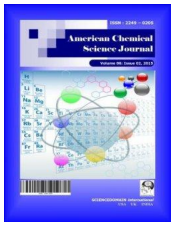

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Chitosan-Grafted Carbon for the Sequestration of Heavy Metals in Aqueous Solution

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AAO, ABA and IEO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AAO, IEO, OSA and ABA managed the analyses of the study. Authors AAO, ABA and OSA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Heavy metals removal from wastewater is totally essential to evade water pollution. The present study showed the performance of chitosan coated carbon for the removal of chromium (VI) and Pb (II) from aqueous solution. The following elements; C, K, Ca, Mg, Al, Si, P and Cl were revealed by Energy dispersive X-ray (EDX) as part of the constituent of the adsorbent while Scanning Electron Microscope (SEM) reveal agglomeration of the adsorbent particle. Batch adsorption experiments were performed in order to examine the removal efficiency under the various factors such as the effects of initial concentration, adsorbent dose, agitation time and particle size. The adsorbent possess good adsorption efficiency for chromium (VI) and lead (II) with optimum agitation time of 90 to 120 min even at low concentration. Experimental data were analysed by Langmuir and Freundlich adsorption isotherms. The characteristic parameters and related correlation coefficients were determined. The isotherm study revealed that the adsorption equilibrium is well-fitted to the

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Langmuir and Freundlich isotherm. The selectivity order of the adsorbent (modified and unmodified) towards the ions was found: Pb (II) > Cr (VI). The method could be successfully employed for removal of toxic metals from industrial effluents and could solve the problem of disposal of agricultural waste materials.

Keywords: Chitosan; chromium (IV); lead (II); heavy metal adsorption; industrial wastewater; coconut shell char; EDX; SEM.

1. INTRODUCTION

Naturally, heavy metals are continuously released into the aquatic environment through processes such as volcanic activity and weathering of rocks. Industrial activities have significantly enhanced the mobilization of heavy metals [1-3]. Among these heavy metals, the two major toxic heavy metals pollutant that found their way into water streams through various industrial processes are chromium and lead. Their toxicity and the tendency for bioaccumulation in the food chain even at relatively low concentrations make the presence of these heavy metals in the environmental a major concern [4,5]. In ionic or compound forms, they are highly toxic; they are soluble in water and may be readily absorbed into living organisms [1]. The possible sources of chromium (VI) wastes are effluents from manufacturing industries such as aluminium electroplating, ink, leather tanning, metallurgy, paint and textile dyeing industries [6,7] while Lead majorly serve as industrial raw material in the manufacture of fuels, leaded glass, photographic materials, pigments, steel products, solder and storage batteries [8,9]. Severe exposure to lead can cause encephalopathy, with permanent damage, while moderate exposure to lead result in neurobehavioral and intelligent deficit [10]. The presence of lead even in low concentrations, in drinking water may cause anaemia, hepatitis and nephritic syndrome [11]. It may also cause severe damage to kidney, nervous system, reproductive system, liver and brain in human [12]. Chromium (VI) is carcinogenic to both humans and animals [13]. Strong exposure of chromium (VI) causes cancer in the digestive tract and lungs and may cause gastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [14]. The World Health Organisation (WHO) and Nigerian Industrial Standard (NIS) permissible limit for total Cr (VI) and Pb (II) are 0.05 mg/L and 0.01 mg/L respectively for potable water while United State Environmental Protection Agencies (USEPA) and Bureau of Indian Standards (BIS) permissible limit for industrial discharge water is 0.1 mg/L [15-17]. Removal of these toxic heavy metals from industrial wastewater is important from the standpoint of environmental pollution control [18]. A number of conventional methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, electrodialysis, precipitation, flocculation and membrane separation processes [19-23]. However, these methods have disadvantages, such as high capital and operational costs, the treatment and disposal of the residual sludge. Adsorption compared with other methods appears to be a favourable process due to its efficiency and the simplicity with which it can be applied in the treatment of heavy metal containing wastewater [24]. In recent years, a number of materials, such as aquatic plants [25], agricultural by-products [26], industry by-product [19], sawdust [27], clay [28], zeolite [29], microorganisms [30] and Shrubs [31] were used for the removal of inorganic and organic contaminants from wastewaters. Agricultural waste materials being economical and eco-friendly due to their exceptional chemical composition, abundance, renewablity, minimal cost and more efficiency seem to be a feasible option for heavy metal remediation.

Modification of agricultural waste or biochar with Chitosan proffers to the waste a better remediation of heavy metal. 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 Fig. 1 [32].

Chitosan in itself has good adsorptive characteristics but because of its slight solubility at low pH, binding sites not readily available for sorption and also tendency of its soft site to agglomerate or form gel in aqueous solutions poses problems for developing commercial applications. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications [33]. The chitosan used for this research was

extracted from natural source and it said that Biochar shows a great affinity and sorption capacity for heavy metals [34].

This present communication is devoted to study the adsorptive removal of Cr (VI) and Pb (II) from synthetic aqueous wastewater by using coconut shell char and modified coconut shell char. It investigated the efficiency of the adsorbents for the removal of heavy metals from industrial effluents and effect of chitosan on the efficiency of the adsorbents was also investigated. This research also compared the efficiency of the adsorbents with commercially available activated carbon.

2. MATERIALS AND METHODS

2.1 Coconut Shell Char Preparation

The coconut shells used for this research were collected from Ilara-mokin and Idanre in Ondo State, Nigeria. The sample was dried ground and sieved to 150 – 300 µm particle size. The char of the coconut shell was carried as previously described with modification [35]. Pulverized sample (15 g) was placed in a furnace at 500°C for 2 h and later soaked in liquid nitrogen for 1 h. The carbonaceous substance was then washed with distilled water and dried.

2.2 Characterization of the Adsorbent

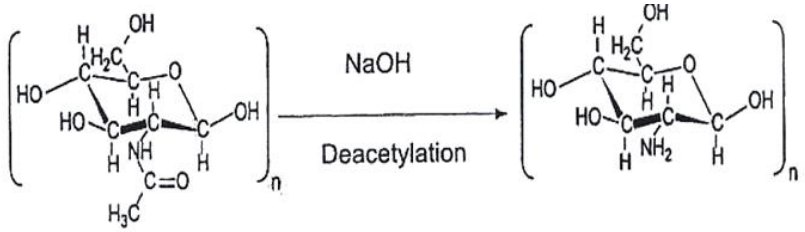
Scanning Electron Microscope (SEM) (High resolution SEM EVO MA 10 carl Zeiss) was used to study the surface morphological characteristics of coconut shell char while the same machine was also used for Energy Dispersive X-ray (EDX) Micro Analysis to study the elemental composition of the coconut shell char.

2.3 Activation of Coconut Shell Char

The carbonaceous samples was treated with 2% H_2SO_4 (v/v) in an incubator at a temperature of 110°C for 24 h. The treated carbonaceous sample was then soaked in distilled water until the pH was stabilized. Then, the sample was soaked in 2% $NaHCO_3$ till residual acid was removed. The acid-treated coconut shell carbon was then dried overnight in an oven (Met-tler, England) at 110°C, cooled and stored in desiccators until use [36].

2.4 Chitosan Preparation

The method of Amuda et al. [32] was modified. 50 g of the less than 2 mm size powdered snail shell was deproteinized by weighing into a 500 ml beaker and 200 ml of 4% (w/v) KOH was added with constant stirring for 6 h at 80°C. The residue was washed with distilled water after filtration until it is free of base and then dried at 100°C for 2 h. The deproteinized snail shell residue was 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. This process is called demineralization. The content was later filtered and the residue was washed until it is free of acid. Litmus paper was used to test if the residue is acid free. 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 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 and stirred at 30°C for 4 hrs. After filteration, the residue, which is Chitosan (2-acetamido-2-deoxy-β-D-glucose-N-(acetylglucosamine)), was then washed and dried at 90°C for 1 hr.



Chitin
2-acetamido-2-deoxy-β-D-glucose-(N-acetylglucan)

Chitosan
2-acetamido-2-deoxy-β-D-glucose-(N-acetylglucosamine)

Fig. 1. Conversion of chitin to chitosan by deacetylation

2.5 Chitosan Gel Preparation

About 5 g of chitosan was slowly added to 100 ml of 10% (w/v) oxalic acid with constant stirring. The mixture was also heated to 40-50°C to facilitate mixing [32]. A chitosan-oxalic acid mixture was formed (a whitish viscous gel).

2.6 Adsorbent Modification

The method of adsorbent modification employed by Amuda et al. [32] was modified. The chitosan gel (100 ml) was diluted with water (~500 ml) and heated to 40-50°C. 50 g of coconut shell 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 gel coated adsorbent were then washed with distilled water and dried. The chitosan coated cocoa husk char was then soaked in 0.5% (w/v) NaOH solution for 3 h. It was then extensively rinsed with distilled water and dried in an oven at 102°C for 2 h, cooled at room temperature and stored in desiccator.

2.7 Batch Biosorption Studies

Experiments were conducted in 250 mL Erlenmeyer flasks containing known 100 ml Cr (VI) synthetic solutions and 1.5 g of the adsorbent. Flasks were agitated on a shaker at 400 osc/m constant shaking. The following parameters were investigated; Biosorbent dose (0.5, 1.0, 1.5, 2.0 and 2.5 g), Contact time (30, 60, 90, 120 and 150 min) and Metal ion concentration (5, 10, 15, 20 and 25 mg/L). The mixture was filtered using Whatman no. 1. and the filterate was analysed spectrophotometrically using atomic absorption spectroscopy (AAS).

The removal efficiency (E) of adsorbent on Cr (IV) are measured as follows:

$$E\,(\%) = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

where C_i and C_f are the initial and final concentration of Cr (VI) (mg/L) in wastewater, respectively. The same procedure was repeated for the adsorption of Pb (II).

2.7.1 Data evaluation

The amount of metal adsorbed by the adsorbent was calculated using a mass balance equation which has been previously used in evaluating the amount of metal ion uptake by maize cob char. The equation is given as

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

where Q is the metal uptake (mg metal per g biosorbent), v is the liquid sample volume (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 biosorbent on the dry basis (g).

2.8 Adsorption Isotherm

Two of the most sorption models were used to fit the experimental data. The Langmuir model assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. The model can be represented as:

$$Q = Q_{max}\, bC_f/\, 1+bC_{f,} \quad (3)$$

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

The linearized equation of Langmuir model is commonly represented by:

$$1/Q = 1/Q_{max}\,(1/b\,C_f + 1) \quad (4)$$

The maximum metal uptake can be obtained if a plot of 1/Q against C_f is made. The second model is Fruendlich model which mathematical equation can be written as:

$$Q = k\,C_f\,(1/\,n), \quad (5)$$

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

Logarithm of Eq. 5 gives rise of the following equation:

$$\text{Log } Q = \text{Log } k + 1/n \log C_f. \quad (6)$$

Plot of 1ogQ against $1ogC_f$, will give a straight line which will confirm the Freudlich Isotherm.

3. RESULTS AND DISCUSSION

Figs. 2 and 3 show the elemental composition and morphological characteristics of coconut

shell char. The presence of the following elements; C, K, Ca, Mg, Al, Si, P and Cl are revealed. These elements have been reported to support adsorption of metals through adsorption mechanism such as ion exchange, chelation, coordination and complexation [37,38]. Morphological characteristics clearly reveal agglomeration of the particles of the adsorbent which encourage retention of metals unto the surface of the adsorbent [39,40].

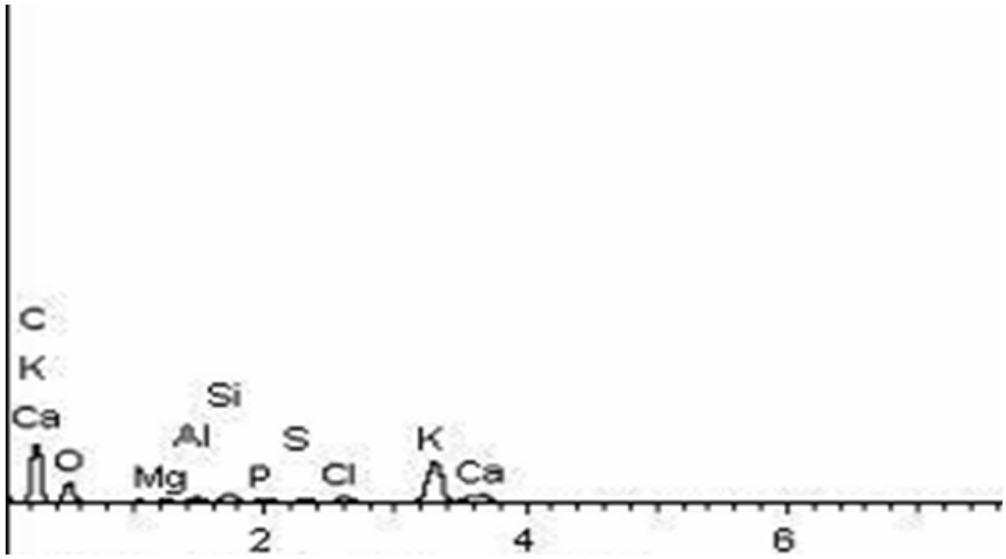


Fig. 2. EDX spectra of coconut shell char

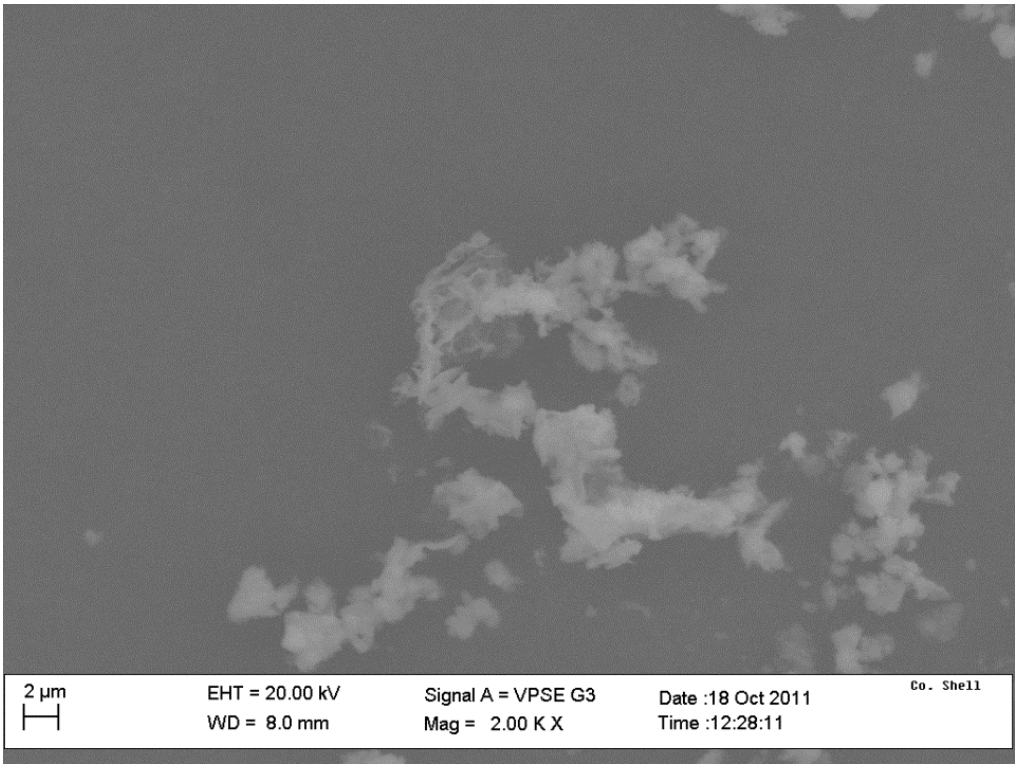


Fig. 3. Coconut shell char SEM image

3.1 Effect of Agitation Time on Removal Efficiency

Agitation time play a vital role in adsorption system irrespective of the other experimental parameters. Fig. 4 depicts that there was an appreciable increase in removal efficiency of chromium up to 90 min and decrease as agitation time increased for unmodified coconut shell char but modified coconut shell char and commercial activated carbon showed in increase the removal efficiency of chromium as agitation time increased. Modified and unmodified coconut shell char also exhibit increase in removal efficiency of Lead as agitation time increases. Equilibrium time for the adsorption of chromium using unmodified adsorbent is reached at 90 min. In the case of lead, the results clearly revealed that as the agitation time increases, the metal uptake increases until the contact time of 150 min (Fig. 5). The implication may be due to the availability of a large number of vacant sites initially for adsorption as the agitation time increased but tailed off due to the saturation of vacant sites at 90 min. This observation agrees with the work of Sugashini and Gopalakrishnan, [41] who studied the performance of protonated Cross linked Chitosan Beads (PCCB) for Chromium removal. The progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbents [42,43].

As shown in the results, the efficiency of the modified is higher than the unmodified adsorbent. The implication is that the enhancement with chitosan increases the binding site available for the uptake of the metals (Cr^{6+} and Pb^{2+}) by the adsorbents. The removal efficiency trend for both metals is commercial activated carbon > modified coconut shell char > unmodified coconut shell char.

3.2 Effect of Adsorbent Dosage on Removal Efficiency

Figs. 6 and 7 show the effect of adsorbent dose on adsorption of Cr(VI) and Pb(II) ions by modified and unmodified coconut shell char respectively. For Cr(VI) ion, a decrease in removal efficiency of 46.1% to 40.06% was observed as the adsorbent dose increased from 0.5 to 2.5 g for modified adsorbent and a decrease of 61.87% to 59.2% was observed as adsorbent dose for commercial activated carbon increased but an increase in removal efficiency from 17% to 21.2% was detected as unmodified adsorbent dosage increased. However, for Pb(II) ion, commercial activated carbon and modified coconut shell char showed increase efficiency as adsorbent dosage increased while unmodified coconut shell char showed a fluctuation in removal efficiency as dosage increases. The increase in efficiency is due to the greater availability of active sites and increase in surface area at higher dose of the adsorbent. These observations are in agreement with previous studies on many other adsorbents [44-47]. The decrease in the 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. Also at high biomass concentration diffusion path length may increase which can give rise to decrease in active sites [48].

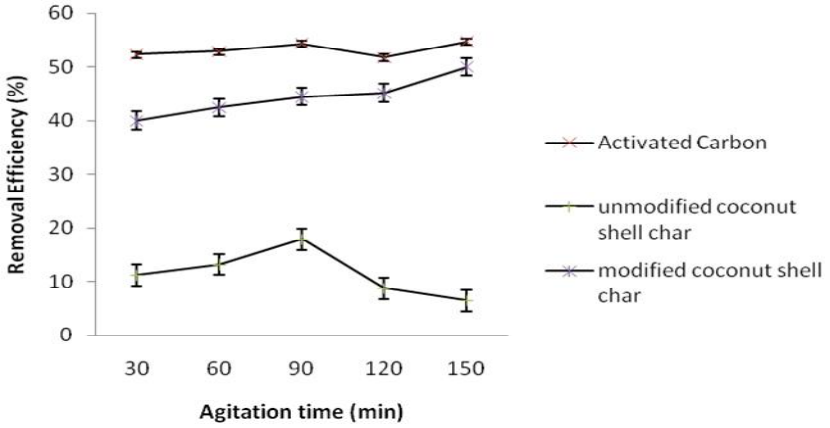


Fig. 4. Effect of agitation time on Cr(VI) removal [Cr(VI) conc = 20 mg/L; adsorbent dose = 1.0 g; agitation speed = 400 osc/m; temp = 25°C]

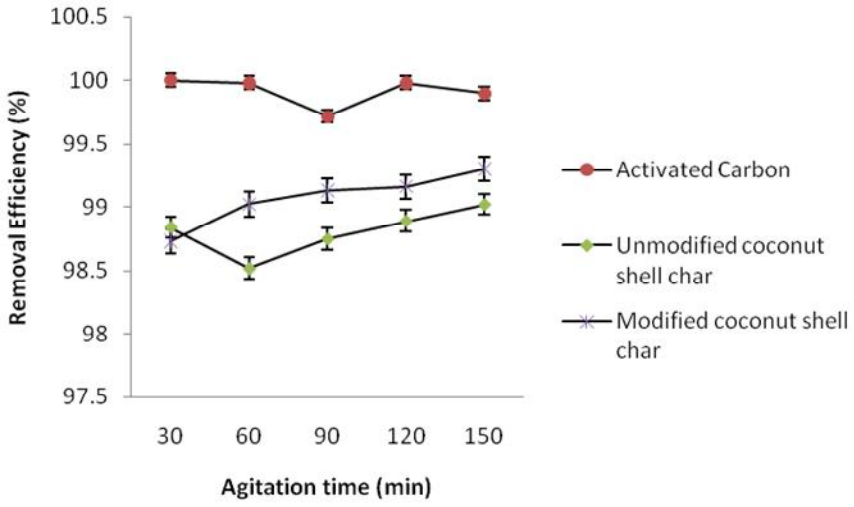


Fig. 5. Effect of agitation time on Pb(II) removal [Pb(II) conc = 20 mg/L; adsorbent dose = 1.0 g; agitation speed = 400 osc/m; temp = 25°C]'

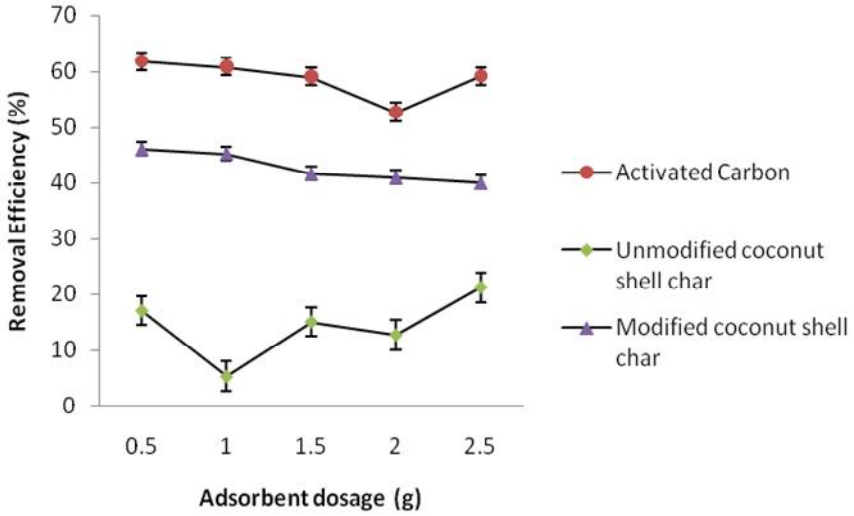


Fig. 6. Effect of adsorbent dosage on Cr (VI) removal [Cr (VI) conc = 30 mg/L; agitation time = 60 min; agitation speed = 400 osc/m; temp = 25°C]

3.3 Effect of Initial Concentration on Adsorption

The results in Figs. 8 and 9 reveal the effect of initial metal ion concentration on adsorption of Cr^{6+} and Pb^{2+} respectively. A range of initial concentrations were used on both modified and unmodified coconut shell char. An increase in the removal efficiency of Cr ion was observed as the initial metal ion concentration increases for commercial activated carbon and modified coconut shell char while a decrease was observe for unmodified coconut shell char as metal ion concentration was increasing. On the other hand, the removal efficiency of Pb^{2+} using unmodified adsorbent increase as metal concentration increases but for modified coconut shell char and commercial activated carbon, the removal efficiency decreases as the initial metal ion concentration increases (Fig. 9). The increase in efficiency may be explained by an increase in the number of metal ions competing for the available binding sites in the adsorbents. The result is in agreement with an earlier study by Olu-Owolabi et al. [49] which reported that Pb (II) adsorption by cocoa pod waste at varying concentration of Pb (II) increased as the initial metal ion concentration increases. However, the decrease

experience in this study may be an indication that at the inception of the experiment, the metal ions are adsorbed fully to the available active sites present on the adsorbents and later no free sites are available to adsorb which agrees with AjayKumar et al. [50] who studied various parameters in the adsorption of four different heavy metals on activated sludge. Waly et al. [51] also experienced the same trend in his work and he concluded that at lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. In this study also, it was observed that the removal efficiency of the chitosan modified adsorbents was higher compared to the unmodified adsorbents (Figs. 8 and 9). This is due to the fact that modification increase the active site that is available for binding metals thereby enhances the performance of the adsorbent [52,53]. Also, the percentage (%) Pb removal efficiency of the modified natural adsorbent was almost the same with that of activated carbon. Commercial activated carbon exhibit a better efficiency than the adsorbent in the adsorption of chromium but modification with Chitosan increases the efficiency.

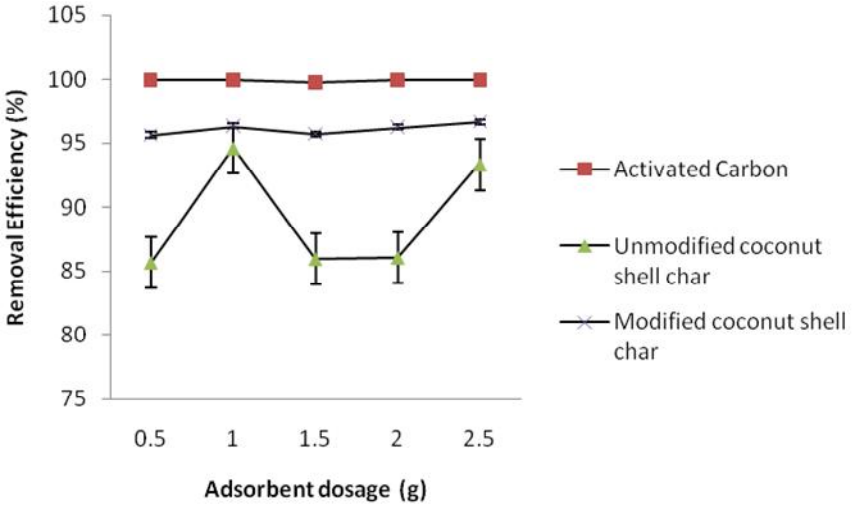


Fig. 7. Effect of adsorbent dosage on Pb(II) removal [Pb(II) conc = 30 mg/L; agitation time = 60 min; agitation speed = 400 osc/m; temp = 25°C]

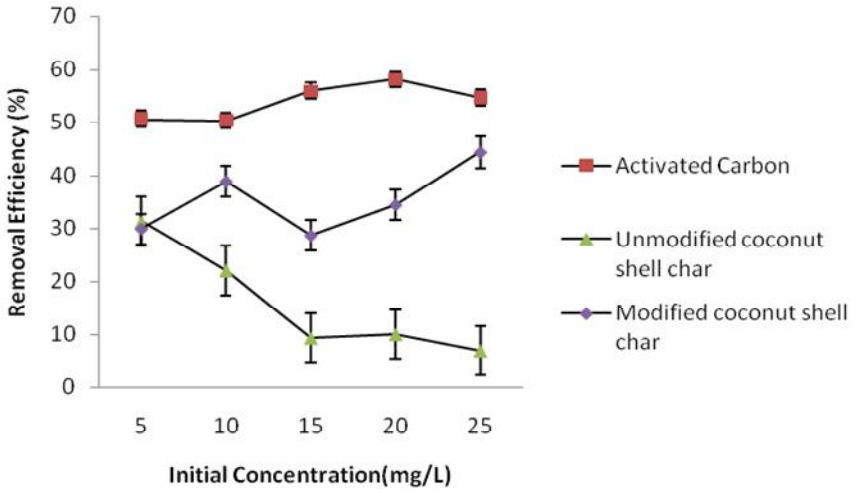


Fig. 8. Effect of initial metal ion concentration on Cr(VI) removal [adsorbent dosage= 1.5 g; agitation time = 45 min; agitation speed = 400 osc/m; temp = 25°C]

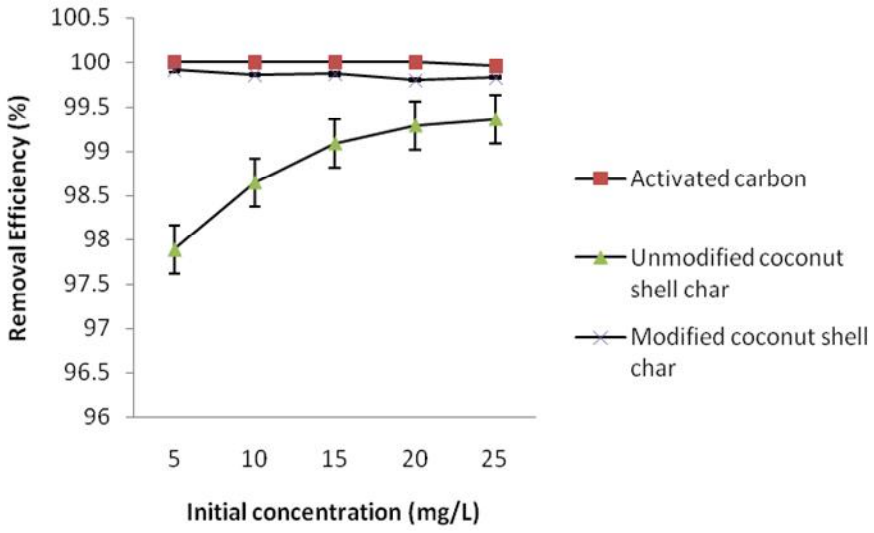


Fig. 9. Effect of initial metal ion concentration on Pb(II) removal [adsorbent dosage= 1.5 g; agitation time = 45 min; agitation speed = 400 osc/m; temp = 25°C]

3.4 Effect of Particle Size on Adsorption

The effect of particle sizes (150, 212 and 300 µm) of the adsorbent on adsorption of the metals were considered in Fig. 10. 150 µm particle size of the unmodified adsorbent showed removal efficiency that is lower compare to the 212 µm particle sizes in the adsorption of Pb but 300 µm particle show the lowest efficiency. However, the removal efficiency of Pb^{2+} ion by the particle sizes of the modified and that of the adsorption of Cr increases as the particle size decreased. The increased adsorption level achieved by smaller particle size of the adsorbent over larger particle size may not be separated from the fact that smaller particles give large surface areas [52]. The trend of adsorption is 150 µm modified > 212 µm modified > 300 µm modified > 150 µm unmodified > 212 µm unmodified > 300 µm unmodified.

3.5 Adsorption Isotherm

The sorption processes applicability as a unit operation can be evaluated using isotherm models. The sorption data obtained were analysed in terms of the Langmuir and Freundlich equations. The data was linearised to fit the Langmuir and Freundlich equation and presents the constants derived by regression analysis for the equation. As shown in Table 1, the Freundlich isotherm had a better fitting than Langmuir isotherm for unmodified coconut shell in the case of Pb but for modified adsorbent, Langmuir isotherm had a better fitting than Freundlich isotherm with respect to Cr and Pb as related to correlation coefficient (R^2). Also, modified coconut shell char has correlation coefficient higher than that of the unmodified. This explains why modified coconut shell char show better adsorption than the unmodified, indicating better suitability of the modified adsorbent [54]. The magnitude of the adsorption capacity, (K) and adsorption intensity, (1/n) shows that it is possible for an easy separation of heavy metal ion from aqueous solution and a high adsorption capacity. The K values for the sorption of Pb (II) ion by the modified and unmodified adsorbent are higher than that of the sorption of Cr (VI) ion by the same modified and unmodified adsorbent (Table 1). 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+}. The higher numerical values of *K* confirm the significant affinity of adsorbate towards the adsorbent [55].

The value of 1/n less than 1 (Tables 1) is indicative of favourable adsorption [56]. Since the fractional value of 1/n in the adsorption of Pb^{2+} (0.6347) is small compared to 1/n value of the adsorption of Cr^{6+} (1.087), it indicates 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 [55,57-58]. The Qmax value which is the maximum value of Q, is important to identify the adsorbent highest metal uptake capacity [51,59-60]. This explain the

reason why Pb^{2+} ion adsorbed more than Cr^{6+} ion as the result showed that Q_{max} value for the adsorption of Pb^{2+} is higher compared to that of adsorption of Cr^{6+} (Table 1). Also, it is therefore concluded that higher capacities of adsorption of Pb (II) was observed for the adsorbents (modified and unmodified) used.

Table 2 compares the Langmuir constants of Pb and Cr (VI) adsorption onto different adsorbents.

Table 1. Langmuir and Freundlich constants for the adsorption of Cr^{6+} and Pb^{2+} at 25ºC using modified and unmodified coconut shell char

	Langmuir constants			Freundlich constants		
	b (L/mg)	Q_{max} (mg/g)	R^2	K	1/n	R^2
Unmodified coconut shell char						
Cr	-3.83	113.64	0.0058	133.84	-0.031	0.0046
Pb	2.6667	1250	0.0774	1281.15	0.6554	0.1539
Modified coconut shell char						
Cr	-12.461	-3.33	0.9711	40.00	1.087	0.8699
Pb	22.22	5000	0.9335	15552.49	0.6347	0.8134

R^2= correlation coefficient

Table 2. Comparison of the Langmuir constants for Pb and Cr (vi) adsorption onto the adsorbents

Lead adsorption		
Adsorbent	**Adsorption capacity qmax (mg/g)**	**References**
Caladium bicolor biomass	53.63	[61]
Wood ash	73.8	[62]
Oryza Sativa L. husk	8.6	[63]
Groundnut husks	39.3	[64]
Corynebacterium glutamicum	2.74	[65]
Chrysophyllum albidum shell	103.42	[66]
Chromium adsorption		
Adsorbent	**Adsorption capacity qmax (mg/g)**	**References**
Coconut Shell fiber	12.23	[67]
Chitosan-coated Acid treated C. Albidum seed shell	84.31	[68]
Chitosan-coated C. Albidum seed shell	76.23	[68]
Acid treated C. Albidum seed shell	59.63	[68]

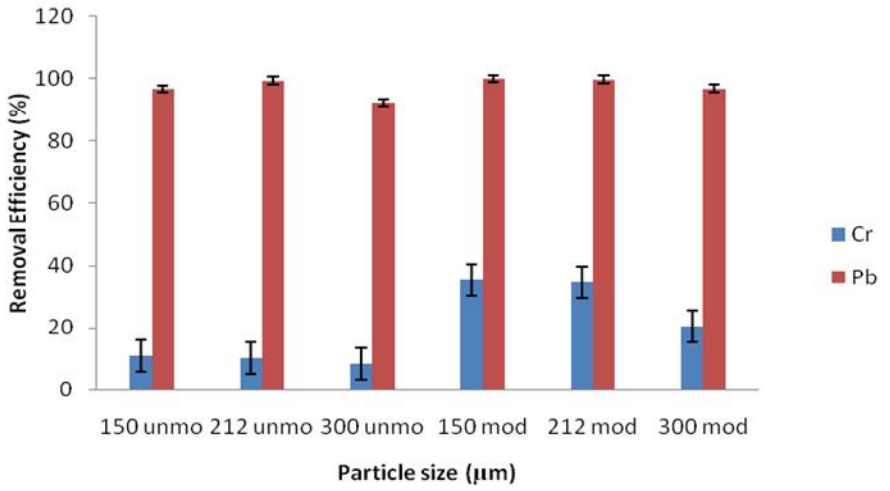


Fig. 10. Effect of particle size on Cr(VI) and Pb(II) removal [metal conc= 20 mg/L; adsorbent dosage= 1.5 g; agitation time = 45 min; agitation speed = 400 osc/m; temp = 25°C]

4. CONCLUSION

This study contributes to waste management by revealing the usefulness of agricultural waste and shell of shell animals in adsorption processes. Coconut shell, instead of becoming nuisance to the environment, can be used as a substitute for commercial activated carbon as an adsorbent. Also the shell of marine animal can serve as an alternative material for the production of Chitosan. In the present work, natural adsorbent showed high adsorption capacity in the removal of Lead ion from aqueous solution compared to chromium. The coconut shell (modified and unmodified) showed better affinity for Lead (II) than Chromium (VI). The adsorbents exhibit high selectivity for metal ion such as Pb^{2+} and when modified with Chitosan gives improved adsorption for Cr^{6+} that is equivalent to that of commercial activated carbon. Application of the Freundlich and Langmuir isotherm models gave good representations of the experimental data for chromium and lead sorption by modified and unmodified coconut shell char. Adsorption of lead and chromium was found to be in good agreements with Langmuir isotherm which indicates monolayer adsorption. Using coconut shells to produce activated carbons potentially provide a less expensive raw material, a highly effective adsorbent as well as production of activated carbon processed from renewable resources instead of non-renewable ones. The composite adsorbent (chitosan-coated acid-treated coconut shells char) exhibited effectiveness in the removal of Pb(II) and Cr(VI) ion from aqueous solution.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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