Activated Periwinkle Shells for the Binding and Recognition of Heavy Metal Ions from Aqueous Media

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Authors' contributions

This work was carried out in collaboration among all authors. Author KNA designed the study. Author ROS performed the laboratory analysis, wrote the protocol and the first draft of the manuscript. Authors VOO and KNA wrote the final draft of the manuscript. Author OMA managed the literature searches. All authors read and approved the final manuscript.

Article Information

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ABSTRACT

The potential of a low-cost periwinkle shell powder (PSP) for the adsorption of Cr(II) and Zn(II) ions from aqueous media was investigated by batch mode. The PSP produced was chemically activated with 0.1M H_2SO_4. Scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetry were used to characterize the structure and morphology of the PSP sorbent. The obtained results showed that PSP possessed good recognition toward Cr and Zn. The effect of various parameters such as contact time, initial concentration, pH and adsorbent dosage was studied to optimize the conditions for maximum adsorption. The optimum contact time, adsorbent dosage and pH, were found to be at 120 min, 1.2g and pH 6 respectively for both metal ion. The

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experiment showed that when the initial metal ion concentration was increased from 20 mg/L up to 100 mg/L, the adsorption capacity of PSP increased from 0.67 to 4.14 mg/g and 0.61 to 3.65 mg/g for Cr and Zn respectively. The mechanism for the adsorption of the metal ions was found to follow Langmuir isotherm model.

1. INTRODUCTION

Toxic heavy metals in air, soil, and water are global problems that are of growing threat to humanity. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, and chloro-alkali industries [1-2]. Under the current regulations in most countries, industries are obligated to treat wastewater and to reduce toxic metal concentration to less than certain designated values [3]. The removal of heavy metal ions from aqueous media has been conventionally carried out by several techniques such as reverse osmosis, adsorption, ion exchange, complexation and precipitation. The use of synthetic resins for chelating toxic metal ions in wastewater is a possible approach for preventing environmental pollution and recycling metals. These resins are mostly composed of petroleum-based synthetic polymers [4-6]. In general, after the adsorption process for metal ions, the chelating resins are discarded in landfills or treated by incineration. Nonetheless, these processes often result in secondary environmental pollution by contaminating the soil or air, because, these synthetic polymers are usually non-renewable and non-biodegradable.

Periwinkle shells are waste obtained from periwinkle. Periwinkles are marine mollusks (gastropods) with thick spiral shells. As they grow, gastropod shells follow a mathematically regular pattern. Thus, as they increase in size, they retain their basic form [7]. Although, few people utilize the shell as coarse aggregate in concrete in areas where there are neither stones nor granite for purpose such as paving of water logged areas [8].

In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity [9].

The use of periwinkle shells will add economic value; provide a potentially inexpensive material that will be used for the removal of metal ions from aqueous media and help reduce the cost of waste disposal.

Therefore, the main objective of this study is to investigate the possibility of using periwinkle shells to develop a new low-cost adsorbent for the recognition and removal of Cr (II) and Zn (II) ions from aqueous media.

2. MATERIALS AND METHODS

2.1 Materials

The periwinkle shells (PS) were collected from a large waste bin at Laketu market Ikorodu, Lagos state, Nigeria. The samples were transported to the laboratory for immediate use. Sulphuric acid, sodium hydroxide, distilled water and heavy metal stock. All chemicals used were of analytical grade. All apparatus were thoroughly washed with detergent followed by tap water and lastly distilled water was used for rinsing.

2.2 Sample Pre-treatment

The PS were washed thoroughly with distilled water to remove adhering dirt and suspended impurities present in it. The shells were sundried for 4-5 days and kept in an oven at 50°C for the next 2 days for complete drying. The dried shells were pulverized (with the aid of mortar and pestles) and was ground to a fine particle using a pm-y44b2 grinder after which it was subsequently sieved through 250 μm analytical sieve to remove larger particles.

The periwinkle shell powder (PSP) obtained was treated with 200 mL of 0.1M sulfuric acid for 24 hours before it was filtered and rinsed with distilled water until the filtrate was near neutral. The reason for treating the adsorbent is to improve removal performance and adsorption capacity for metal ions. The PSP was oven dried at 65°C for 24 hours and then kept in an air tight plastic container at room temperature.

2.3 Adsorption Experiment

The adsorption experiment of metal ions was performed at room temperature by adding an optimal quantity of the PSP (600 mg) into 30 mL
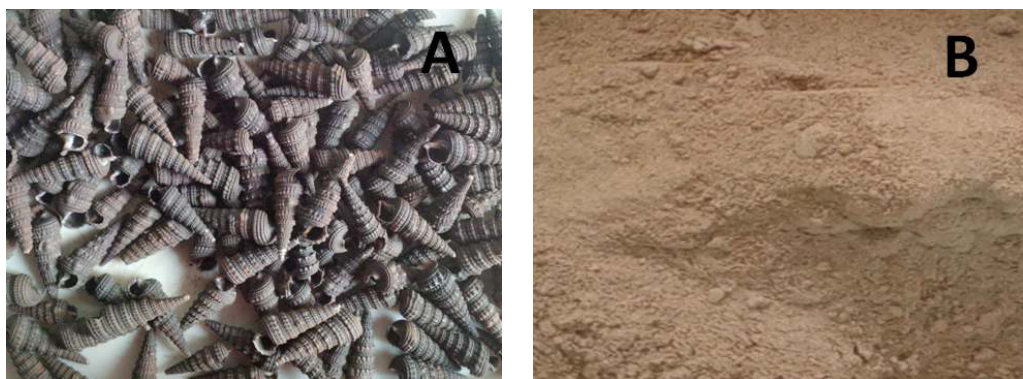
Fig. 1. Photographs of periwinkle shell (A) and periwinkle shell powder (B)

of metal ion solution with initial concentrations of metal ion in aqueous media ranging from 20 to 100 mg/L. Initial pH of the solutions was adjusted to desired pH by adding 0.1M HCl and/or NaOH solutions to the medium to maintain a constant pH. After shaking consistently for 2 h on an orbital shaker, PSPs were separated by centrifugation at 8 000 rpm for 15 min. Content of each flask were filtered and the amount of heavy metal content in the filtrate were analyzed by using Atomic Absorption Spectrophotometer. The adsorption capacity (Q_e mg/g) was calculated before and after adsorption according to the Eq. 1;

$$Q_e = \frac{V(C_i - C_e)}{M} \tag{1}$$

where C_i is the initial metal ion concentration (mg/L), C_e is the metal ion concentration at adsorption equilibrium (mg/L), V is the volume of metal ion solution (L), and M is the weight of the PSP (g). The adsorption capacity values were evaluated using Langmuir equation (Eq. 2) and Freundlich equation (Eq. 3), respectively [10].

$$^1/_{Q_e} = {}^1/_{Q_m} + {}^1/_{(KC_eQ_m)} \tag{2}$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where C_e (mg/L) and Q_e (mg/g) are metal ion concentration and adsorption amount at adsorption equilibrium, respectively, and Q_m (mg/g) and K (L/mg) are the theoretical maximum adsorption capacity and Langmuir equilibrium constant related to the theoretical maximum adsorption capacity and energy of adsorption, respectively. K_f and n are the Freundlich constants that are indicators of adsorption capacity and adsorption intensity, respectively.

K_f and n can be determined from a linear plot of $\log Q_e$ against $\log C_e$.

2.4 Scanning Electron Microscopy

To determine the surface morphology of the PSP, the powder was taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using Vega Tescan SEM fitted with an Oxford instrument INCAPentaFETx3 EDS.

2.5 FT-IR Spectroscopy

The Fourier transform infrared (FT-IR) spectra of the PSP was obtained using a PerkinElmer (Waltham, MA, USA) Spectrum 100 FT-IR spectrometer with an AutoIMAGE system.

2.6 Thermogravimetric Analysis (TGA)

Approximately 5 mg of the PSP was placed in an open aluminum pan. The sample was heated at a heating rate of 10°C min^{-1} from 30 – 500°C temperature range under nitrogen atmosphere (flow rate = 20 ml mn^{-1}) using a Diamond TG/DTA (Perkin-Elmer).

3. RESULTS AND DISCUSSION

3.1 Structural Characterization Studies

The morphology of the obtained PSP before and after adsorption of the metal ions was observed on scanning electron microscopy (SEM) as shown in Fig. 2. It can be seen in Fig. 2A that the PSP before adsorption exihibits a smooth surface and a uniform network structure with randomly distributed gaps (open structure) on the

surface. Thus, this open structure is of benefit because it can increase the adsorption capacity of the PSP. The morphology of the PSP after adsorption (Fig. 2B) had drastically different size and shape with porous structure. Interestingly, the surface of the PSP was shrunk with wrinkles and this could be attributed to the presence of metal ions on the surface of the sorbent material. In addition, it is evident that the PSP after adsorption had more compact and a rougher surface compared with that of the PSP before adsorption.

FT-IR spectroscopy can be applied in a similar fashion to elemental micro analysis to extract quantitative information on the composition of the PSP [11]. The result of FT-IR analysis of PSP before and after adsorption in the range of 650 – 4000 cm^{-1} are shown in Fig. 3, in which there are residual features of PSP, such as SiO_2 and CaO skeletal peaks appearing at 1422 cm^{-1} and 848 cm^{-1} (Fig. 3A). After adsorption of the metal ions, the spectrum (Fig. 3B) exhibits an alteration around 688 cm^{-1}, which might be due to steric effect resulting from the adsorption of metal ions. In addition, there are band shifts from 1422 cm^{-1} to 1442 cm^{-1}, 848 cm^{-1} to 859 cm^{-1}, these shifts in frequency suggest that there were metal binding formations taking place on the active sites of the PSP sorbent.
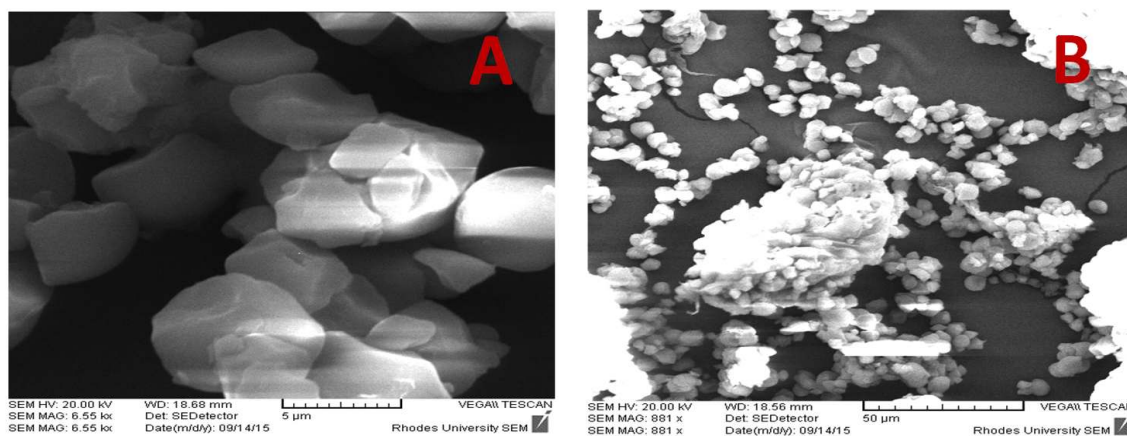

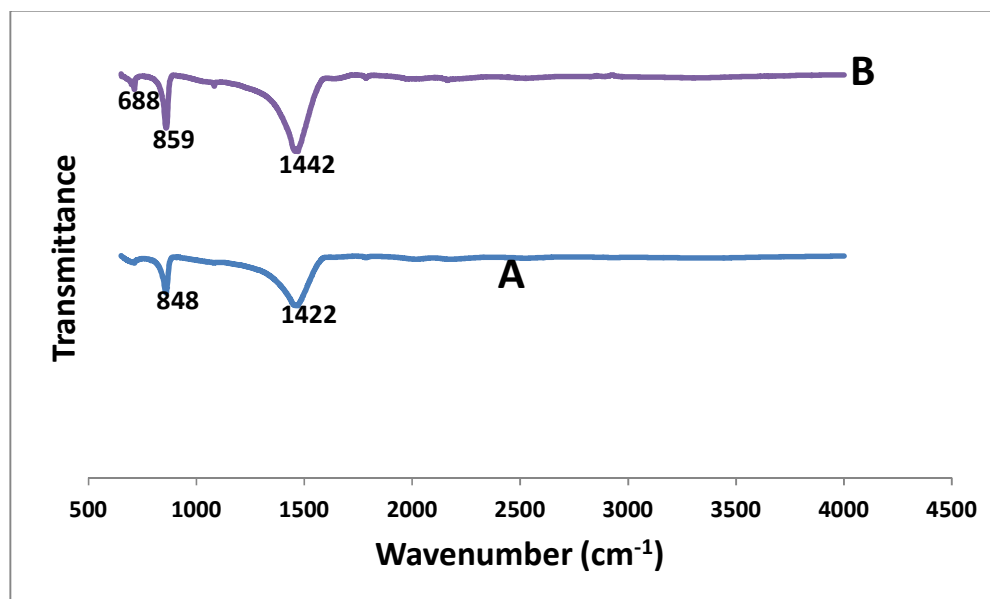**Fig. 2. SEM micrographs of the PSP before (A) and after (B) metal ions adsorption**

Fig. 3. FT-IR spectra of PSP (A) before adsorption (B) after adsorption of metal ions
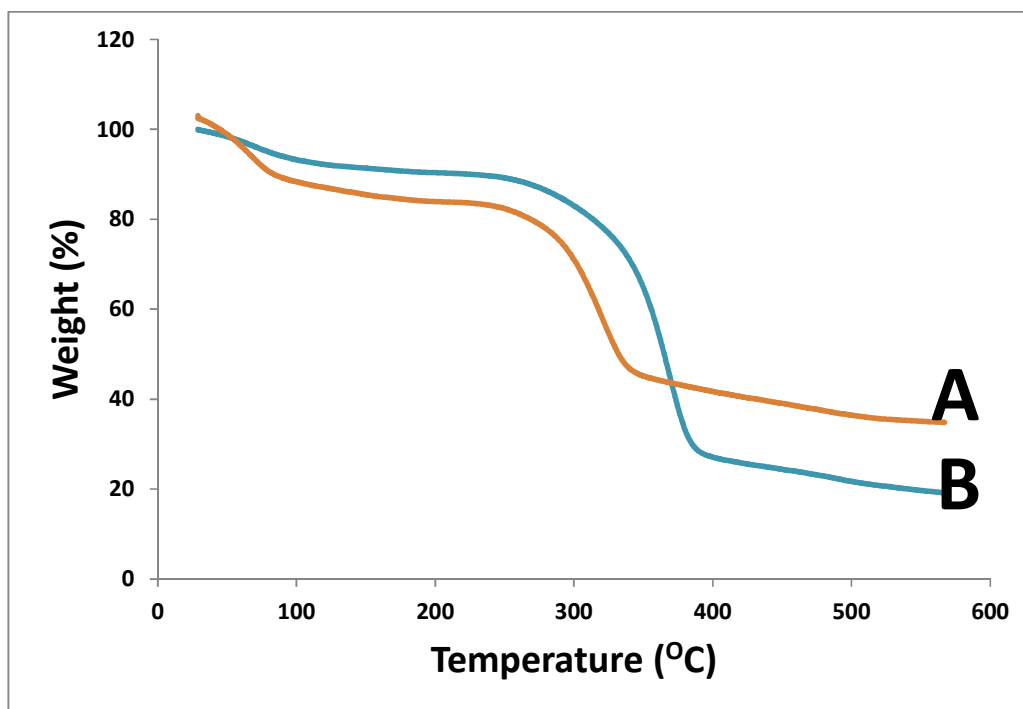
Fig. 4. Thermogravimetric analysis PSP: (A) before adsorption (B) after adsorption of metal ions

Fig. 4 shows TGA thermograms of PSP before and after adsorption of the metal ions. As shown in Fig. 4A for pure PSP i.e PSP before adsorption, three weight loss stages are seen, the first stage is related to loss of physically adsorbed water around 80℃, the second stage around 280℃ is associated with decomposition of PSP elemental framework. The third and the final stage occurred around 350℃ which might be due to further degradation of PSP elemental framework. Moreover, the results reveal that the thermal stability in PSP after adsorption (Fig. 4B) is higher (final decomposition around 390℃) – possibly an effect of metal binding formations.

3.2 Adsorption Isotherm

3.2.1 Effect of the initial metal ions concentration

In order to determine the adsorption strength of the PSP adsorbent for Chromium and Zinc adsorption, the effect of initial concentrations of Cr (II) and Zn (II) ions were investigated by varying the initial concentrations of the metal ions at optimum pH values and 2 h of equilibration time. As shown in Fig. 5, the adsorbed amount of metal ions by the PSP adsorbent was dependent

on the initial metal ion concentration in the solution. When the initial metal ion concentrations were increased from 20 mg/L up to 100 mg/L, the adsorption capacity of PSP for Cr and Zn increased. Maximum adsorption capacity of PSP towards Cr (4.14 mg/g) was higher than that of Zn (3.65 mg/g). In addition, the PSP got saturated faster for Zn compared to Cr. The increasing adsorption capacity of PSP might be attributed to the fact that the increasing initial concentration could increase the contact of surface solid-liquid, resulting in the higher collision between metal ions and the PSP sorbent material.

Adsorption isotherms are important for describing how adsorbates could interact with adsorbent. Thus, the correlation of equilibrium data using either a theoretical or empirical equation is essential to practical adsorption process. In this study, the equilibrium data for Cr (II) and Zn (II) onto PSP were evaluated with the Langmuir and Freundlich models.

The easiest and more often used model in adsorption studies is the Langmuir isotherm [12]. Langmuir proposed his theory by making assumptions: (1) fixed number of adsorption sites

are available on the surface of solid, (2) all the surface binding sites are of equal size and shape on the surface of adsorbent and can hold, at most, one adsorbed molecule, (3) there are no interactions between adsorbate molecules on adjacent sites and (4) adsorption is monolayer or unilayer [13].

The adsorption data fitted with both the Langmuir and Freundlich isotherm models are shown in Table 1, Figs. 6 and 7. The plot $1/Q_e$ versus $1/C_e$ was used to validate the linearized Langmuir isotherm as shown in Fig. 6. Langmuir constants Q_m and K were determined from the slope and intercept of the plots. The values of the correlation coefficients for Cr ($R^2 = 0.954$) and Zn ($R^2 = 0.973$) are higher than those calculated by Freundlich model, showing that the adsorption in the experiment obeyed the Langmuir model.

The results showed that the value of n was greater than unity i.e (n >1), which represent good adsorption and that the adsorption is a physical process. The difference in the k_F values for the metal ions might be in relation to interaction between the PSP and the analytes. A comparison based on Langmuir saturation adsorption capacity and equilibrium constant (Qm and K) for both metal ions, indicated that the PSP was more efficient for Cr (4.72 mg/g). This may be due to the fact that generally at room temperature Cr shows antiferromagnetic ordering compared to Zn (i.e magnetic moments, usually related to the spins of electrons). In addition, it could be concluded that the Langmuir isotherm model was more suitable for the experimental data than Freundlich isotherm because of the higher value of the correlation coefficient, suggested that the adsorption took place at specific homogeneous sites.
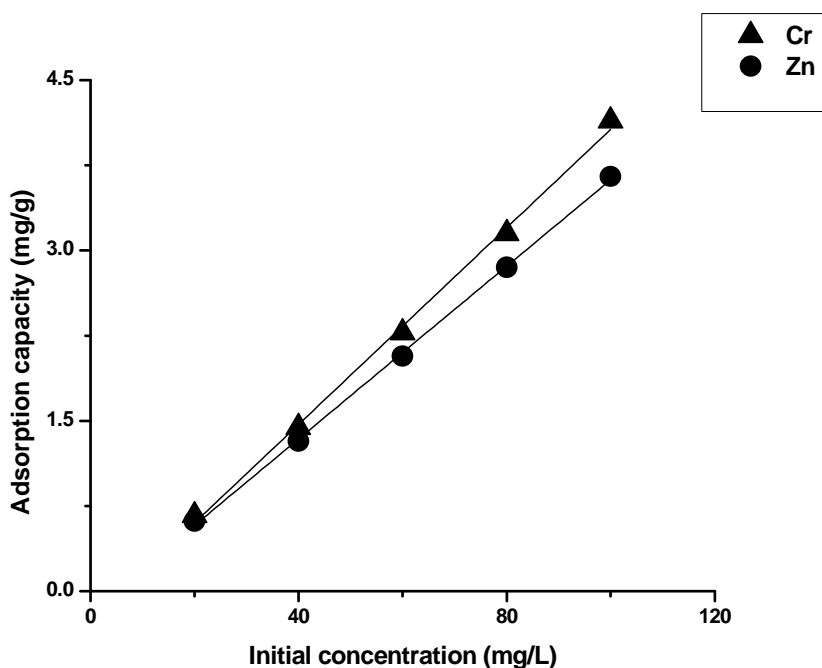

Fig. 5. Effect of initial concentration for the adsorption of Cr (II) and Zn (II) ions by PSP adsorbent at room temperature for 2 h

Table 1. Parameters of Langmuir adsorption equation and Freundlich isothermal equation for adsorption experimental data

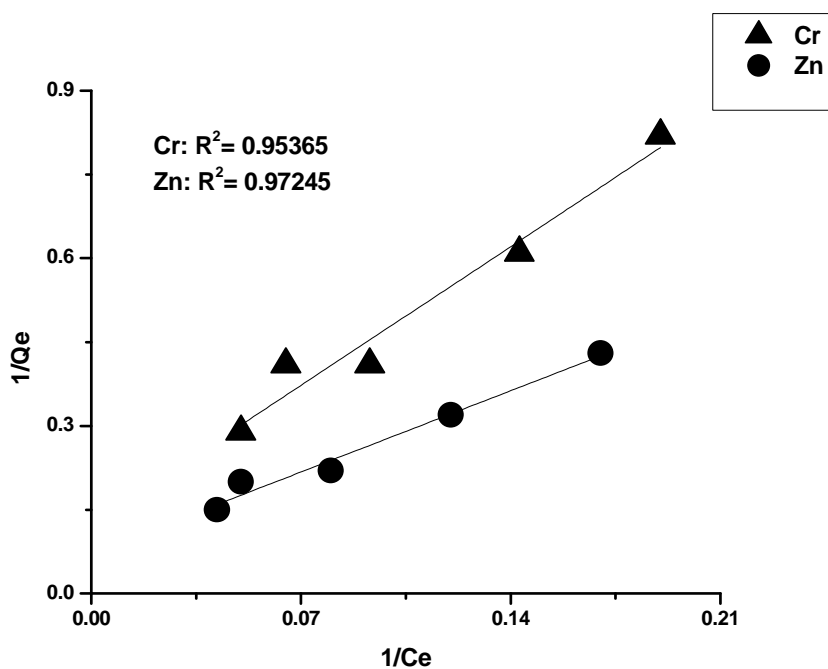| Metal ion	Langmuir parameters			Freundlich parameters		
	Q_m(mg/g)	K(mg/L)	R^2	k_F	n	R^2
Cr	4.72	0.56	0.954	3.63	1.4954	0.922
Zn	3.83	0.49	0.973	2.74	1.4762	0.943

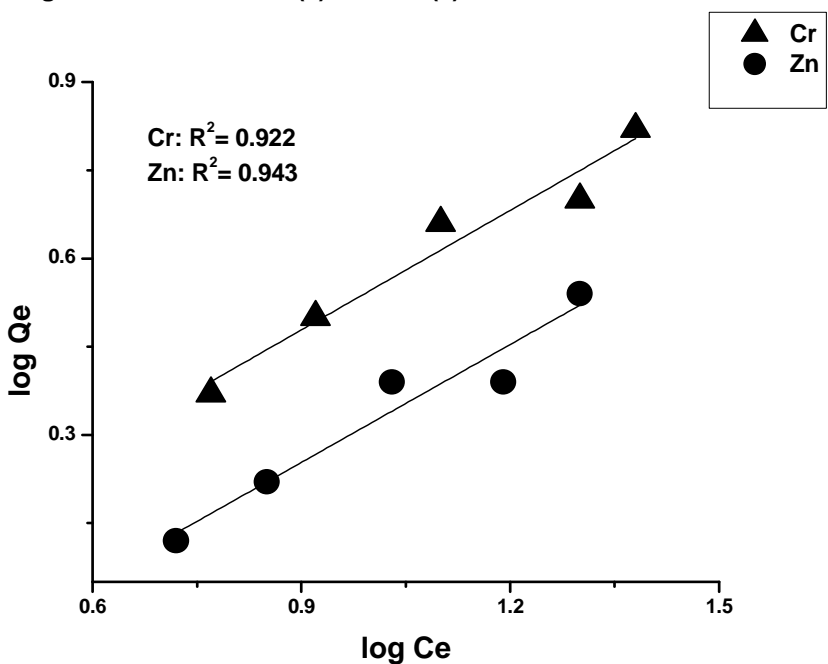**Fig. 6. Langmuir isotherm of Cr (II) and Zn (II) ions adsorbed onto PSP sorbent**

Fig. 7. Freundlich isotherm of Cr (II) and Zn (II) ions adsorbed onto PSP sorbent

3.2.2 Effect of initial pH

The pH of the metal ion solution is one of the imperative factors governing the adsorption of the metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during adsorption [14]. The adsorption characteristics of metal ions by PSP were studied at varying pH range from 2 to 9 under the precise conditions (contact time of 1 hour and 0.6 g of the

adsorbent). From Fig. 8, the least metal adsorption was observed at pH 2, and increased as pH is increasing. The maximum adsorption was more pronounced at pH 6 for the two metals with 81.24% removal for Cr and 74.23% for Zn but decreased when pH was increased. The minimum adsorption at low pH may be due to the higher concentration and high mobility of H^+ present in the solution which favours the preferential adsorption of H^+ ions rather than metal ion; the adsorbent surface being surrounded by H^+, thereby preventing the metal ions from approaching the binding sites on the adsorbent. A similar trend was observed in the removal of Pb (II) ions from industrial wastewaters using activated carbon [9].

3.2.3 Effect of contact time for the adsorption of metal ions by PSP

The relationship between contact time and heavy metal removal using PSP is shown in Fig. 9. The effect of contact time was studied at room temperature, at intervals of 20 min. From the result obtained, it is evident that the removal of metal ions increased as contact time increased. The percentage metal ions removal approached equilibrium within 120 min for both metal ion solution.

The amount of metal ions adsorbed sharply increased for 60 mins as a result of large and unrestricted available binding sites on the

samples, thereafter the adsorption slowed down as more sites were filled up within 60-100 min. The slowest adsorption occurred between 100-120 min at which equilibrium was attained after which further increase in time did not bring about any further adsorption for the metal ions. This is similar to the adsorption of metal ions on waste chinese herbs reported earlier [15].

3.2.4 Effect of adsorbent dose

The effects of adsorbent dose on the removal of metal ions ion is shown in Fig. 10. Adsorbent dose was varied between 0.2 g to 1.4 g, under the specific conditions (pH 6, initial concentration of 100 ppm and contact time of 120min). Increasing the adsorbent dose increased the percentage removal of the both metal ions until mass of the adsorbent reached 1.2 g, with maximum removal for Cr and Zn at 94.13% and 87.91% respectively after which further increase in adsorbent dose brought about no increase in adsorption.

This is an expected result because as the adsorbent dose increases, the number of adsorbent particles surrounding the metal ions or ratio of adsorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites [16,17].
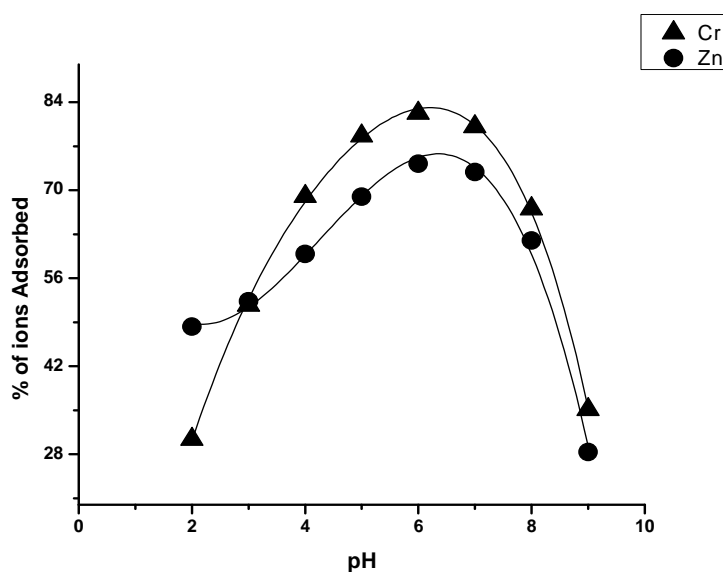

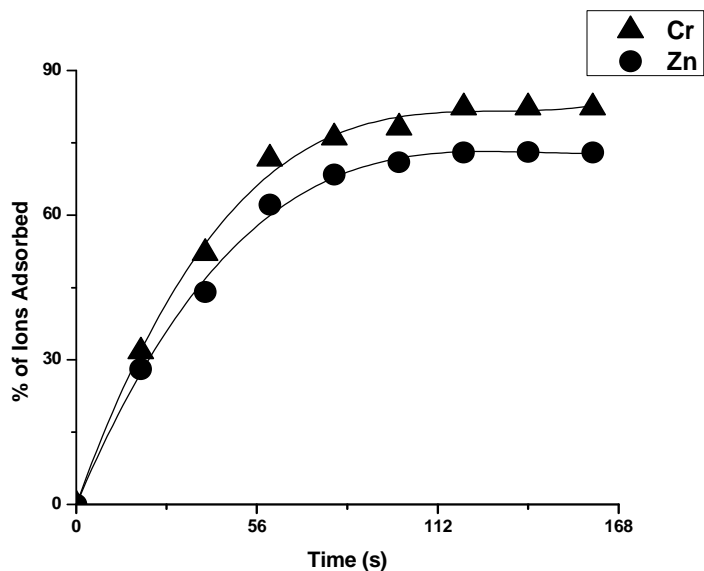**Fig. 8. Effect of pH on adsorption of metal ions by PSP**

Fig. 9. Effect of contact time for the adsorption of metal ions by PSP
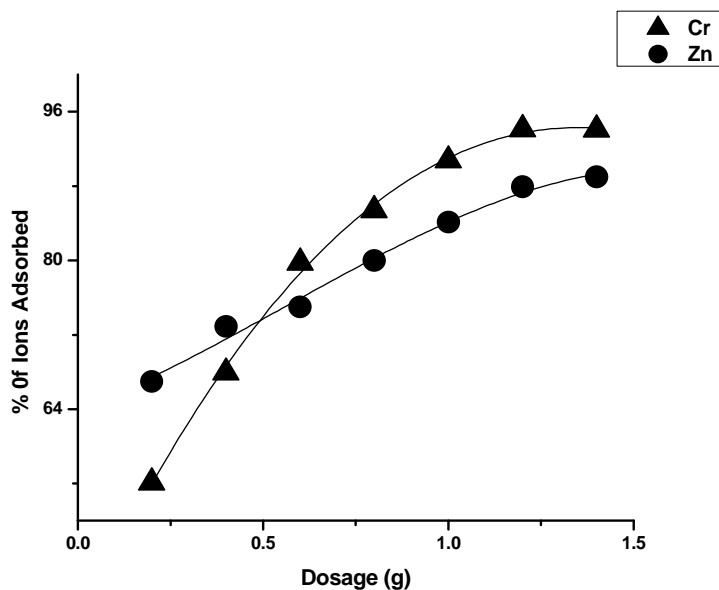

Fig. 10. Effect of amount of adsorbent for the removal of metal ions using PSP

4. CONCLUSIONS

In conclusion, a high ordered sorbent material (PSP) has been prepared from periwinkle shells through a simple chemical activation. As a result of the investigation of influence factors on the adsorption, such as the initial metal ion concentration, contact time, the pH and the dosage of sorbent material, it was found that these factors have a good promoting effect on the adsorption process. The adsorption activity increased with increase in pH value until it reaches optimum at pH 6 and then decreased. In a word, the results indicated that PSP exhibited a high recognizable capacity for both Cr abd Zn metal ions. The adsorption isotherm studies suggested that Langmuir model was more suitable for adsorption of Cr and Zn metal ions onto PSP than Freundlich model because of the higher correlation coefficients ($R^2 = 0.9537$ for Cr and $R^2 = 0.9725$ for Zn), suggesting that adsorption takes place at specific homogeneous

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sites. The adsorption of metal ion increased the PSP thermal stability, while its morphology had drastically different size and shape with porous structure after adsorption.The sorbent material described in this study has great potential for future application in extraction of metal ions or related compounds from organic media both at the academic and industrial settings.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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