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KINETIC STUDIES OF THE ADSORPTION OF MANGANESE (II) AND NICKEL (II) IONS ONTO MODIFIED OIL PALM MESOCARP FIBER

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ABSTRACT

The removal of Mn^{2+} and Ni^{2+} from aqueous solutions onto chemically modified oil palm mesocarp fiber using the batch adsorption method at 30, 60, 90, 120 and 150 minutes were studied. The influence of contact time was used to determine experimental, $q_{e(exp)}$ and theoretical, $q_{e(cal)}$ values. Three adsorption kinetic models: pseudo first-order, pseudo second-order and elovich models were tested. The correlation coefficient (R^2) values for first order kinetics were 0.4630 and 0.1020 for Mn^{2+} and Ni^{2+} respectively. R^2 values obtained for pseudo second kinetics of Mn^{2+} and Ni^{2+} adsorption were 0.9950 and 0.9970 respectively and were higher than 0.9710 and 0.9260 obtained for elovich model. Large difference existed between the $q_{e(exp)}$ and $q_{e(cal)}$ values (0.1632 and 0.0033) of pseudo first order and low difference was obtained for pseudo second order (0.1653 and 0.1676) for the adsorption of Ni^{2+}. Similar trend was observed for the adsorption of Mn^{2+}. The sum of square of error calculated to compare the fitness of the adsorption kinetics indicated that the adsorption of Mn^{2+} and Ni^{2+} followed a pseudo second-order kinetics.

Keywords: Adsorption, Fiber, Ions, Kinetics, Mesocarp, Oil Palm

INTRODUCTION

Heavy metals can cause grave health to human and pose danger to aquatic and other terrestrial lives if their concentrations in the environment exceed tolerable limits. Concentrations below these limits have potentials for long term effect, because heavy metals are known to be accumulative within biological systems. Increased industrialization, agricultural activities, emissions from coal-burning plants, metallurgy, mining, chemicals and domestic wastes have all contributed to the increase in the presence of these metals in the environment. Poor waste management and disposal methods which include incineration of solid wastes on open fields and dumping of industrial wastes in water ways have also contributed to the amount these metals in the environment and exposure.

Heavy metals are elements whose densities are greater than 5 g/cm^3 and could be toxic even at low concentrations and are non-biodegradable (Nwankwo and Mogbo, 2014). These metals have been reported to be present in industrial wastewater and detected at distance of over 90 meter away from point of discharge (Idris *et al*., 2013). Heavy metals can also enter the environment through naturally occurring geological processes and mining activities (Mathew *et al*., 2022). The high amount of heavy metals employed in industrial processes and poorly discharged into the environment is capable of affecting human health and causing great environmental disasters (Shanmugam and Arabi, 2016).

The need for less expensive and effective methods of removing heavy metals from waste water has giving rise to the search for

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unconventional readily available materials that may be used to remove heavy metals from wastewater. Byproducts of agricultural practices are among materials that are available in large quantities which can be modified for use as low cost adsorbents. In view of this, chemically modify oil palm fiber with acid was used to study the adsorption efficiency of Ni^{2+} and Mn^{2+} in aqueous solutions by determining the adsorption kinetic to establish the best fitted model with the adsorption study.

Adsorption Kinetics

Adsorption kinetics describes the rate at which adsorbate is adsorbed into adsorbent and how long the adsorbate is resident in the liquid-solid interphase (Javadian *et al.,* 2015).

***Pseudo First Order* (*Largergren Model*)**

The model assumes that the rate of change that occurs in the uptake of adsorbate as time is directly proportional to the difference in the concentration and rate of sorbate uptake with time and that binding could originate from physical adsorption (Musah *et al*., 2022). The model is expressed by the following equations:

$$\frac{dqt}{dt} = k_t(q_e - q_t) \qquad (1)$$

Where:

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

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

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

$$\log(q_e - q_t) = \log(qe) - \frac{k_t}{2.303}t \qquad (2)$$

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_t and q_e can be determined from the slop and intercept of the plot, respectively.

Pseudo Second Order

The adsorption kinetics rate equation for the pseudo second is expressed as:

$$\frac{dq_t}{dt} = k_2(qe - q_t)^2 \qquad (3)$$

Where:

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

An integrated form of the equation for boundary conditions *t*=0 to *t*=*t* and q_t=0 to q_t=q_e becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \qquad (4)$$

Equation 4 is the integrated rate law for the pseudo second-order reaction, and can be rearranged to the linear form below (Ademiluyi and Nze, 2016):

$$\left[\frac{t}{q_t}\right] = \frac{1}{k_{2q_e^2}} + \frac{1}{q_e}(t) \qquad (5)$$

If the initial adsorption rate, h (mg.g^{-1}.min^{-1}) is:

$$h = k_2(q_e) \qquad (6)$$

Equations 5 and 6 becomes:

$$\left[\frac{t}{q_t}\right] = \frac{1}{h} + \frac{1}{q_e}(t) \qquad (7)$$

The plot of (t/qt) vs t of equation 7 yields a linear relationship from which q_e and k_2 are determined from the slope and intercept of the plot.

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Test of Kinetic model of Pseudo first-order and Pseudo second-order

The applicability of these kinetic models is verified by Sum of Square Error (SSE, %).

$$SSE\ (\%) = \sqrt{(qe(exp) - qe(cal))^2 / N} \quad (8)$$

Where N = number of data point (Javadian *et al*., 2015)

$q_{e(cal)}$ = Adsorption capacity at equilibrium-calculated (mg/g)

$q_{e(exp)}$ = Adsorption capacity at equilibrium-experimental (mg/g)

Elovich Model

With the assumption that surface of sorbent is energetically heterogeneous, Elovich model can be used further describe the pseudo second order kinetic (Edet and Ifelebuegu, 2020). The equation is expressed as:

$$\frac{dq_t}{d_t} = \propto e^{-\beta q_t} \quad (9)$$

Where:

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

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

To simplify the Elovich equation, it is assumed that (Farouq and Yousef, 2015):

αβt >> t and by applying boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, equation 9 becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (10)$$

If adsorption fits the equation, a plot of q_t versus *ln(t)* should yield a linear relationship with a slope of (1/β) and an intercept of (1/β)In(αβ).

MATERIALS AND METHODS

Preparation of Solution

Manganese stock solution was prepared by dissolving 3.608 g of manganese chloride ($MnCl_2.4H_2O$) in 50 cm^3 conc. HCl and the volume made up to the mark with distilled water while Nickel stock solution was prepared by dissolving 4.953 g of Nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 100 cm^3 then diluted with distilled water to 250 cm^3 in volumetric flask. Solution used for experiments were prepared by dilution of the stock solution (using dilution factor).

Adsorbent and Adsorption

Activated carbon employed for the study was prepared from oil palm mesocarp fiber using the two step activation method and H_3PO_4 was used as activating reagent (Musah *et al*., 2018; Rahman *et al*., 2014). The fiber was the byproduct of palm oil extraction obtained from a local oil extraction site. Interaction of the solutions with adsorbent was done using the batch adsorption method where 0.2 g of the adsorbent interacted with 20 cm^3 of adsorbate solutions. This was allowed to shake for 30 minutes at 250 rpm. The process was repeated at 60, 90, 120 and 150 minutes. Each mixture was filtered separately using Whatman filter paper (No.42), the filtrates were collected into separate sample bottles. Concentrations of metal ions in the solutions were determined before and after interactions with the adsorbent using the AA320N Atomic Absorption Spectrometer (Shaba *et al*., 2021).

Adsorption capacity at time t (q_t) was calculated using the formula (Javadian *et al*., 2015):

$$q_t = \frac{(C_o - C_t)\,v}{} \quad (11)$$

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m

Where:

C_o and C_t = initial and equilibrium metal concentrations;

v = volume of aqueous solution sample;

m = mass of adsorbent used.

Equations 2, 7, 8 and 10 were used to determine the kinetic parameters in pseudo first order, pseudo second order, sum of square error (SSE, %) and elovic model.

RESULTS AND DISCUSSION

Results of the kinetic study of the adsorption of zinc and nickel ions are presented in Tables 1-3.

To evaluate the kinetics for adsorption of Mn^{2+} and Ni^{2+}, the pseudo first-order, pseudo second-order and Elovich models were employed to analyze the experimental data obtained. Sample having correlation coefficient (R^2) value close or equal to one (1) is considered acceptable for a given model and relatively high R^2 value indicates that the model successfully describes the adsorption kinetics.

The optimum correlation coefficient (R^2) value for pseudo first-order in the adsorption of Mn^{2+} as presented in Table 1 was 0.4630 which was higher than the 0.1020 obtained for the adsorption of Ni^{2+}. These values are lower than the 0.819 and 0.643 reported for Fe^{3+} and Cu^{2+} respectively (Shaba *et al*., 2021). The first order rate constant (k_1) were low; 0.0172 and 0.0021 were obtained for the adsorption of Mn^{2+} and Ni^{2+} respectively. A wide variation in value was observed between the experimental q_e value ($q_{e(exp)}$) and calculated q_e value ($q_{e(cal)}$). The values obtained were 0.1470 ($q_{e(exp)}$) and 0.0029 ($q_{e(cal)}$) for Mn^{2+} while 0.1632 ($q_{e(exp)}$) and 0.0033 ($q_{e(cal)}$) were obtained for Ni^{2+}. These low values indicate that adsorption of Mn^{2+} and Ni^{2+} onto chemically modified oil palm mesocarp fiber does not follow pseudo first order kinetics. Similar observations were reported for the adsorption Mn^{2+}, Cd^{2+} and Cr^{6+} (Musah *et al*., 2018; Rout *et al*., 2015).

Table 1: Pseudo first order parameters for adsorption of Mn^{2+} and Ni^{2+}

Parameter	Mn^{2+}	Ni^{2+}
k_1 (min^{-1})	0.0172	0.0021
R^2	0.4630	0.1020
$q_{e(exp)}$ (mg/g)	0.1470	0.1632
$q_{e(cal)}$ (mg/g)	0.0029	0.0033
SSE (%)	0.0648	0.0714

Further analysis of the experimental data using pseudo second-order (Table 2) revealed correlation coefficient (R^2) values for pseudo second-order were higher than those obtained for pseudo first order and Elovich model with 0.9950 and 0.9970 for Mn^{2+} and Ni^{2+} adsorption respectively. These values were higher than the 0.9203 reported for the adsorption of Mn^{2+} onto untreated Venus shell but slightly lower than 0.9999 for the adsorption of Cr^{6+} onto nano-scaled avocado seeds (Mahmoud *et al*., 2022; Yusuff *et al*., 2017). The values of $q_{e(cal)}$ were close to $q_{e(exp)}$ for both Mn^{2+} and Ni^{2+}. 0.1491 $q_{e(exp)}$ and 0.1453 $q_{e(cal)}$ for Mn^{2+}; 0.1653 $q_{e(exp)}$ and 0.1676 $q_{e(cal)}$ for the adsorption of Ni^{2+}. Compared to pseudo first-order kinetic model, the R^2 values of pseudo second-order kinetic model were higher and values of $q_{e(exp)}$ and $q_{e(cal)}$ were closer than those of pseudo first order. Values obtained revealed that the adsorption of Mn^{2+} and Ni^{2+} followed pseudo second-order kinetic model. Khamwichit *et al.* (2022), Shaba *et al*. (2021) and Musah *et al.* (2018) also reported adsorption that followed pseudo second order kinetic model for the

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removal of Cu^{2+}, Zn^{2+}, Cr^{6+} and Cd^{2+} respectively.

Table 2: Pseudo second order parameters for adsorption of Mn^{2+} and Ni^{2+}

Parameter	Mn^{2+}	Ni^{2+}
$k_{2)}$ (mg.g^{-1}min^{-1})	0.7980	0.7912
R^2	0.9950	0.9970
$q_{e(exp)}$ (mg/g)	0.1491	0.1653
$q_{e(cal)}$ (mg/g)	0.1453	0.1676
SSE (%)	0.0017	0.0010

Beside the values of correlation coefficient (R^2) and closeness of $q_{e(exp)}$ value to $q_{e(cal)}$, the application of pseudo first-order and pseudo second-order kinetic models were verified using the sum of squares error (SSE %). The higher the value of R^2, the closer the value of $q_{e(exp)}$ to $q_{e(cal)}$ and the lower the value of % SSE, the better will be the fit. Sample with the lowest % SSE value is accepted for a given model. Results obtained indicate that % SSE value for pseudo second-order (0.0017 and 0.0010 for Mn^{2+} and Ni^{2+}) were lower than 0.0648 (Mn^{2+}) and 0.0714 (Ni^{2+}) obtained for pseudo first-order which further confirms that the adsorption of Mn^{2+} and Ni^{2+} followed pseudo second-order kinetic model. Similar processes were reported for the adsorption of Cu^{2+} onto mussel shell activated carbon and adsorption of Cd^{2+} onto zeolite (Farouq and Yousef, 2015; Javadian *et al*., 2015).

Values of α and β for the adsorption of Mn^{2+} and Ni^{2+} onto oil palm mesocarp fiber presented in Table 3 were obtained from the slope and intercept of linear plots *qt* versus *lnt*. α represent the initial rate of adsorption and β relates to the extent of surface coverage (Mahmoud *et al*., 2022).

Table 3: Elovich model parameter for adsorption of Mn^{2+} and Ni^{2+}

Parameter	Mn^{2+}	Ni^{2+}
R^2	0.9710	0.9260
α (mg/g.min)	0.1465	0.2731
β (mg/g)	4.3670	4.8610

Higher values of α (0.2731 mg/g.min) and β (4.8610 mg/g) were obtained for the adsorption of Ni^{2+} compared to those for the adsorption of Mn^{2+} by the same adsorbent. Correlation coefficients (R^2) values for the adsorption of Mn^{2+} and Ni^{2+} were 0.9710 and 0.9260 respectively. The values were higher than 0.9383 and 0.8983 reported for the adsorption of Cr^{6+} and Cu^{2+} onto nano- scaled avocado seed and venus shells adsorbents (Mahmoud *et al*., 2022; Khamwichit *et al*., 2022). The Correlation coefficient (R^2) values were also lower than those obtained for pseudo second adsorption model.

CONCLUSION

Chemically modified oil palm mesocarp fiber with H_3PO_4 was used as adsorbent to study the kinetics of the adsorption of Ni (II) and Mn (II) ions from aqueous solutions. The adsorption kinetic parameters studied indicated the overall adsorption process is best described by the pseudo second order kinetic model and also indicate that the adsorption is majorly physisorption and a non-specific process. The overall result indicate the suitability of adsorbent in the adsorption of adsorbates (Ni^{2+} and Mn^{2+}) from aqueous solution.

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