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Removal of Heavy Metals from Aqueous Solutions using Snail Shell Powder as available Adsorbent

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ABSTRACT

This study focused on the heavy metals adsorption capability of snail shell (*Helix aspersa*) powder as a technique for treating heavy metals polluted water. Cadmium (II) and Iron (II) salts were used to prepare the synthetic wastewater of which their adsorption on the snail shell powder was investigated as a function of pH, contact time, snail shell powder dosage and agitation speed in order to establish the physical conditions for optimum adsorption. The initial and after-adsorption concentrations of the metals were determined using Atomic Absorption Spectroscopy, AAS (Varian SpectraAA600). The study on pH factor showed that the adsorption is pH dependent as optimum result was recorded circa pH 7 at 25^{0}C. It also showed that the adsorption depends on duration as maximum adsorption of 93% and 71.9% for Cd(II) and Fe(II) respectively were obtained with increased contact time of the process. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherms models; the correlation factors for Freundlich are 0.9425 and 0.9402, while the Langmuir correlation factors are 0.9668 and 0.954, for cadmium and iron respectively. The study further showed that an increase of snail shell powder results in increase of adsorption just as 99% removal efficiency was achieved at agitation speed of 150 – 180 rpm. These results indicate that snail shell, a waste material; have good potential as an adsorbent to remove heavy metal like Cd (II) and Fe (II) from industrial wastewater.

Keywords: *Snail shell, Cadmium, Iron, Adsorption.*

1. INTRODUCTION

Excessive release of heavy metals into the environment through industrial effluents and urbanization has posed a great problem worldwide and removal of such pollutants has been a great concern in the last few decades. Unlike organic pollutants, heavy metals are non- biodegradable and thus, undergo bioaccumulation in organisms resulting numerous diseases and disorder such as high blood pressure, anemia, lead poisoning, coma and host of others as documented by Yu (2005).
Conventional methods for removing heavy metals from aqueous solutions include chemical precipitation, ion exchange (Gode and Pehlivan, 2006), adsorption (Sari and et al, 2007), sedimentation (Song et al; 2004), electrochemical processes (Falim et al; 2006), coagulation/flocculation (Lai and Lin, 2003), filtration and membrane processes (Fabiani et al, 1996) and solvent extraction (Macchi et al; 1991).

Among them, adsorption method proves simple and cost-effective in both energy requirement and environmental friendliness thus has caught the attention of researchers. Last decade witnessed a growing knowledge in the subject as researchers directed effort to finding low-cost, readily available but efficient adsorbents. Consequent upon that, most natural adsorbents have deeply studied. Agricultural wastes, *inter alia*, were mostly considered as follow: tea waste and coffee (Orhan and Buyukgungor, 1993); hazelnut straws, Peanut hull, saw dusts Lusk (Babarinde; 2002); corncobs and apple wastes (Maranon and Sastre, 1991); wool fibers, tea leaves banana, orange peels, papaya wood, maize leaf powder (Hanafali et al; 2007); grape stalk wastes and different agricultural by-products (Pehlivan et al; 2006). The above highlighted reports tend to suggest that adsorption, which utilizes plants and animals remains (agricultural waste) in their natural or preconditioned form as adsorbents, is a promissory technique for the treatment of heavy metals polluted water; especially adsorbents derived from lingno cellulosic material (Coelho et al; 2007).

While adsorption technique has demonstrated significant potential in the laboratory, its technological application in the industry remains a challenge owing to some technical issues not yet addressed. These issues include the versatility and robustness, ease of regeneration in a continuous process line under time constraint, requiring minimum energy and retaining its known eco-friendly characteristics. However, a good number of adsorbents like activated carbon have been deployed in large scale to treat wastewaters particularly organic constituents and decolourisation of water.(Babel, S and Kurniawan, T.A.2003).

In line with the quest to discover a cheap and readily available adsorbent, this study attempts to investigate the capability of snail shell, which till now remains unutilized, as an adsorbent for heavy metal removal from wastewater and to establish the conditions for optimum result.

2. MATERIALS AND METHODS

Apparatus: Measuring cylinder (1000mL), Drying Ovens, Funnel, Spatula, Dropper, 250ml Erlenmeyer Flask, 100mL

Conical Flask, 120ml amber glass wide mouth jar PVC gloves, pH Meter (EUTECH pH510), orbital shaker (Stuart SSLI), AAS (Varian spectraAA.600),Whatman 0.45µm filter paper, mechanical sieve and analytical balance.

Reagents and Materials: All the chemicals and reagents used in this study were of analytical reagent grade, essentially as specified by the committee on Analytical Reagents of the American Chemical Society. They included HNO_3 (AR) – Riedel-deHaën, Germany; H_2SO_4 (AR) – Rochelle Chemicals, SA; NaOH, Cadmium acetate and Iron (II) ammonium sulfate, (R&M marketing Essex U.K).

Preparation of the Adsorbent (Snail Shell Powder): Snail shell was collected from dump site, and was washed carefully first with tap water and then de-ionized water to remove particulate material from their surface. Thereafter was dried in oven at 100˚C for 24hrs before pulverizing to powder form and sieved with the aid of a mechanical sieve.

Preparation of Synthetic Wastewater: A 1000mg/L stock solutions of Cadmium acetate and Iron (II) ammonium sulphate respectively were prepared in de-ionised water containing 1% HNO_3. This was further diluted accordingly to obtain the working synthetic wastewater.

Quality Control: The distilled water was digested and analyzed with every sample group to track any possible contamination source and obtain a baseline values. A duplicate analysis was carried out for every sample to track experimental error and show reproducibility.

Adsorption Experiments: After each adsorption, the residual Cd and Fe were determined by digesting the filtered synthetic wastewater followed by AAS analysis as a standard method. The percentage and capacity adsorption of snail shell powder were estimated using the following equations:

$$\% = \frac{(Co - Ce)}{Co} \quad \ldots\ldots (1)$$

$$\frac{X}{M} = \frac{\mathbf{V}\,(Co - Ce)}{m} \quad \ldots.. (2)$$

Where,

V = Volume of solution (mL).
M = mass of adsorbent (mg).
Co = Initial metal Concentration.
Ce = Final metal Concentration at equilibrium (mg/L).
$\frac{X}{M}$ = The adsorbate Concentration/adsorption Capacity of Snail shell powder (mg/g).

Determination of Optimum pH for Adsorption

A mixed solution of Cd (II) and Iron (II) solutions with concentration of 50mg/L respectively was prepared from the stock solutions. Samples of 25mL from the mixed solution were poured into five 100mL conical flasks labeled A - E. The pH in each flask was varied in the range of 3 to 9. Thereafter, 50mg of snail shell powder was added to each flask. After 1 hour 15 minutes of agitation with orbital shaker at 25˚C and speed of 150rpm, an aliquot was taken for Cd and Fe analysis using the aforementioned standard method.

Study of Adsorption Isotherms

Five mixed solutions with concentrations 50mg/L, 75mg/L, 100mg/L, 125mg/L and 150mg/L of Cd and Fe were made by proper dilution of stock solution of. The pH was adjusted and maintained at 7 throughout the experiment. 25mL of the prepared samples was poured into five conical flasks. 50mg of adsorbent was introduced to each conical flask and was agitated for 1 hour 15 minute. Thereafter the concentration of Cd and Fe was determined and noted.

Determination of Optimum Contact Time

To determine the optimum contact time, 50mg of snail shell powder was added to 5 different conical flasks containing 25ml of 50mg/L of the metals at pH value of 7 and then agitated at 150 rpm. An aliquot was withdrawn from each flask at a time for Cd and Fe determination in every 15 minutes interval.

Effect of Adsorbent Dosage

The effect of absorbent dosage on the equilibrium uptake of Cadmium and Iron ions were determined by adding 25mg, 50mg, 75mg, 100mg and 125mg to five conical flasks respectively containing 25ml of the 50mg/L mixed solution. The flasks were shaken at 150rpm and 25˚c for 1 hour 15 minute.

Effect of Agitation Speed

To determine the effect of agitation speed, 50mg of snail shell power was added to five conical flasks containing 25mL of prepared sample with known metal concentrations of 50mg/L and pH of 7. The agitation speed was set at 50, 100, 120, 150 and 180rpm respectively for each flask at 25˚C orbital shaker for 1hour 15 minutes. Thereafter, an aliquot was taken for AAS analysis.

3. RESULTS AND DISCUSSION

Effect of Optimum pH

The adsorption capability of the snail shell adsorbent was observed to be influenced by pH change. At pH 4, adsorption percentage was 80% of Cd (II) and 75% of Fe (II) and rose to about 96% of Cd (II) and 89% of Fe (II) at pH 7.Further increase in pH above 7 resulted a decline in adsorptions of Cd (II) and Fe (II) as shown in figure 1. This adsorption trend is consistent with that observed by Olayinka et al (2009). The result revealed that adsorption efficiency of snail shell powder is optimum at about pH 7.

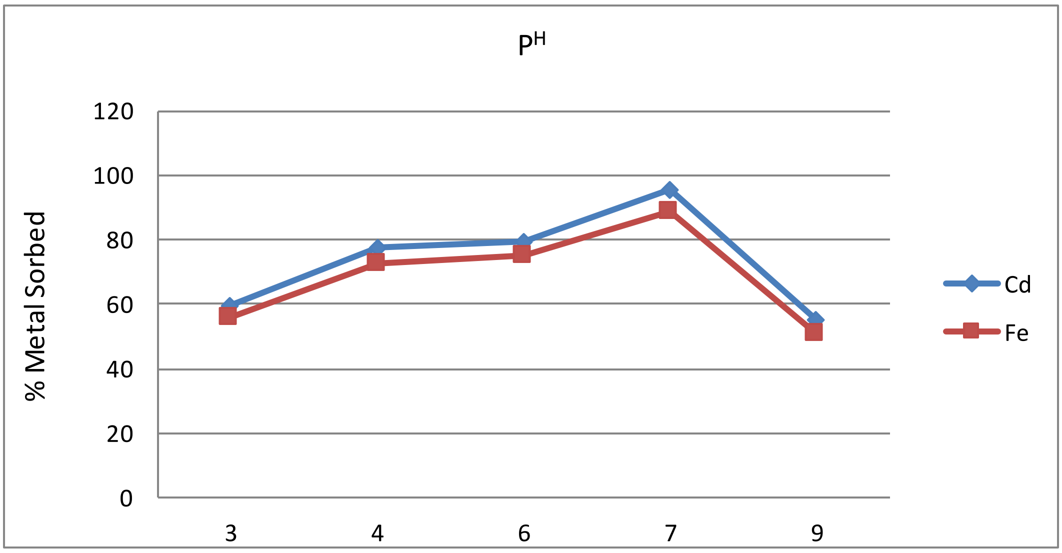

Figure1: Effect of pH for % removal of Cadmium (II) and Iron (II)

Low adsorption of the metal ions at higher pH values could be attributed to the formation of their hydroxides which form precipitates and inhibit further adsorption as revealed by Lisa *et al*.(2004) and Xiao and Ju-Chang(2009).

Effect of Contact Time on Adsorption of the Metal Ions

The contact time profile for the adsorption of Cadmium and Iron is shown in figure 2. The result clearly showed that adsorption efficiency increases with contact time. Cadmium removal progressed with time as 55.3%, 59.0%, 60.7%, 62.3 and 93% percentage adsorption was achieved with 15, 30, 45, 60 and 75 minutes respectively. Similarly, percentage adsorption of Iron with respect to contact time was 50.5%, 55.0%, 56.3%, 58.7 and 71.9% for the time lapse of 15, 30, 45, 60 and 75 minutes. This showed that adsorption is a function of contact time; it increases with contact time but it is expected to level up despite longer duration due to adsorption–desorption equilibrium soon established in the process (Metcalf and Eddy; 1991).

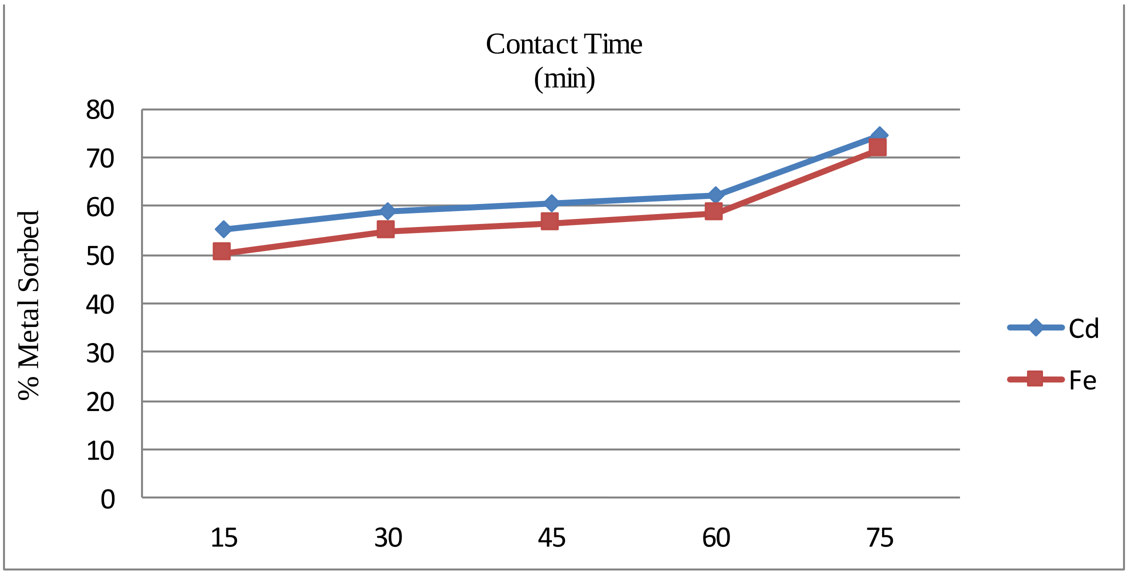

Figure 2: Time required by snail shell powder to remove cadmium (II) and Iron (II) from synthetic waste water.

Equilibrium Study and Adsorption Isotherms

The equilibrium study has been conducted based on the commonly used monolayer and multilayer adsorption isotherm models of Langmuir and Freundlich. To examine the relationship between Sorbed (x/m) and aqueous concentrations (Ce) at equilibrium, sorption isotherm models are widely employed test the data.

The equilibrium data obtained from this study were tested to follow Langmuir and Freundlich models as shown by the plots of Ce/(x/m) against Ce for Langmuir isotherm and Log x/m against Log Ce for Freundlich isotherm (figure 3, 4 and 5, 6 respectively). The sorption affinity (n) of cadmium and iron was found to be 1.96 and 1.76 respectively which implies effective adsorption. The maximum adsorption capacity and sorption affinity for cadmium is greater than that for Iron. And this can be linked to the greater affinity of the active sites for cadmium. According to Kadirvelu *et al*. (2001), the essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (R_L), defined by:

$$R = \frac{1}{1+K_f Ce}$$

Where K_f is the Langmuir constant and Ce is the final concentration of metal ion. Langmuir isotherm is irreversible when $R_L= 0$, favourable when $0<R_L<1$ and linear when $R_L=1$ while $R_L>1$ indicates unfavourable. And in this case, Langmuir isotherm is favourable as R_L is 0.966 and 0.954 for Cd and Fe respectively as shown in figure 3, 4; 5, 6 and Table 3.

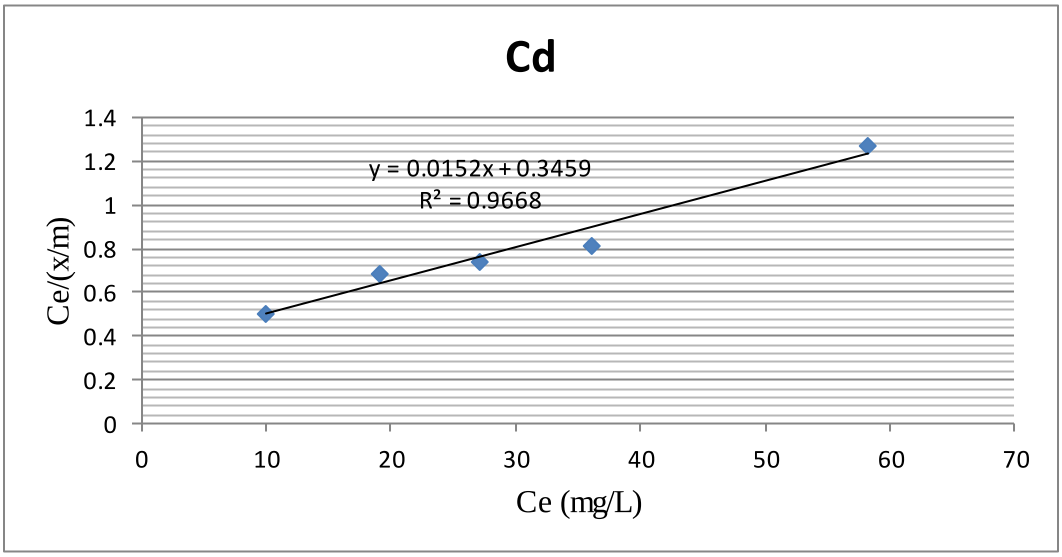

Figure 3: Show Langmuir isotherm for Cd removal by snail shell powder, for pH = 7.

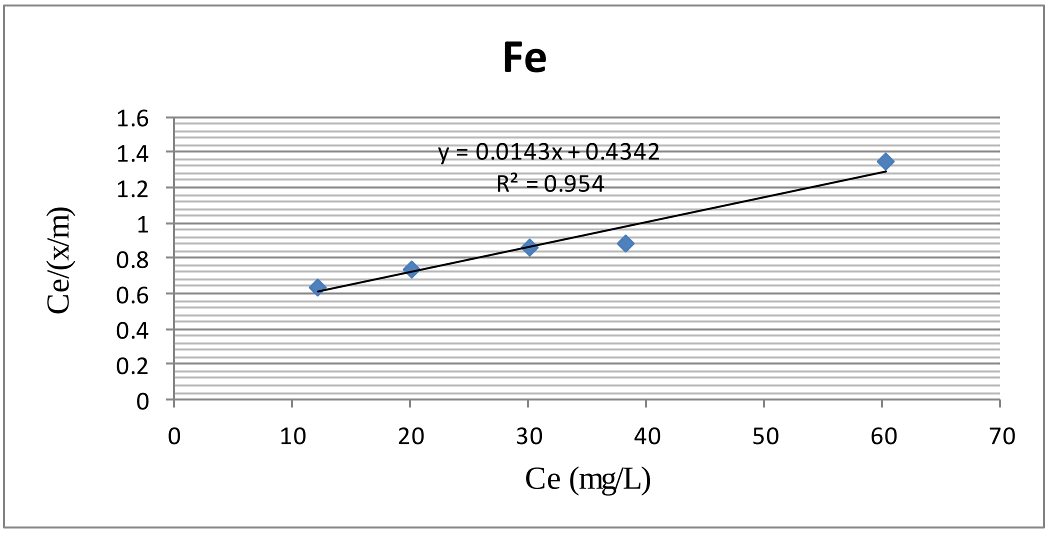

Figure 4: Show Langmuir isotherm for Iron removal by snail shell powder, for pH =7.

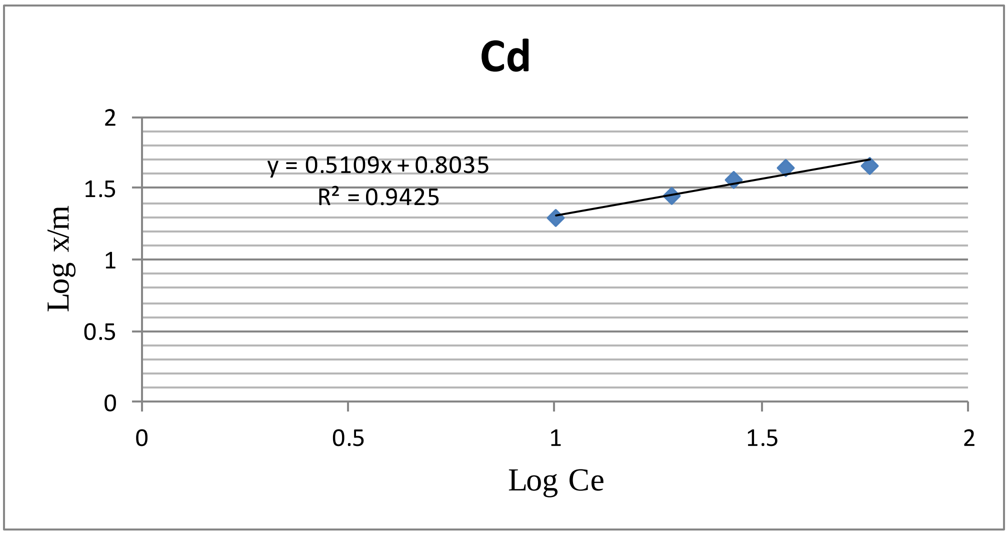

Figure 5: Show Freundlich isotherm for Cd removal by snail shell powder, for pH = 7.

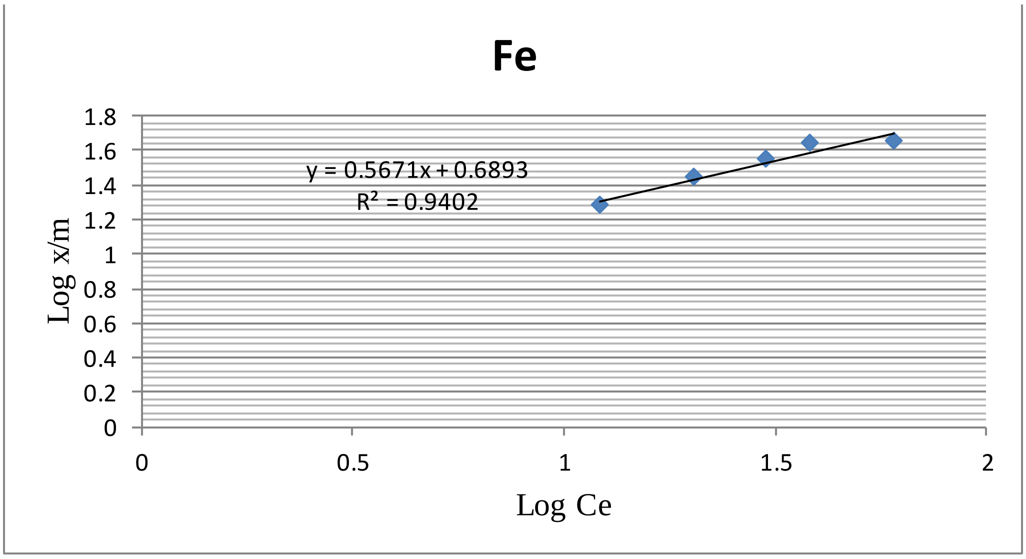

Figure 6: Show Freundlich isotherm for Iron removal by snail shell powder, for pH = 7.

Table 3: Parameters for Langmuir and Freundlich Adsorption Models

Metals	**Parameters of the Langmuir model**			**Parameters of the Freundlich model**		
	a_{max}(mg/g)	b (1/mg)	R^2	K_f	1/n	R^2
Cadmium	65.79	0.044	0.97	6.36	0.51	0.94
Iron	69.93	0.033	0.95	4.89	0.57	0.94

Effect of Adsorbent Dosage

This was done by varying the adsorbent dosage from 25mg to 125mg while keeping other physical parameters constant. The graph in figure 7 shows an increase in the percentage adsorption as dosage of adsorbent increases. This is attributed to the increased binding sites and surface area brought about by the increase in dosage.

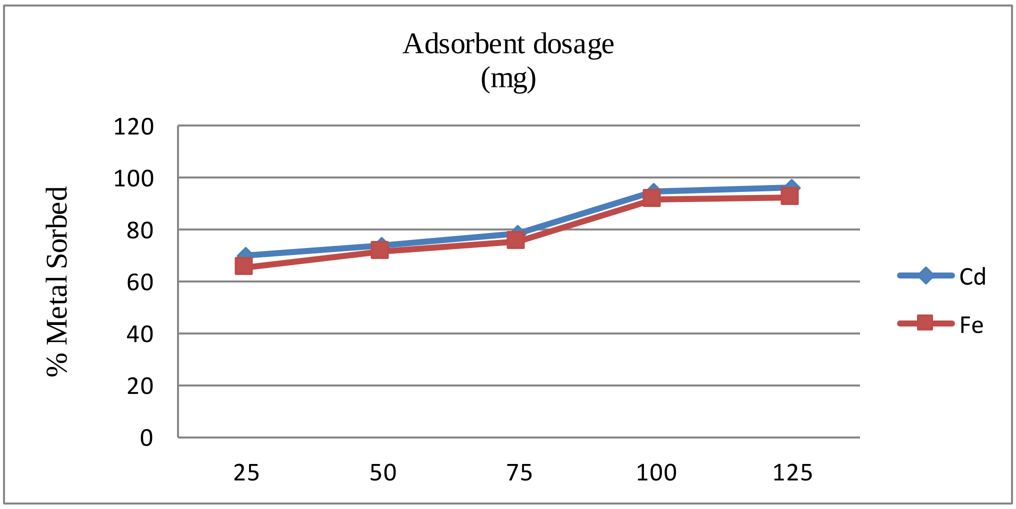

Figure 7: Effect of adsorbent dosage for the removal cadmium (II) and iron (II) from synthetic waste water.

Effect of Agitation Speed

The effect of agitation speed on removal efficiency was examined under constant optimum dose of adsorbents and optimum pH and the result presented in Figure 8.The result proved Cd and Fe removal efficiency increase with increasing agitation speed. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of Cd and Fe ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 150-180 rpm sufficiently ensure that all the binding sites are made readily available for Cd and Fe uptake. The effect of external film diffusion on adsorption rate can also be assumed but not significant.

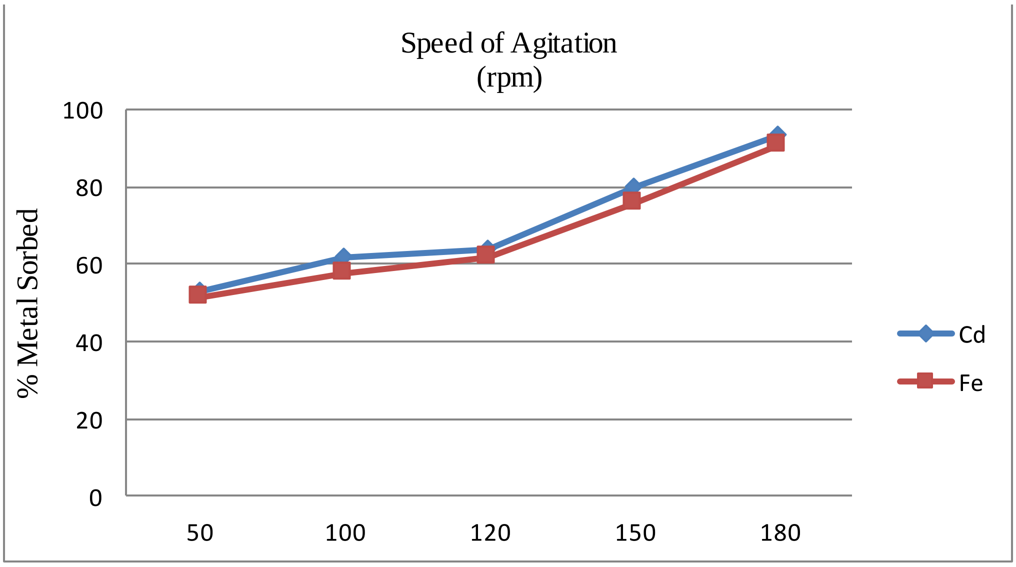

Figure 8: Effect of agitation speed on the adsorption of Cd and Fe by Snail Shell Powder.

4. CONCLUSIONS

On optimizing all the conditions studied in this work, it was discovered that snail shell powder can compete favorably well with known commercial adsorbents such as activated carbon and zeolite. The percentage removal of the ions was found to be 98.3% for Cd (II) and 98.9 for Fe (II) respectively using 125mg of the adsorbent with pH of 7, contact time of 75 minutes or more and agitation speed in the range of 150 – 180rpm.

When subjected to further adsorption isotherm analysis usingLangmuir and Freundlich models, the sorption affinity (n) calculated proved that snail shell adsorption is effective and is supported by the values of separation factor, R_L which fell between 0 and 1 to indicate favourable adsorption.

The result is not only important for industries but also to the planet earth in general due to the resultant social and environmental benefits. This study has, therefore, shown that instead of chemicals, nonhazardous agro-waste materials like snail shell can be used as heavy metal adsorbent to treat wastewaters and industrial effluents without putting the environment in danger.

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