

Adsorption of Ni(II) and Zn(II) ions onto Activated Carbon derived from Agricultural Waste.

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Abstract: The adsorption of Ni²⁺ and Zn²⁺ ions from aqueous solutions by batch process onto activated carbon prepared from palm kernel shell was studied. The influence of contact time was experimentally verified. Optimum adsorption of 85.61% and 79.34% were obtained for Ni²⁺ and Zn²⁺ ions. Three kinetic models: pseudo first-order, pseudo second-order and elovich models were used to analyse the adsorption process. Sum of square of error was also calculated to compare the fitness of pseudo first-order and pseudo second-order kinetics. Results showed that the adsorption mechanism in the sorbate/adsorbent system follow a pseudo second-order kinetics.

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Introduction

The presence of heavy metals in the environment may be caused by air emissions from coal-burning plants, smelters and industrial facilities; dumping of industrial wastes in water ways and incineration of solid wastes on open fields. Heavy metals can also enter the environment into the environment through naturally occurring geological processes and mining activities (Ademoroti, 1996; Musah, 2010).

Heavy metals are known to pose grave health dangers to human, terrestrial and aquatic lives if their concentrations exceed the maximum permitted limits. Concentrations below these limits have potentials for long term contamination, because heavy metals are known to be accumulative within biological systems (Malakootian and Hossaini, 2008). The need for economical and effective methods of removing heavy metals from waste water has necessitated the search for unconventional materials that may be useful in the adsorption of heavy metals waste water (Akporhonor and Egwaikhide, 2007). Wastes from agricultural practices are among natural materials available in large quantities which may have potential to be used as low cost adsorbents, as they represent unused resources widely available and environmentally friendly (Abdel- Ghani *et al.*, 2007).

This paper narrates the use of activated carbon prepared from palm kernel shells (cheap and undesirable by products of kernel oil production) to remove Ni²⁺ and Zn²⁺ from aqueous solution and their adsorption kinetics

Mechanism of adsorption

Adsorption of solute to the interior surfaces of adsorbent may take four steps (Ibrahim and Hassan, 2008):

Bulk transport: The adsorbates are transported to the boundary layer of water surrounding the adsorbent particle from the bulk solution. The transport occurs by diffusion if the adsorbent is suspended in quiescent water, such as in a sedimentation basin, or by turbulent mixing, such as during turbulent flow through a packed bed of granular activated carbon (GAC), or when powdered activated carbon (PAC) is being mixed in a rapid mix or flocculator.

Film transport: Adsorbates are transported by molecular diffusion through the stationary layer of water (hydrodynamic boundary layer) that surrounds adsorbent particles when water is flowing past them. The distance of transport and thus the time of this step is determined by the rate of flow past the particle: the higher the rate of flow, the shorter the distance.

Intraparticle transport: After the adsorbates pass through the hydrodynamic boundary layer, they are transported through the adsorbent's pores to the available adsorption sites. Intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion), or by diffusion along the adsorbent surface (surface diffusion), then adsorption takes place.

Adsorption of the solute on active sites: After the adsorbates reach an available site, the adsorption bond is formed between the adsorbate and adsorbent. This step is very rapid for physical adsorption and so one of the preceding diffusion steps will control the

rate at which molecules are removed from the solution. If a chemical reaction that changes the nature of the molecules takes place during the adsorption step, this chemical reaction may be slower than the diffusion steps and thereby control the rate of compound removal.

Batch Adsorption Studies

Solutions of Ni^{2+} and Zn^{2+} were prepared by dissolving known quantities of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and ZnO was dissolved in 5mL distilled water followed by 25mL of 5M HCl then diluted to 1dm^3 (DeLloyd, 2000) and used as stock solutions. The solution was subsequently diluted (using dilution factor) to required working concentration. The batch adsorption method was used (to determine adsorption) were 0.5g of activated carbon was interacted with 10cm^3 of aqueous solution in a beaker and covered. This was allowed to stand for 60 minutes. The process was repeated for 120, 180, 240 and 300 minutes. Each mixture was filtered separately using Whatman filter paper (No.42) and filtrate was collected (Shama *et al.*, 2010). The instrument used for determining heavy metal ions from the filtrates is Atomic Absorption Spectrophotometer (Buck AAS, model 210 VGP).

The amount of metal ion adsorbed during the series of batch investigations was determined using a mass balance equation (Badmus *et al.*, 2007):

Where q is the metal uptake (mg/g); C_o and C_t are the initial and equilibrium metal concentrations in the aqueous solution sample (mg/l), respectively; v is the volume of aqueous solution sample and m is the mass of adsorbent used (g).

The percentage of ions adsorbed from aqueous solution on activated carbon was determined using the expression (Erdem *et al.*, 2004):

$$\% \text{ adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \dots \dots \dots 1$$

Where C_i and C_f are the initial and final concentrations of the metal ions in mg/l at given time t .

Kinetic Studies

Adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the adsorption in a system (Shahryari *et al.*, 2010). Adsorption kinetics was ascertained using the following models:

Pseudo First Order Equation

The model also known as Lagergren model assumes a first order adsorption kinetics and is represented by the equation below

Where:

q_e and q_t are adsorption capacity at equilibrium and at time t , respectively ($\text{mg} \cdot \text{g}^{-1}$).

K_1 is the rate constant of pseudo first order adsorption (min^{-1}).

After integration and applying the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the integrated form becomes:

The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot (Demirbas *et al.*, 2004).

Pseudo Second Order Equation

The adsorption kinetic rate equation for pseudo second order is expressed according to Ho *et al.* (2000) as:

Where:

K_2 is the rate constant of the pseudo second order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the integrated form of the equation becomes:

Equation (5) is the integrated rate law for the pseudo second-order reaction, and can be rearranged to the linear form as:

The plot of (t/q_t) and t of equation (6) should give a linear relationship from which q_e and k_2 can be

determined from the slope and intercept of the plot, respectively (Zawani *et al.*, 2009).

The applicability of both kinetic models is verified by Statistical Sum of Error (%SSE).SSE (%)

=7

Where N is number of data point (Hameed *et al.*, 2006)

The Elovich Equation

The Elovich equation is generally expressed as (Badmus *et al.*, 2007):

Where:

is the initial adsorption rate ($\text{mg.g}^{-1}.\text{min}^{-1}$)

is the desorption constant (g.mg^{-1}) during any one experiment.

To simplify the Elovich equation, it is assumed that $t \gg t$ and by applying boundary conditions $qt = 0$ at $t = 0$ and $qt = qt$ at $t = t$, equation (8) becomes:

A plot of qt versus $\ln(t)$ should yield a linear relationship with a slope of $(1/)$ and an intercept of $(1/) \ln()$.

Results and Discussion

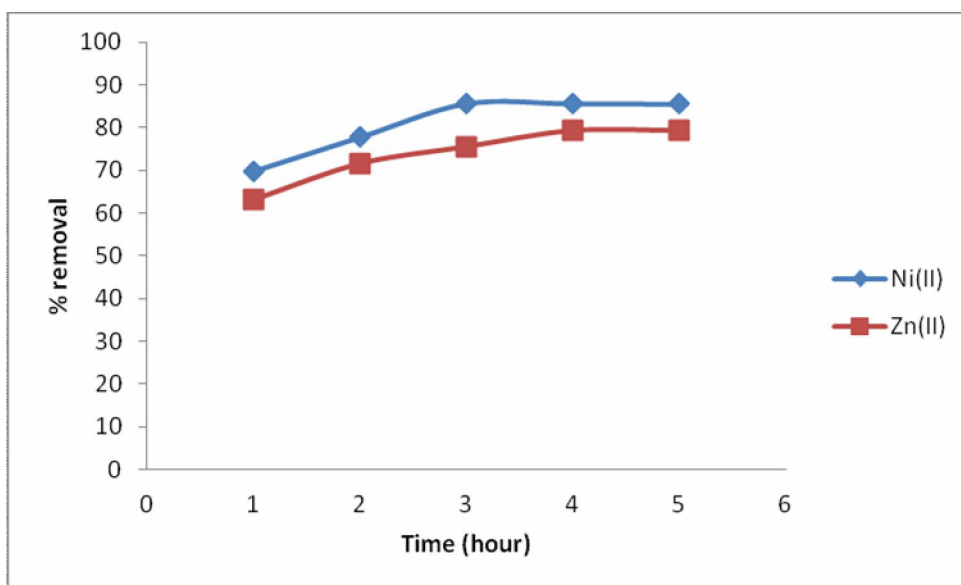


Fig 1: effect of interaction time on adsorption of Ni^{2+} and Zn^{2+}

The adsorption of ions was rapid within the first 60minin (1hour) after which the process proceeds very slowly. Hameed (2009) assert that this may be due to vacant sites available at the initial stage. Optimum percent removal of Ni^{2+} ions was attained at 180 minutes and after 240minutes for Zn^{2+} . The

optimum percent removal (RE%) of Ni^{2+} and Zn^{2+} were higher than 68.75% and 58.40% adsorbed onto neem leaves (Oboh *et al.*,2009) but lower than the over 95% obtained for Zn^{2+} when *Eichhornia crassipes* is used (Shama *et al.*, 2010).

Table 1a: Pseudo first order parameters for adsorption of Ni²⁺ and Zn²⁺ onto chemically modified palm kernel shells

Sample	R ²	K ₁	q _e (cal)	q _e (exp)	SSE(%)
Ni ²⁺	0.012	-0.0042	0.0035	0.1752	0.0768
Zn ²⁺	0.558	-0.0184	0.0030	0.1590	0.0698

Table 1b: Pseudo second order parameters for adsorption of Ni²⁺ and Zn²⁺ onto chemically modified palm kernel shells

Sample	R ²	K ₂	q _e (cal)	q _e (exp)	SSE(%)
Ni ²⁺	0.995	0.6938	0.1786	0.1752	0.0015
Zn ²⁺	0.994	0.6939	0.1613	0.1590	0.0010

Table 1c: Elovich model parameter for adsorption of Ni²⁺ and Zn²⁺ onto chemically modified palm kernel shells

Sample	R ²
Ni ²⁺	0.9164
Zn ²⁺	0.9815

Evaluating the adsorption kinetics of heavy metal ions studied, the pseudo first-order, pseudo second-order and elovich kinetic models were employed to analyse the experimental data obtained. Sample with correlation coefficient (R²) values close or equal to one is accepted for a given model and relatively high R² value indicates that the model successfully describes the adsorption kinetics (Hameed, 2009). The optimum correlation coefficient (R²) for pseudo first-order is 0.4837. The first order rate constant (k₁) was low (-0.010). A wide range of variation also exist between q_{e(cal)} and q_{e(exp)}. These low values indicate that adsorption of the heavy metal ions does not follow pseudo first order kinetics.

Experimental data were further analyzed using pseudo second-order. Correlation coefficient (R²) values for pseudo second-order was higher with values greater than 0.99 and the values q_{e(cal)} were closer than q_{e(exp)}. When compared to elovich kinetic model, the R² values of pseudo second-order kinetic model were higher. The study therefore revealed that the adsorption of these heavy metal ions followed pseudo second-order kinetic model. Hameed (2009), Kongsuwan *et al* (2006) and, Ho and Mc Kay (2002) also reported pseudo second-order adsorption kinetic model.

Beside the values of R², the applicability of pseudo first-order and pseudo second-order kinetic models were verified through the sum of error squares (SSE %). The higher the value of R² and the lower the values of %SSE, the better will be the goodness of the fit; sample with least %SSE is accepted for a given model. The findings indicate that %SSE for pseudo second-order is lower than that of pseudo first-order which further confirms that the adsorption of these heavy metal ions followed pseudo

second-order model (Hameed *et al.*, 2006). Similar processes were reported for the adsorption of lead onto periwinkle shell activated carbon and adsorption of chromium (IV) onto cornelian cherry, apricot stone and almond shells activated carbons (Badmus *et al.*, 2007; Demirbas *et al.*, 2004).

Conclusion

This study revealed the effectiveness of palm kernel shell activated carbon as adsorbent for Ni²⁺ and Zn²⁺ uptake from aqueous solutions. The results indicate that the activated carbon can be employed in the removal of heavy metal ions from aqueous solutions. The kinetics of Ni²⁺ and Zn²⁺ adsorption on the adsorbent was found to follow a pseudo second-order model.

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