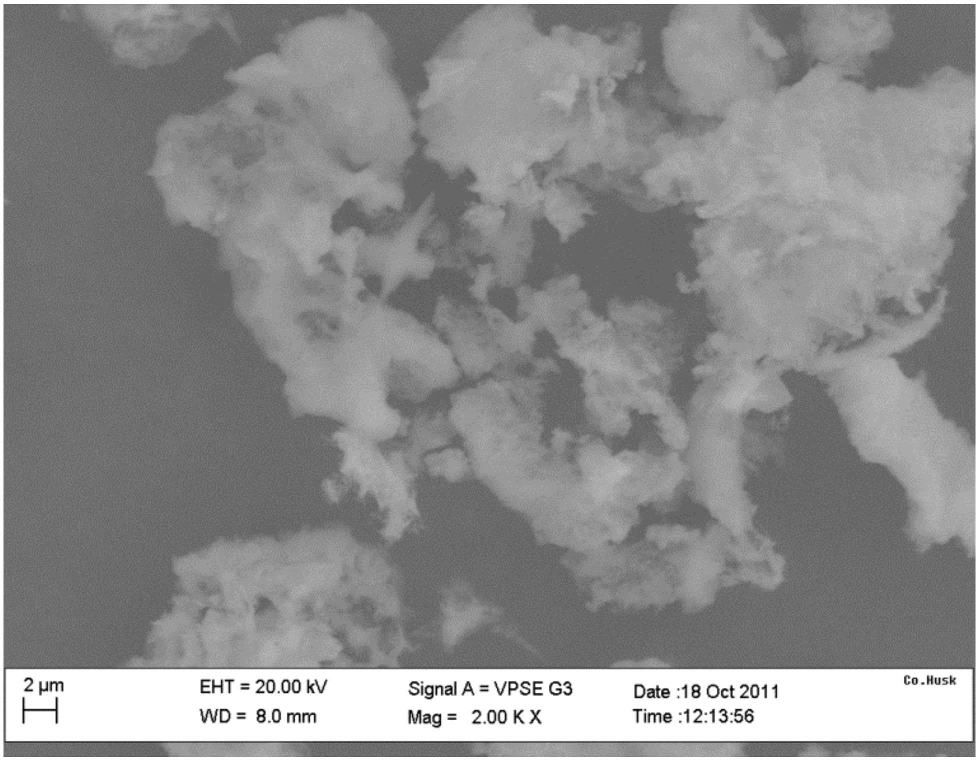


Figure 1. SEM image of cocoa husk char.

$$E\% = ((C_i - C_f)/C_i) \times 100 \qquad (1)$$

Where C_i and C_f are the initial and final concentrations of Cr^{+6} and Pb^{+2} (mg/L), respectively, (Amuda et al., 2007).

DATA EVALUATION

The amount of metal bound by the adsorbent was calculated as follows:

$$Q = v\,(C_i - C_f)/m \qquad (2)$$

Where Q is the metal uptake (mg metal per g adsorbent), v is the volume of solution containing the metal (ml), C_i is the initial concentration of the metal in the solution (mg/L), C_f is the final (equilibrium) concentration of the metal in the filtrate (mg/L) and m is the amount of the added adsorbent on the dry basis (g) (Jun et al., 2012).

RESULTS AND DISCUSSION

Sample characterisation

Scanning electron micrographs (SEM) clearly revealed the surface texture and morphological characteristics of the adsorbent (cocoa husk char). The SEM image in Figure 1 reveals the porous structure of the cocoa husk char. It also shows the agglomeration of the particles of the cocoa husk char and the distinctive irregular material with large surface area. As shown in Table 1, the Energy Dispersive X- ray spectroscopy (EDX) reveals the presence of elements such as Carbon C, Potassium K, Calcium Ca, Magnesium Mg, Aluminium Al, Silicon Si, Phosphorus P and Chlorine Cl in the adsorbent. The porosity and agglomeration of cocoa husk char particles enhance metal uptake and encourage mass transport of heavy metals through the inside of the sorbent (Grabriela et al., 2006; Edwin, 2008; Zhang et al., 2009; Alayande et al., 2011; Gholami et al., 2006). While the presence of the elements mentioned above had been reported to enhance adsorption metals through ion exchange, chelation, coordination and complexation reactions. Elements such as Al, K, Ca, and Mg could exchange for the heavy metals while elements like P, O and Si could prompt chelation, coordination and complexation (Grabriela et al., 2006; Edwin, 2008; Michaud, 2011) (Figure 2).

Effect of initial concentration

Figures 3 and 4 show the effect of Initial metal ion concentration on the removal efficiency exhibited by the adsorbents with increase in metal ion concentration. From these Figures, commercial activated carbon show an outstanding removal efficiency over modified and unmodified cocoa husk char. In fact it exhibit 100%

Table 1. Elemental composition of cocoa husk char.

Element	Cocoa husk	
	Weight %	Atomic %
C	42.04	54.13
O	37.95	36.69
Mg	2.47	1.57
Al	1.07	0.61
Si	3.36	1.85
P	1.25	0.62
K	4.71	1.86
Ca	6.32	2.44
Fe	0.82	0.23

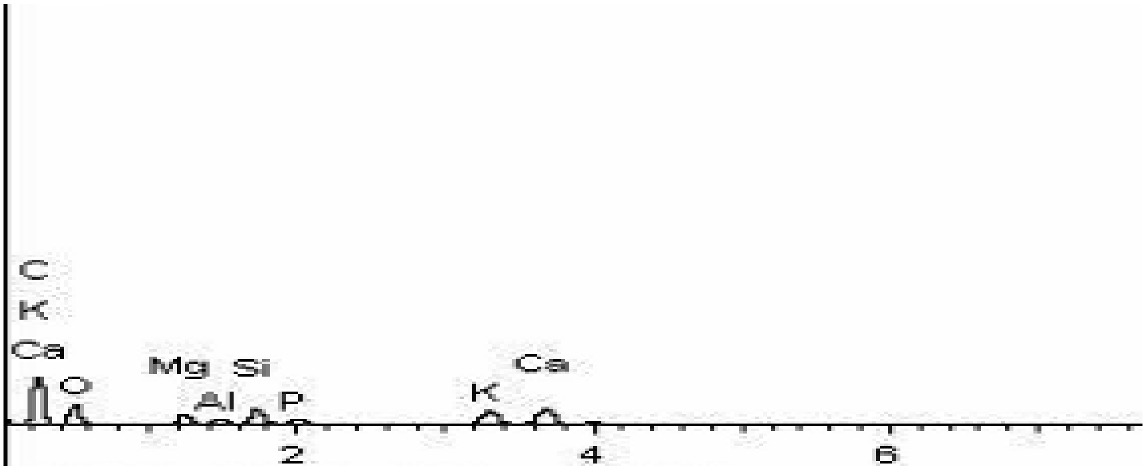


Figure 2. EDX spectra of cocoa husk char.

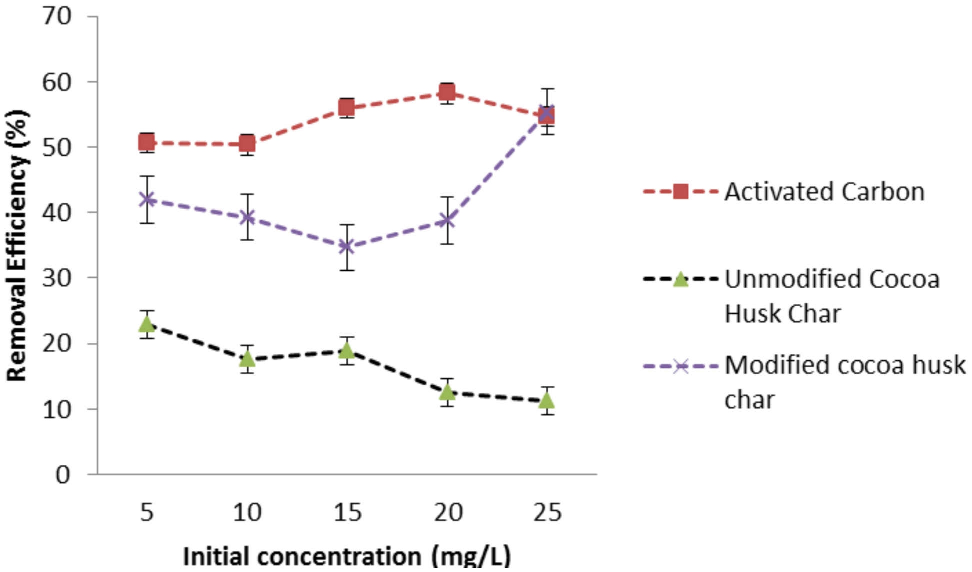


Figure 3. Effect of initial concentration on the removal efficiency of Cr (VI). Agitation time: 60 min; Adsorbent dose: 1.5; Agitation speed 400 osc/min.

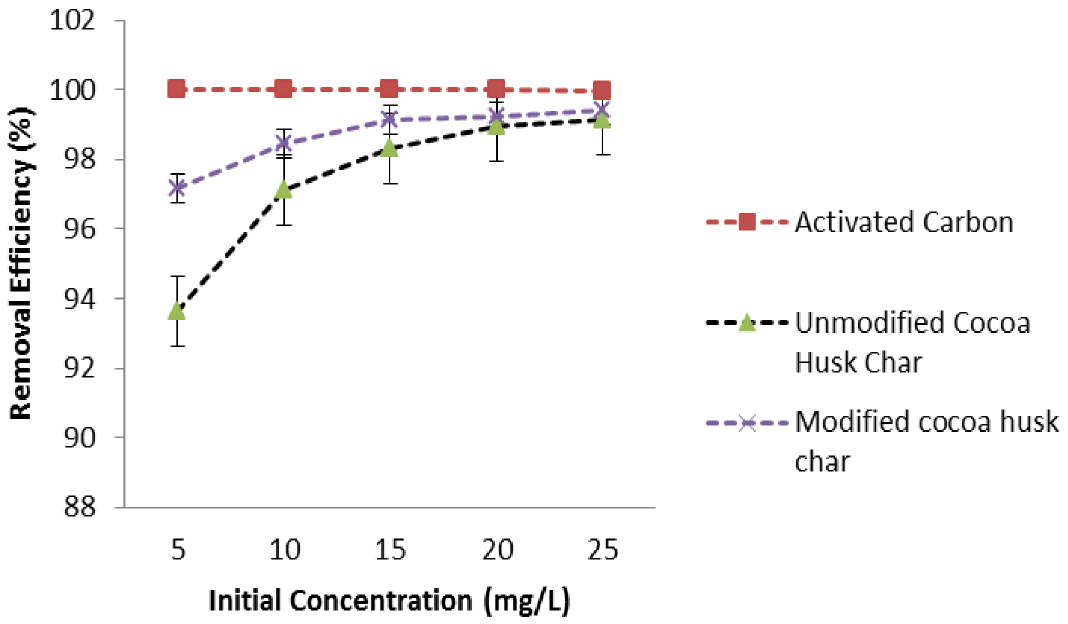


Figure 4. Effect of initial concentration on the removal efficiency of Pb (II). Agitation time: 60 min; Adsorbent dose: 1.5; Agitation speed 400 osc/min.

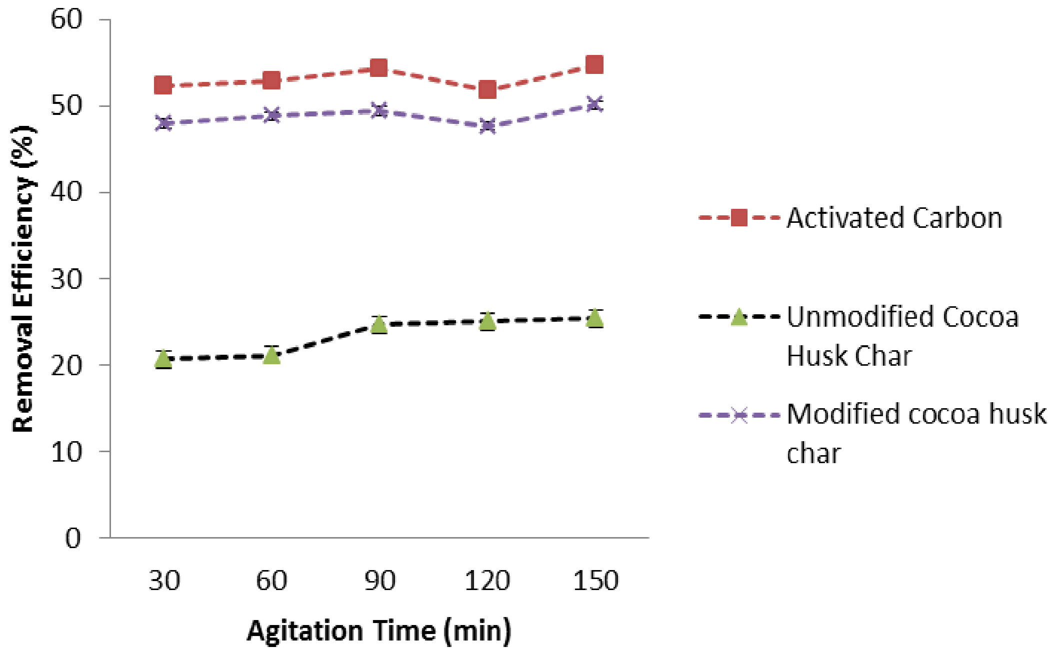


Figure 5. Effect of agitation time on removal efficiency of Pb (II) by the adsorbents. Pb (II) Concentration: 20 mg/L; agitation speed: 400 osc/min; dose of each adsorbent: 1.0 g.

removal efficiency for Pb^{+2} ion (Figure 5). In Figure 4, the removal efficiency of unmodified cocoa husk char decreased as the metal ion concentration increases while the removal efficiency of the modified adsorbent initially decreased as metal ion concentration increased from 5 to 15 mg/L and later increased as metal ion concentration increased. The decrease in removal efficiency may be due to the limited number of active sites in the adsorbent as it attained saturation above certain concentration (Sugashini and Gopalakrishnan, 2012). However, in the

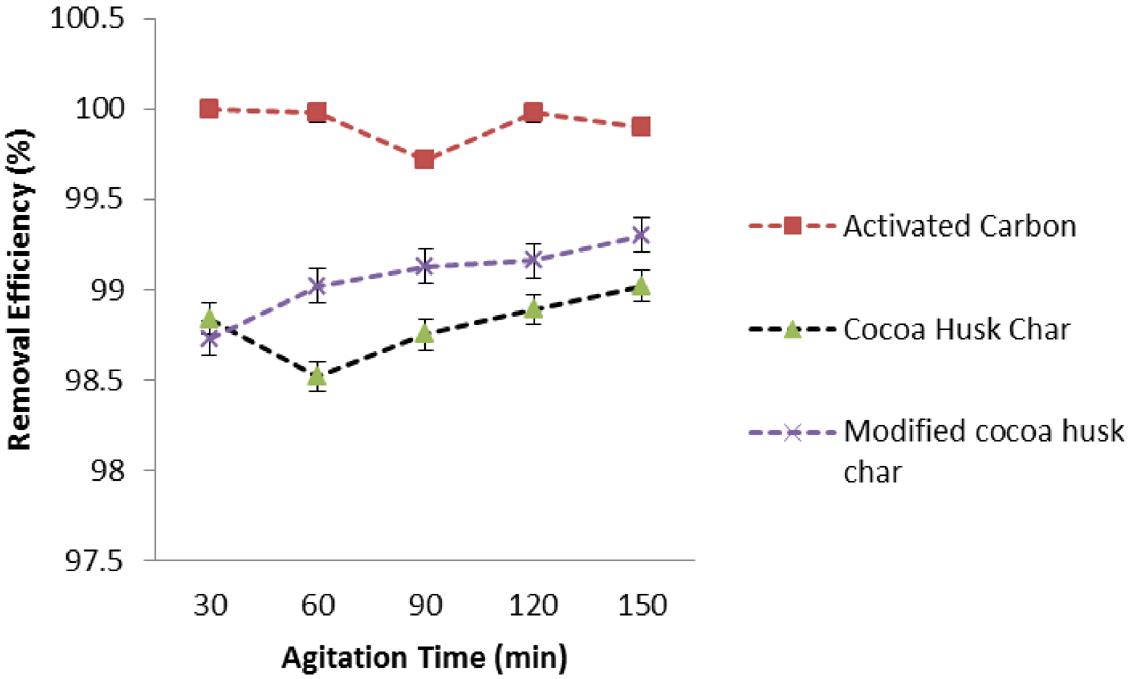


Figure 6. Effect of agitation time on removal efficiency of Cr (VI) by the adsorbents. Cr (VI) Concentration: 20 mg/L; agitation speed: 400 osc/mim; dose of each adsorbent: 1.0 g.

case of Pb^{+2}, the removal efficiency of both modified and unmodified adsorbent increase as initial metal ion concentration increases. The increase in removal efficiency as metal ion concentration increases may be as a result of competition for the available binding site on the adsorbent by the metal ion as the concentration increases (Olu-owolabi et al., 2012; Gholami et al., 2006). Also, the initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase (Aksu and Akpinar, 2000). The results show that feasibility and efficiency of adsorption process depends not only on the properties of the adsorbents, but also on the concentration of the metal ion solution. It was observed that the removal efficiency of the chitosan modified cocoa husk char was higher compared to the unmodified adsorbents (Figures 3 and 4). This may be due to the fact that modification increases the available active binding sites for metals thereby enhancing the performance of the adsorbent (Igwe and Abia, 2007; Amuda et al., 2009). Development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. Among these low cost adsorbents, chitosan has the highest sorption capacity for several metal ions (Amuda et al., 2007; Amuda et al., 2009). Yang and Zall (1984) reported that chitosan can chelate five to six times greater concentrations of metals than chitin. They further reported this property to be related to the free amino groups exposed in chitosan because of deacetylation of chitin.

In addition, removal efficiency of Pb^{2+} with the modified cocoa husk char is relatively close to that of activated carbon (Figure 4).

Effect of contact time

As shown in Figure 5, the removal efficiency of Cr^{6+} by unmodified cocoa husk char increases with adsorbent contact time from 30 to 90 min. However, it remained constant within the adsorbent contact time of 120 and 150 min, meanwhile that of modified cocoa husk char and commercial activated carbon increased as contact time increases. In Figure 6, the removal efficiency of Pb^{2+} using modified and unmodified cocoa husk char increased with increase in contact time while for commercial activated carbon, equilibrium was reached within 30 min. These results showed that initially the number of vacant sites was large which later reduced as the vacant active site is been saturated (Sugashini and Gopalakrishnan, 2012). Also, the fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of available binding sites on the adsorbent surface at the beginning while the decrease in efficiency may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbents (Onundi et al., 2011). Also greater availability of various functional groups on the surface of the chitosan, which are required for

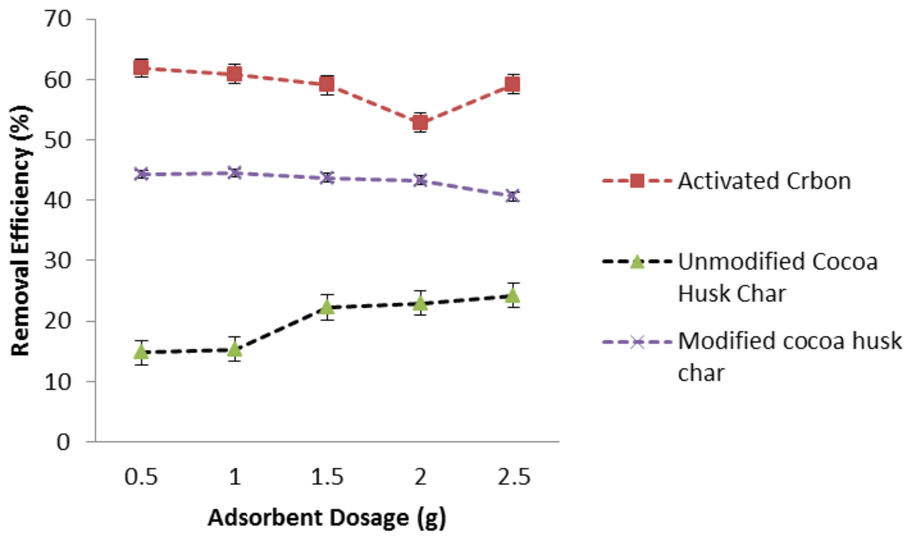


Figure 7. Effect of dose of the adsorbents on the removal efficiency of Cr (VI). Cr (VI) Concentration: 30 mg/L; Agitation time: 60 min; Agitation speed 400 osc/min.

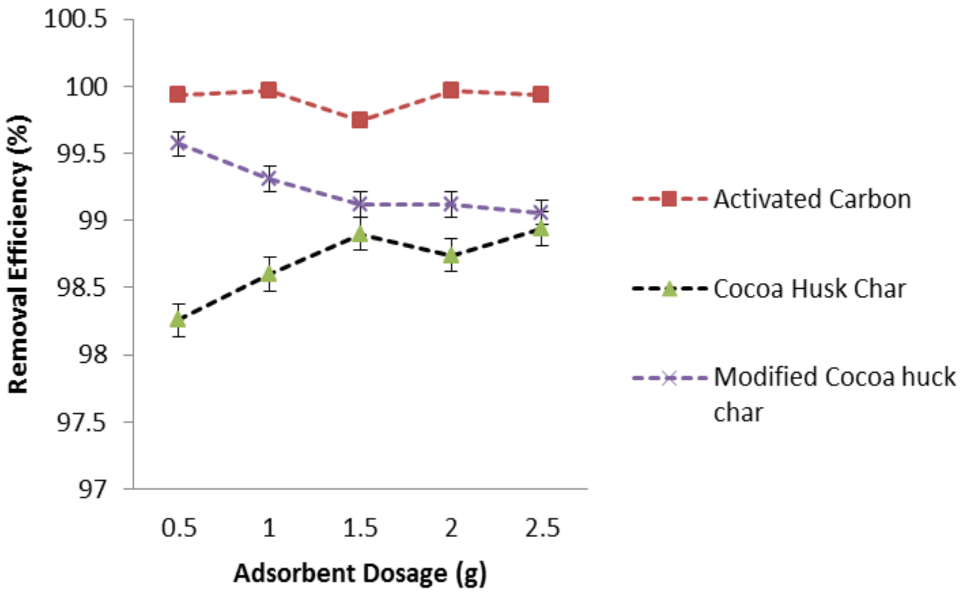


Figure 8. Effect of dose of the adsorbents on the removal efficiency of Pb (II). Pb (II) Concentration: 30 mg/L; Agitation time: 60 min; Agitation speed 400 osc/min.

interaction with anions and cations, could significantly improve the binding capacity of an adsorbent and adsorption proceeds rapidly (Amuda et al., 2009; Nomanbhay and Palanisamy, 2005).

Effect of adsorbent dosage

Effect of adsorbent dosage on adsorption of Cr^{6+} and Pb^{2+} is studied by varying the adsorbent dosage from 0.5 to 2.5 g and other parameters like initial metal ion concentration were kept constant. The Figures 7 and 8 show increase in the removal efficiency of Cr^{6+} and Pb^{2+} as dosage of unmodified cocoa husk char increases. This is because of the availability of more binding sites in the surface of the adsorbent as the dosage increase (Asubiojo and Ajelabi, 2009; Choi et al., 2009; Dhabab, 2011). However, there is a decrease in removal efficiency as commercial activated carbon and modified cocoa husk char increases (Figures 8 and 9). The decrease in the

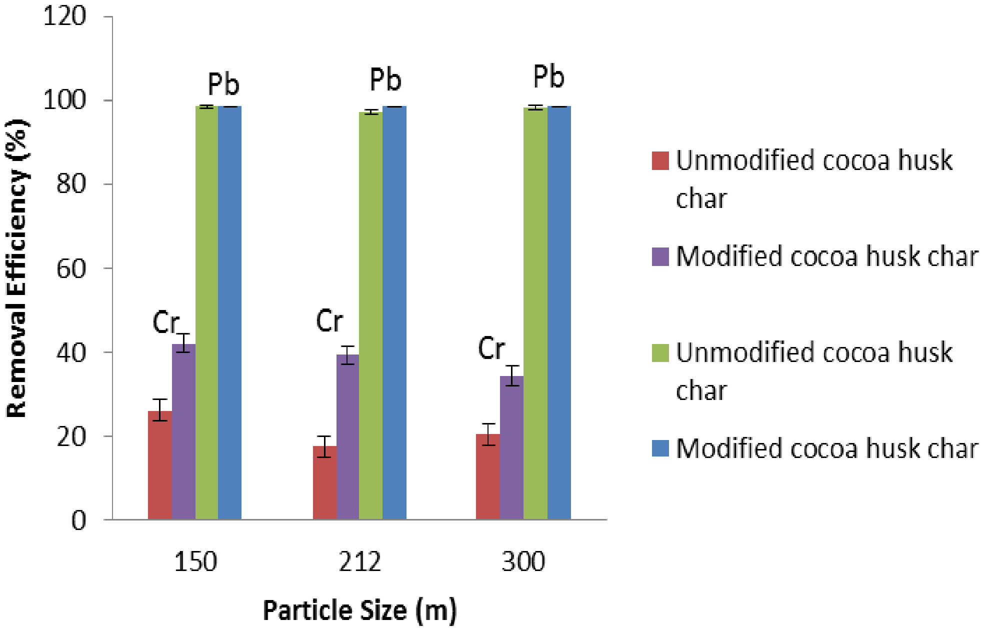


Figure 9. Influence of the adsorbent particle size on the removal efficiency of Cr^{6+} using modified and unmodified cocoa husk char. Metal concentration: 10mg/L; Agitation time: 45 min; agitation speed: 400 osc/min; adsorbent dosage: 1.5 g.

sorption efficiency with the increasing adsorbent dose may be as a consequence of a partial overlapping or aggregation of adsorbent surface area available to ion and an increase in diffusion path length, which occurs at high biomass concentration given rise to a decrease of active sites (Gönen and Serin, 2012; Souundarrajan et al., 2012; Sudha et al., 2012). Also, differential adsorption capacities of the adsorbents depend on the extent of surface modification (Amuda et al., 2009; Nomanbhay and Palanisamy, 2005).

Effect of particle size

The results of the effects of particle size on the removal efficiencies of Cr^{6+} and Pb^{2+} is presented in Figure 10. The particle sizes used were 150, 212 and 300 µm, respectively. Other parameters such as adsorbent dose, initial ion concentration and agitation time were kept constant; temperature and agitation speed were kept at 25°C and 400 osc/min, respectively. The removal efficiency of Cr^{6+} and Pb^{2+} by modified cocoa husk char decreased as particle size increased while for the unmodified cocoa husk char, 300 µm particle size show higher efficiency than 212 µm. This increased efficiency as particle size decreased may be due to the fact that smaller particles give large surface areas. Sometimes, larger particle size can show higher removal efficiency over smaller particle if the particles are spherical in shape. Larger particles with spherical shape, in general, present higher external mass transfer than small particle size which therefore responsible for the higher removal efficiency (Leusch and Volesky, 1995).

Adsorption isotherm

Langmuir and Freundlich models are the most commonly used theoretical model to generate adsorption isotherm. Langmuir model assumption state that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions while the assumption of Freundlich model is based on adsorption on heterogenous surface. The experimental data were analyzed according to the linearized form of the Langmuir and Freundlich model. The linearized equation of Langmuir model is represented by:

$$1/Q = 1/Q_{max} (1/b\ C_f + 1) \qquad (3)$$

Where Q_{max} is the maximum metal uptake under the given conditions, b is a constant related to the affinity between the adsorbent and sorbate.

The linearized equation of Freundlich model is represented by:

$$\text{Log } Q = \text{Log } k + 1/n \log C_f \qquad (4)$$

Where k and n are Freundlich constant, which correlated to the maximum adsorption capacity and adsorption intensity, respectively.

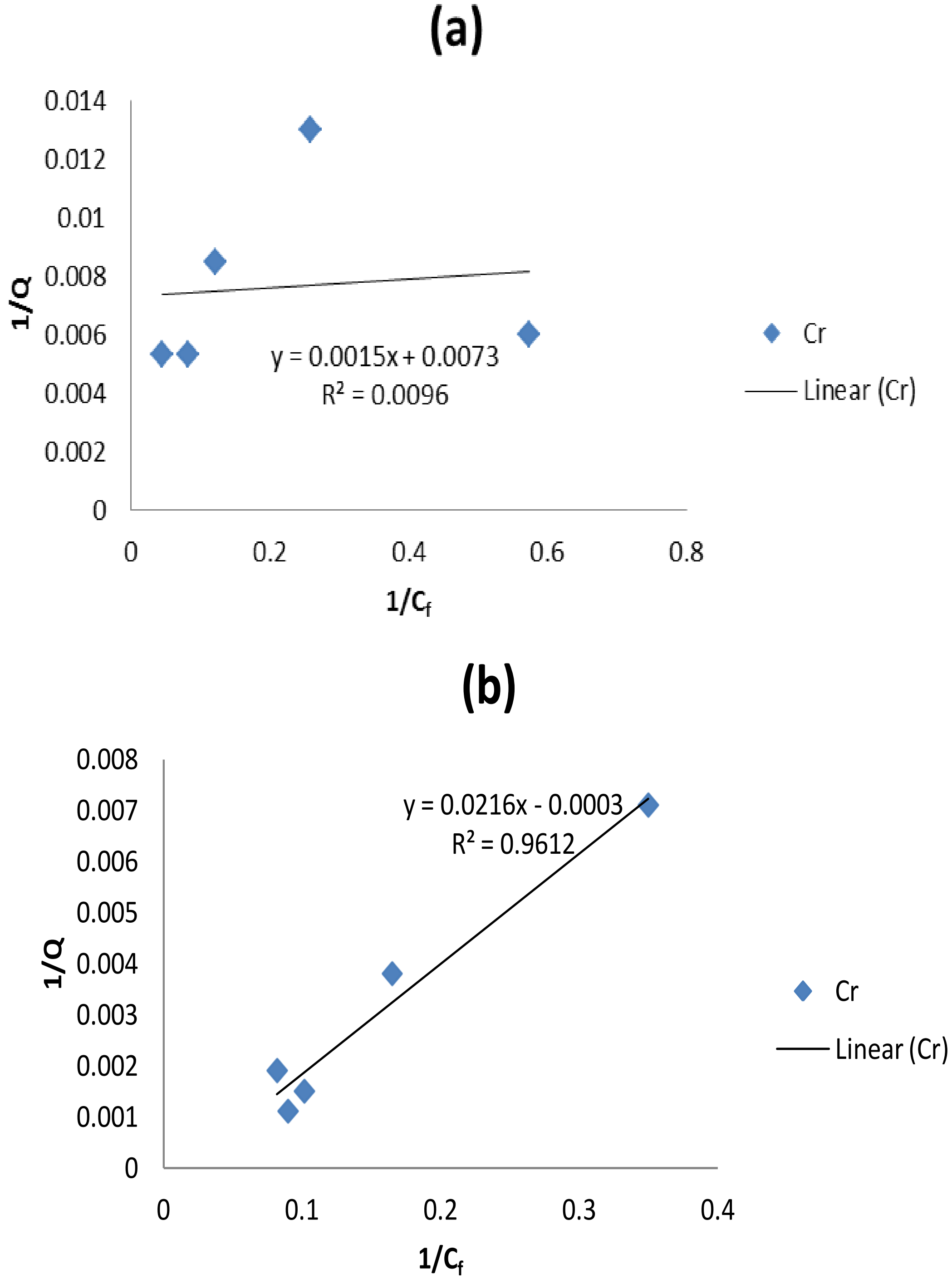


Figure 10. Langmuir adsorption isotherms for the adsorption of Cr^{6+} by (a) unmodified cocoa husk char (b) modified cocoa husk char.

Figures 10 to 13 and Table 2 shows the applicability of Langmuir and Freundlich model to the metals using cocoa husk char adsorbent. The two models fitted well for the adsorption studies of Cr^{6+} and Pb^{2+} using modified adsorbent while Freundlich model fitted well for the adsorption study of the two metals than Langmuir. This is because of the higher correlation coefficient depicted by the two models (Table 2). Q_{max} value which is the adsorption capacity determined from the slope of Langmuir indicate a good adsorbing capacities of the

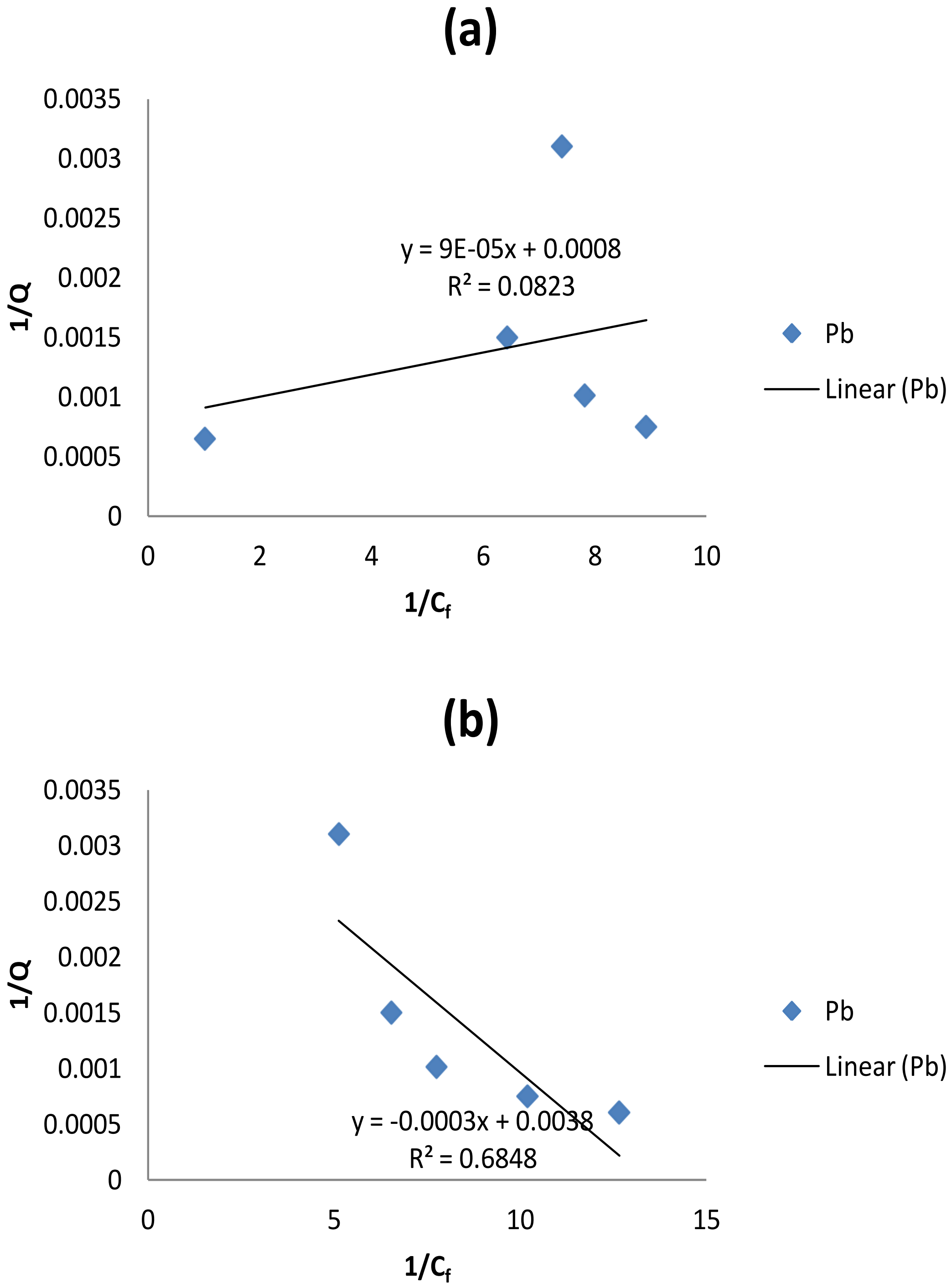


Figure 11. Langmuir adsorption isotherms for the adsorption of Pb^{2+} by (a) unmodified cocoa husk char (b) modified cocoa husk char.

adsorbent for Pb^{2+} than Cr^{6+}. The K values for the sorption of Pb^{2+} by the cocoa husk char adsorbents are higher (1500.7) than that of the sorption of Cr^{6+} (39.138) by the adsorbent (Table 2). The higher the value of K, the greater the adsorption intensity (Vaishnav et al., 2012). The higher K-values exhibit by the sorption of Pb^{2+} suggests that Pb^{2+} has greater sorption tendency towards the adsorbents than Cr^{6+} (Kose et al., 2012).

The fractional value of *1/n* indicates the surface of adsorbent is of heterogeneous type with an exponential distribution of energy sites (Kose et al., 2012). The value of 1/n less than 1 (Table 2) is indicative of favourable

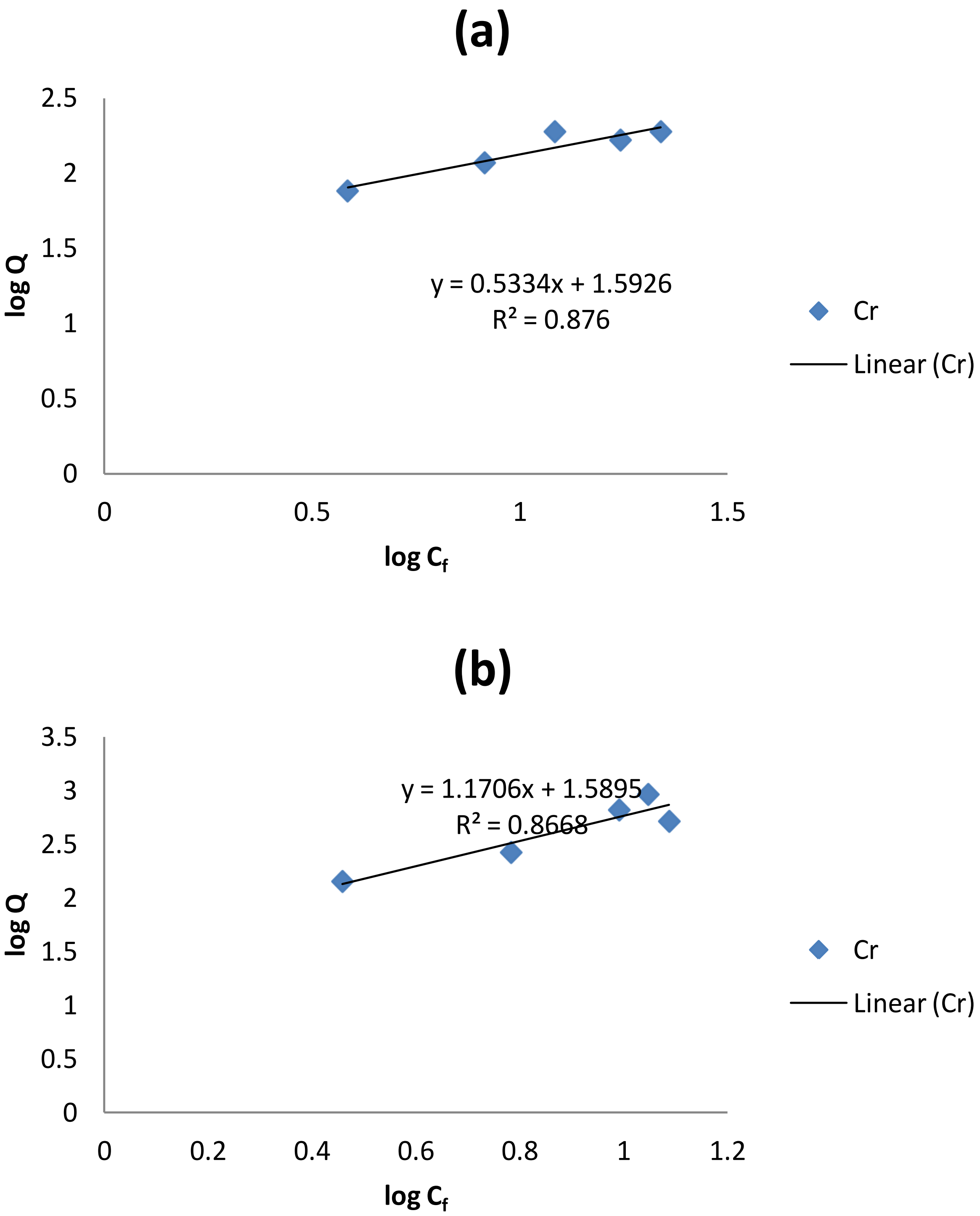


Figure 12. Freundlich adsorption isotherms for the adsorption of Cr^{6+} by (a) unmodified cocoa husk char (b) modified cocoa husk char.

adsorption (Onwu and Ogah, 2010). The fact that the value of 1/n in the adsorption of Pb^{2+} is small (< 1 even some tend towards negative) (-1.7634, 0.3464) compared to 1/n value of the adsorption of Cr^{6+} (1.1706, 0.5334), is indicative of favourable adsorption for Pb^{2+} than Cr^{6+}. A smaller value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent Tables 3 and 4 (Al-Sultani and Al-Seroury, 2012; Alfa et al., 2012; Patil et al., 2006).

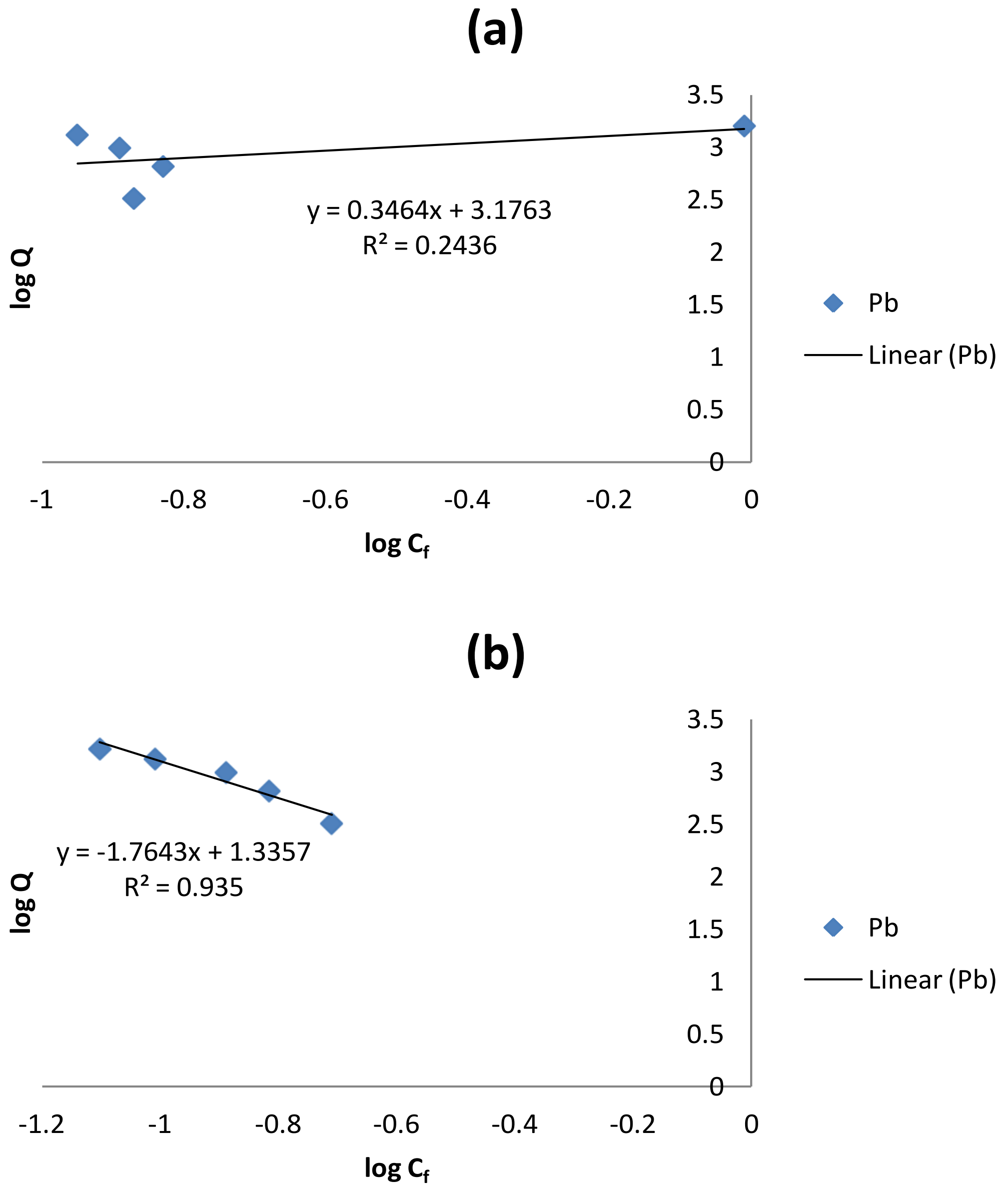


Figure 13. Freundlich adsorption isotherms for the adsorption of Pb^{2+} by (a) unmodified cocoa husk char (b) modified cocoa husk char.

Table 2. Langmuir and Freundlich constants for the adsorption of Cr^{6+} and Pb^{2+} at 25°C using modified and unmodified cocoa husk char.

Element	Langmuir constants			Freundlich constants		
	b (L/mg)	Q_{max} (mg/g)	R^2	K	1/n	R^2
			Unmodified cocoa husk char			
Cr	4.867	136.98	0.0096	39.138	0.5334	0.876
Pb	0.1125	1250	0.0823	1500.7	0.3464	0.2436
			Modified cocoa husk char			
Cr	-13.903	333	0.9612	38.86	1.1706	0.8668
Pb	-12.667	263.16	0.6848	21.6621	-1.7643	0.935

R^2= correlation coefficient.

Table 3. Comparisons of the Langmuir constants for cr adsorption onto adsorbents.

Adsorbent	Qmax ((mg/g)	References
Caladium bicolor biomass	53.63	Horsfall and Spiff (2005)
Wood ash	73.8	Chirenje et al. (2006)
Oryza Sativa L. husk	8.6	Zulkali et al. (2006)
Sago waste	46.6	Quek et al. (1998)
Sphagnum moss peat	30.7	Ho and McKay (2000)
Groundnut husks	39.3	Okieime et al. (1991)
Corynebacterium glutamicum	2.74	Choi and Yun (2004)
Peat moss	76.7	Akinbayo (2000)
Chrysophyllum albidum shell	103.42	Amuda et al., (2009)
Chitosan modified Cocoa husk carbon	333	This study

Table 4. Comparisons of the Langmuir constants for Pb adsorption onto adsorbents.

Adsorbent	Qmax (mg/g)	References
Chitosan impregnated with Microemulsion	85.59	de Castro Dantas et al., 2001
Chitosan–coated acid treated C. albidum seed shell (CACASC)	84.31	Amuda et al., 2009
Chitosan–coated C. albidum seed shell (CCASC)	76.23	Amuda et al., 2009
Chitosan modified Cocoa husk carbon	263.16	This study

Conclusion

This study shows that the use of chitosan coated cocoa husk char for metal ion removal is technically feasible, eco-friendly and with high efficacy. Besides that, cocoa husk and even the snail shell being agricultural industry waste makes the study to be relevant in the management of cocoa husk and snail shell waste. The preparation of chitosan from snail shell is cost effective. Cocoa husk char could be used for waste water treatment.

Conflict of Interest

The authors have not declared any conflict of interest.

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