Sorption Kinetics and Intraparticle Diffusivities of Cd (II) and Fe (III) Ions on Unmodified Snail Shell Powder

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Abstract: Sorption kinetics of Cd (II) and Fe (III) ions in aqueous solution by unmodified snail shell powder was carried out through time dependent studies. Maximum percent adsorption capacity of the metal ions based on contact time was found to be 62.3% and 58.74% for Cd and Fe respectively at 60 minutes. The kinetic behaviour of the metal ions towards the adsorbent was studied with seven kinetic and diffusion models: pseudo-first order and pseudo-second order, mass transfer kinetics, intraparticle diffusion (external film, particle diffusion and penetrant transport). The pseudo first order rate constants k_1 (g/mg min) were determined to be 2.203×10^{-3}, for both Cd (II) and Fe (III). The pseudo-second order rate constant, k_2 for Cd and Fe (III) were found to be 2.256×10^{-2} and 2.792×10^{-1} g/mg min respectively. Sorption capacities based on the pseudo-first order model were found to be 4.7315mg/g and 6.4565mg/g for Cd (II) and Fe (III) respectively. Pseudo-second order sorption capacities for Cd (II) and Fe (III) were 5.3763 and 4.9261 respectively. Correlation coefficient R^2, for Cd (II) and Fe (III) were greater than 0.99 for pseudo-second and greater than 0.95 for the pseudo-first order. All diffusion models used correlated well over 0.94 with a maximum of 0.9917 for the penetrant transport model for Cd (II) ion.

Keywords: Adsorption, Pseudo-First and Pseudo-Second Order, Mass Transfer Kinetics, Intraparticle Diffusion

1. Introduction

One of the impurities in water is the heavy metals from sewage and industrial waste water (Rattan, 2012). Heavy metals in water constitute a part of inorganic pollutants of water or the aqueous phase. Heavy metals in the aqueous phase have been known to be toxic for decades. They constitute a threat to environmental health because of their lethal effects on marine and aquatic organisms as well as humans. Cadmium for instance is a nephrotoxic metal, cancerous and hypertensive agent (Hanafiah *et al*., 2007). Discourses and research interest have centred mostly on removal, recovery and remediation of heavy metals from the aqueous phase. Practical approaches or methods have been utilized over the years for removal or recovery, however, they are not without setbacks .These setbacks have been one of the prompts to further researches in the recovery, removal or remediation of heavy metals especially from the aqueous media. To this end, agricultural and agro-based waste and other low cost plant materials have been extensively utilized in adsorption or biosorption of heavy metals. Batch and column processes have been applied for recovery or removal, and both have proved to have high adsorption efficiency and kinetics. Agricultural materials which have been used for adsorption research include: cassava waste (Abia *et al*., 2003) maize cob and husk (Abia and Igwe, 2003), fluted pumpkin waste (Horsfall and Spiff, 2005), nipah palm shoot (Wankasi *et al*., 2006) and many others which are not captured here.

The extent to which metal ions will adsorb on the surface of an adsorbent depends among other factors on the rate of transfer of the metal ions from the bulk fluid phase to the adsorbent surface. The attainment of equilibrium also depends on the rate of diffusion of the adsorbate from the bulk fluid phase. These are the reasons the kinetics of the process becomes important in the treatment of adsorption. Rate studies of adsorption are important in obtaining the optimal sorption conditions and the best adsorbate transfer dynamics for the process (Abasi *et al*., 2012). Kinetic models have been developed over the years to explain the dynamics of adsorption. These include the first – order and second – order rate equations. The rate of transfer of adsorbates from the solution to the adsorbent is dependent on some other solution processes as bulk diffusion, film diffusion, chemical reaction and intraparticle diffusion (Ho *et al*., 2000). Therefore, rate transfer models are useful in explaining the controlling transfer dynamics of a particular adsorption process.

This paper presents the kinetic properties and the intraparticle diffussivities of the adsorption of Fe (III) and Cd (II) on unmodified snail shell powder.

2. Materials and Methods

Adsorbent Preparation

Snail shells were collected from a dump site in Amassoma in the south-south region of Nigeria. They were first washed in tap water and then in distilled water. They were then dried in the oven at 100°C for 24 hours. The oven-dried sample was ground and sieved through a mechanical sieve.

Adsorbate / Instruments

Aqueous solution of cadmium and iron were prepared in the laboratory from analytical grade cadmium acetate and iron (II) ammonium sulphate (R & M marketing, Essex). Other reagents used for work included HNO_3 (AR-) Riedel-de-Hen,Germany; H_2SO_4 (AR)- Rochelle Chemicals, SA and NaOH-(R & M marketing, Essex). All polyethylene sample bottles were washed with liquid detergents and rinsed with distilled water. Agitation of solutions was carried out with Barnstead/Labline, UK,

maxQ 2000 Orbital shaker (20-500 rpm). Centrifuging work was done with B. Bran Scientific & Instument Co., UK, 80-1 Electric Centrifuge. Analysis of filtrate was done with Unicam photon atomic absorption spectrophotometer.

Experimental Procedure

Stock solutions of 1000mg/L of Cadmium and Iron were prepared from Cadmium acetate and Iron (II) ammonium sulphate respectively in deionised water.

A working concentration of 50mg/L was prepared from the stock and used for a series of batch adsorption for both metal ions with respect to the contact time of 15,30,45 and 60 minutes . A volume of 25mL from the working solution was added to 50mg of the snail shell powder and shaken in an orbital shaker at 150 rpm for the times indicated.

The mixtures were filtered to obtain the filtrates which were stored in plastic bottles and further analyzed for metal ion concentration in atomic absorption spectrophotometer.

3. Results and Discussion

Sorption Capacity

The effect of contact time required for maximum adsorption of metal ions by Snail shell powder is represented in **figure 1.** The percent adsorbed against time is shown in **figure 2**. Maximum adsorption for all the two metal ions was attained after 60 minutes. The time curve increased steadily from the starting batch up to that at 60 minutes. The sorption efficiency increased with rise in contact time up to 60 minutes. The steady rise in adsorption indicates the availability of adsorption sites on the adsorbent. This continuity indicates the formation of a monolayer on the outer interface of the adsorbent (Karhikeyan *et al*., 2005). It has been observed by previous workers (Ho *et al*., 1995; Gardea-Torresday *et al*., 1998) that a short contact time necessary to reach equilibrium in adsorption studies indicates that the predominant mechanism is chemisorption.

From **figures 1** and **2**, the order of adsorption is Cd > Fe. The percent adsorption for all the contact times is higher for Cd which indicates that its rate of transfer and adsorption was higher than the Fe(III) ions. The results also show a differentiated adsorption of the metal ions. Differentiated adsorption of metal ions from aqueous solutions has been ascribed to some factors (Ho *et al*., 1995): (i) sizes of metal ions (ii) affinity of the metal ions for some active groups on the biomass and (iii) nature of anions of the salt of the metals. Of these three factors, the third one, that is, the anions of the salt of the metals may have taken precedence over the rest. As reported by Abasi *et al*., (2011), the anions of the metal ions played more significant role in the extent of the adsorption than other influencing factors. The basic strength of the anion SO_4^{2-} is less than NO_3^-. As expected SO_4^{2-} has a higher tendency to remain in solution than NO_3^-. Therefore, the rate of adsorption of Cd^{2+} is higher than Fe^{3+} though the size of Fe^{3+} (0.64Å) is less than Cd^{2+} (0.97Å).

The kinetic study was performed based on pseudo first order, pseudo-second order, Elovich and intraparticle diffusion equations. The data indicated that the adsorption kinetics followed the pseudo-second order and the Elovich rate equations with Intraparticle diffusion (penetrant transport) as one of the rate determining steps**.** Pseudo-first order rate model was applied using the Lagergren's equation (Lagergren in Abia et al., 2007) given as (1)

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

The pseudo-second order rate model (Ho *et al*. 1995), took the form of equation 2:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where qt is the amount of metal ion adsorbed on the biomass surface (mg/g) at time, t, qe is the amount of metal ion adsorbed at equilibrium (mg/g). k_1 and k_2 are pseudo-first and-second order rate constants respectively.

Another kinetic model used in data analysis is the Elovich equation, which is simplified (Chien and Clayton 1980) as equation 3:

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln\left(t\right) \qquad (3)$$

where α is the initial adsorption rate (mg/g-min), β is the desorption rate constant (g/mg) during one experiment. The plot for Elovich equation is shown in **figure 6**.

The linearised mass transfer equation (Qadeer and Akhtar, 2005) is generally expressed as equation 4:

$$\ln(C_0 - C_t) = \ln D + K_0 t \qquad (4)$$

Where C_o is the initial metal ion concentration (mg.dm^{-3}), C_t is the metal ion concentration at time t, t is the shaking time (mins), D is a fitting parameter, K_o is the adsorption constant.

Three equations for intraparticle diffusivity in respect of external film diffusion, particle diffusion, and percent adsorbed (penetrant transport) were applied to the data. The intraparticle diffusivity for particle diffusion mechanism was estimated using the linear driving force concept equation (Vinod and Anirudhan 2002) in which the fractional attainment to equilibrium (FATE) factor α is used.

This is given by equation 3.

$$\ln\left(1-\alpha\right) = -k_p t \qquad (5)$$

where,

$$\alpha = \left[M\right]_t^{n+} / \left[M\right]_\infty^{n+} \qquad (6)$$

kp is the rate constant for intraparticle diffusivity and t is the time in minutes, $\left[M\right]_t^{n+}$ is the amount of metal ion of charge n+ adsorbed at time t and $\left[M\right]_\infty^{n+}$ is the amount of metal ions of charge n+ adsorbed at infinity or equilibrium. Intraparticle diffusivity for particle diffusion for all the metal ions from this equation is shown in **figure 8**

The intraparticle diffusion by external film diffusion mechanism was tested using equation 7 (McKay and Poots, 1980). This equation is given as:

$$q_t = X_i + K_i t^{\frac{1}{2}}$$

$$(7)$$

where q_t is the amount adsorbed at time t, X_i is the boundary layer thickness and K_i is the initial rate constant of adsorption. The plot of this e quation is shown in **figure 7**

Intraparticle diffusivity (penetrant transport) applied to the data is that expressed as equation 8 (Weber and Morris, 1963; Srivastava et al., 1989):

$$R = K_{id}(t)^a \qquad (8)$$

This is linearised to equation (14) as

$$\log R = \log K_{id} + a \log(t) \qquad (9)$$

where R is the percent metal ion adsorbed, t is the contact time in minutes, a is constant that depicts the adsorption mechanism. The plot of this model is shown in **figure 5.**

The plots of the kinetic and diffusion models applied to data are shown in figures **3** to **9**. Adsorption data fitted well to almost all models applied, as correlation coefficients were all greater than 0.94. For the kinetic plots, the Elovich and pseudo-second order were the best correlated at 0.9985 for Cd^{2+} and Fe^{3+} respectively. The pseudo-second order was also highly correlated for Cd^{2+} at 0.9917. All the diffusion models applied were also well correlated to the adsorption data with a penetrant transport maximum at 0.9973 for Cd^{2+} ions. This implies that the dominant rate limiting mechanisms for the sorption were the pseudo-second order, Elovich and penetrant transport models.
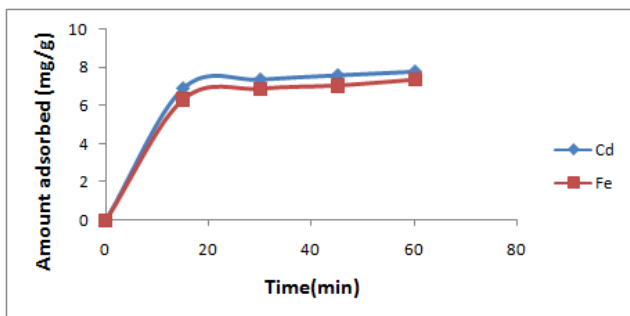

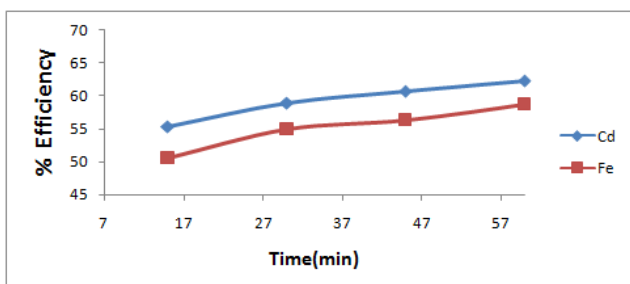**Figure 1:** Effect of contact time on adsorption of Cd (II) and Fe (III) ions by unmodified snail shell powder

Figure 2: Percent Efficiency of adsorption of Cd (II) and Fe (III) ions with contact time
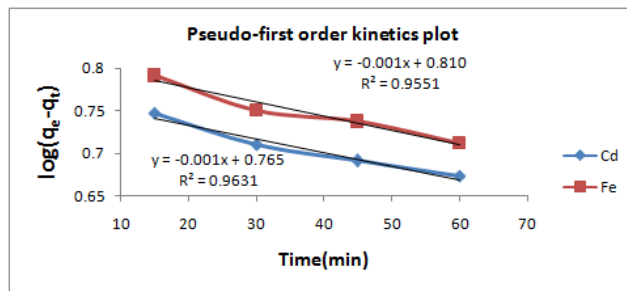

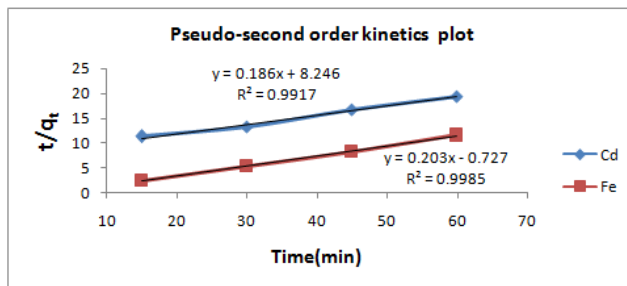**Figure 3:** Pseudo- first order rate plot for Cd (II) and Fe (III) ions adsorption on unmodified snail powder

Figure 4: Pseudo-second order rate plot for Cd (II) and Fe (III) ions adsorption on unmodified snail shell powder
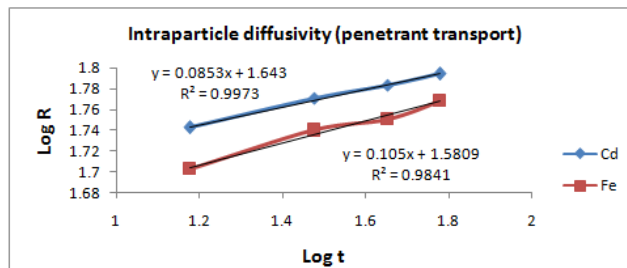

Figure 5: Intraparticle diffusivity (penetrant transport) plot for Cd (II) and Fe (III) ions adsorption on unmodified snail shell powder
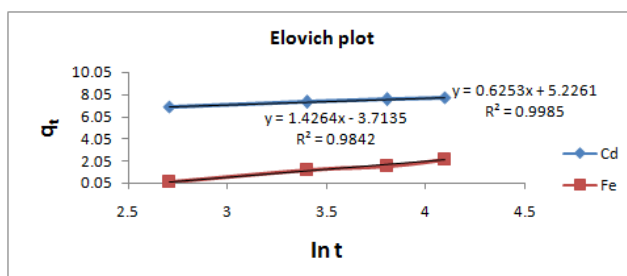

Figure 6: Elovich plot for Cd (II) and Fe (III) ions adsorption on unmodified snail shell powder
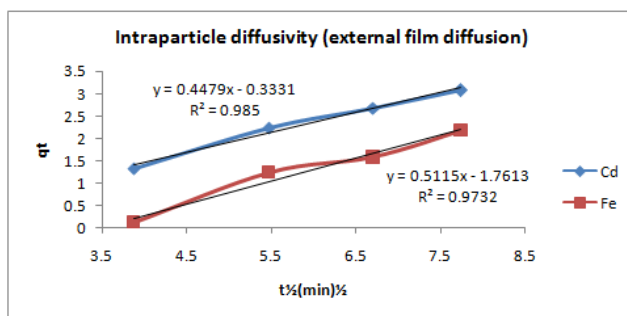

Figure 7: Intraparticle diffusivity (external film diffusion) plot for Cd (II) and Fe (III) ions adsorption on unmodified snail shell powder
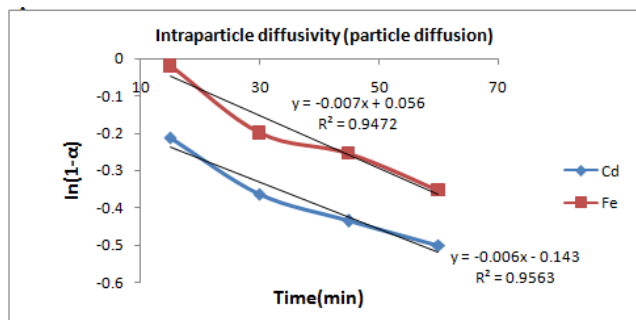
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Figure 8: Intraparticle diffusivity (particle diffusion) plot for Cd (II) and Fe (III) ions adsorption on unmodified snail shell powder
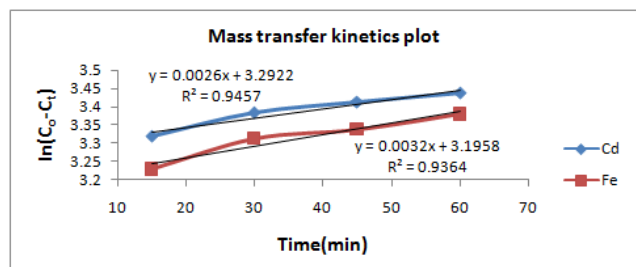

Figure 9: Mass transfer kinetics plot for Cd (II) and Fe(III) ions adsorption on unmodified snail shell powder

Table 1: Kinetics and diffusion parameters of adsorption of on unmodified snail shell powder

Type	Parameters	Metal ion	
		Cd^{2+}	Fe^{3+}
Pseudo -1ST Order	q_e (mg/g)	4.7315	6.4565
	K_1	2.203×10^{-3}	2.203×10^{-3}
	R^2	**0.9631**	**0.9551**
Pseudo -2ND Order	q_e (mg/g)	5.3763	4.9261
	K_2	2.256×10^{-2}	-2.792×10^{-1}
	R^2	**0.9917**	**0.9985**
Elovich	α	2665.9	9.4716
	β	1.5992	0.7011
	R^2	**0.9985**	**0.9842**
Mass transfer	D	26.902	24.4297
	K_0	2.6×10^{-3}	3.2×10^{-3}
	R^2	**0.9457**	**0.9364**
Intraparticle Diffusion (External film)	K_i	0.4479	0.5115
	X_i	-0.3331	-1.7613
	R^2	**0.9732**	**0.9732**
Intraparticle Diffusion (particle diffusion)	K_P	0.007	0.006
	R^2	**0.9472**	**0.9563**
Intraparticle Diffusion (Penetrant transport)	a	0.0853	0.105
	k_{id}	1.643	1.5809
	R^2	**0.9973**	**0.9841**

4. Conclusion

A total of seven kinetic and diffusion models were applied to the adsorption data to determine the controlling kinetics and the rate limiting mechanism. The correlation coefficients(R^2 = 0.9985) of the plots of equations applied showed that the pseudo-second order and the Elovich models were the most fitting for the description of Fe^{3+} and Cd^{2+} ions transport from the bulk solution onto the surface of the adsorbents respectively . These models were

therefore, the controlling kinetics of the sorption. The intraparticle diffusion (percent adsorbed) plot with the highest correlation coefficient (R^2 = 0.9985) confirmed that the rate limiting diffusion process was penetrant transport or pore diffusion.

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