



KINETIC STUDY OF THE ADSORPTION OF HEAVY METAL IONS FROM WATER USING CACTUS ASH ADSORBENT



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Abstract: With rapid global economic, population growth and accelerated industrialization, heavy metal pollution has become increasingly severe, with the heavy metal content in many rivers and groundwater exceeding safety standards. The aim of this study is to evaluate the kinetic models of heavy metal adsorption from water using cactus ash adsorbent. Three kinetic models i.e., pseudo-first-order, pseudo-second-order and power function were applied to study the reaction pathways and potential rate determining steps of the adsorption of Cr, Ni, Pb and Cd onto Cactus ash residue. The pseudo-first-order model did not provide a good fit to the experimental data, rather the adsorption of Cr, Ni, Pb and Cd by cactus ash residue followed the pseudo-second-order kinetics. Suitability of pseudo-second-order model suggests chemisorptions as the rate limiting step. The study therefore shows that the adsorption of Cr, Ni, Pb and Cd ions onto cactus ash residue adsorbent was best fitted in the pseudo second order model for the evaluation of kinetic parameters of the adsorption process, which R^2 values of the ions tends towards 1.

Key Words: Kinetics, Adsorption, Cactus, Model, Metals

Introduction.

With rapid global economic growth, rapid population growth, and accelerated industrialization, heavy metal pollution has become increasingly severe, with the heavy metal content in many rivers and groundwater exceeding safety standards. Moreover, because heavy metals are enriched and difficult to degrade, they cause significant harm to human health when they enter the human body. Heavy metal refers to group of metal pollutants with atomic density greater than $4 \pm 1 \text{ g/cm}^3$ (Igberase *et al.*, 2018). Studies confirmed heavy metals to be a major problem faced by our natural environment to the devastating effect it causes to human health through the food and water consumed. Heavy metals get their source from human activities such as industrialization, waste disposal, and mining and indiscriminate agricultural activities practice by quakes (Gao *et al.*, 2018). For instance, industrialization was discovered to be a major cause of water pollution which is on the increase because of the large volume of influent water from industries released to the environment and because of the limited fresh water sources, treatment of water for drinking and industrial use is now common practice globally (Vishali and Karthikeyan, 2015). The major sources of heavy metal contaminations bedeviling our ecosystem, specifically water bodies are these effluents of these factories, waste treatment plants and refineries and because of wide encroachment of the pollutants entering bodies of water to a larger extent, they are seen as a major challenge or threat to human health and the wellbeing of the environment (Jaishankar *et al.*, 2014). For instance, the literatures show that effluents of leathers industries, metallurgy, paints, electroplating, metallurgy and pigments are the major sources of lead and chromium found in large or concentrations in wastewater polluting our ecosystem such as water used for drinking or cooking. Studies confirmed that the aforementioned heavy metals (chromium and lead) are mostly found in concentrations above their threshold or permissible levels of 0.05 mg/l and 0.01 mg/l, respectively (Ince and Ince, 2017). Nickel (II) finds its way into water bodies through effluents from industries. It is present in the effluents of silver refineries, zinc base casting and storage battery industries. As it resists corrosion even at high

temperature, it can also be used in gas turbines, rocket engines and desalination plants. It is also used in coinage and costume jewelry. Skin contact with nickel causes a painful disease called "nickel itch" which is fatal (Bailey *et al.*, 2005).

Adsorption is a mass transfer process in which pollutants move from the liquid phase to the solid adsorbent. Adsorption is one of the most widely used technologies in water and waste water treatment, because it has many advantages, such as simple design, low price, easy maintenance, and high efficiency (Anastopoulos *et al.*, 2016). The adsorption kinetic study provides information of the adsorption rate, the performance of the adsorbent used, and the mass transfer mechanisms. Knowing the adsorption kinetic is essential for the design of the adsorption systems (Amari *et al.*, 2020). Biomasses obtained from post-harvest waste or agricultural waste are common and available for production of adsorbents used for heavy metal adsorption. Bio-adsorbents produced from agricultural waste has much advantages compared to the conventional one such as: high adsorption rate, environmentally friendly, can be regenerated after use, no need of enrichment, economically affordable, high effectiveness and non-toxic (Othman and Mohd-Asharuddin, 2012).

Agricultural biomass are common and abundant of various species of plant generally referred to as biomaterials which were found to be suitable for adsorption of heavy metals. Studies shows that, using biomaterials for heavy metal capture or removal has better advantage than conventional process. Such advantages include: High adsorption rate, economically feasible, can be regenerated after use, no need for nutrient enrichment, void of toxic sludge and environmentally friendly (Ashtaputrey and Ashtaputrey, 2016). In recent years, researchers give due attention on the use of natural adsorbents obtained from natural materials as an alternative to replace commercial activated carbon in the removal of toxic heavy metals effluent from different sources of wastewater due to their environmental and the economic advantages (Özsin *et al.*, 2019). The literatures from previous studies show several biomaterials have been used for the development of bio-adsorbent for heavy metal removal. For instance, Werkneh *et al.*, (2014) developed a bio-adsorbent using

sugarcane with 3.8 mg/g adsorption capacity using 20 g/L adsorbent doses, 99% heavy metal removal was observed. Also Sugashini and Begum (2015) developed bio-adsorbent using Rice husk with 8.9 mg/g adsorption capacity using 4 g/L adsorbent dose, 94% heavy metal removal was observed. In another similar study Arulkumar et al., (2012) development a bio-adsorbent using prawn shell having absorption capacity of 8.9 mg/g and 98% heavy metal was obtained.

The prediction of kinetics is necessary for the design of adsorption systems. The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. Successful application of the adsorption demands innovation of cheap, easily available and abundant adsorbents of known kinetic parameters and sorption characteristics. (Espinoza-sánchez et al., 2019). The kinetic of adsorption studies predict the progress of dyes adsorption during the adsorption to reach the equilibrium. In addition, the estimate of the adsorption mechanism is important for design purposes. To analyze the adsorption mechanism of the anionic dyes on the pseudo-first order, pseudo-second order, and intra-particle diffusion models were used (Afroze & Sen, 2018).

Pseudo-First-Order Kinetic Model

Lagergren's kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity. In order to distinguish kinetics equation based on concentration of solution and adsorption capacity of solid, Lagergren's first order equation has been called pseudo-first order. The linear form of the pseudo-first-order kinetic mode is represented by (Acharya et al., 2018)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

Where q_e and q_t are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium and at various time t , respectively, k_1 is the Pseudo-first-order adsorption rate constant (min^{-1}). The values of k_1 and calculated q_e can be determined from the slope and intercept respectively, of the linear plot of $\ln(q_e - q_t)$ versus t .

Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model is expressed by (Vaid et al., 2013)

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

Where k_2 is the pseudo-second-order adsorption rate constant (g/mg.min) and q_e is the amount of adsorbate adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate, h (mg/g.min) is expressed as:

$$h = k_2^2 q_e \quad (3)$$

The plot of t/q_t versus t gives a linear relationship which allows computation of k_2 , h and calculated q_e . Among these models, the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e , (Igberase et al., 2018).

Power Function Kinetic Model

The power function kinetic equation (model) is represented by: (Sun and Chakraborty, 2015)

$$\log q_t = \log a + b \log t \quad (4)$$

Where: the constant, a , represents the initial rate ($\text{mg.g}^{-1}.\text{min}^{-1}$) and the constant b represents the rate constant of the reaction (g/mg/min). If the adsorption fits the power function model, a plot of $\log q_t$ versus $\log t$ should yield a linear relationship with a slope of b and intercept $\log a$.

Methodology

Sample Collection and Pretreatment

The cactus plant was collected from the environs of Girei L.G.A, Adamawa State, washed and identified by plant botanist in the Department of Botany, Modibbo Adama University Yola. The plant was washed with distilled water to remove dirt, according to the method adopted from.

Preparation of Cactus Ash Residue

The clean plant sample was cut into strips of 1 - 2 cm, dried in an oven at 60°C for 24 hours. Ash was obtained as dry plant material was heated in a furnace at 600°C with excess air for 24 hours. Ash residue was prepared by dissolving the ash in distilled water to remove the soluble alkali, filtered, washed with distilled water and dried in an oven at 100° . Table 1 and 2 show the reagents and equipment that were used for the preparation of cactus ash residue

Table 1: List of reagents used

Reagent	Purity/Model	Manufacturer
Hydrogen Chloride	35-38%	BDH Limited, Poole, England
Sodium Hydro Oxide	96.0%	Central Drug House P Ltd, India
Potassium Chromate	99.0%	Labtech Chemicals
Lead Acetate	99.0%	Labtech Chemicals
Cadmium (metal)	99.0%	Lobal Chemie
Nickel Chloride	99.0%	Lobal Chemie

Experimental Method

Experimental data was tested by the kinetic models so as to provide a good correlation for the adsorption kinetics of Cr, Ni, Pb, Cd ions onto ash residue. Three kinetic models i.e., pseudo-first-order, pseudo-second-order, and power function model were applied to study the reaction pathways and potential rate determining steps of the adsorption of Cr, Ni, Pb and Cd onto Cactus ash residue.

Results and Discussion

Kinetic Model for Cr, Ni, Pb, and Cd ion Removal

Three kinetic models i.e., pseudo-first-order, pseudo-second-order and power function were applied to study the reaction pathways and potential rate determining steps of the adsorption of Cr, Ni, Pb and Cd onto Cactus ash residue. The pseudo-first-order model did not provide a good fit to the experimental data, in the present case, kinetic data is in good agreement with pseudo second order in terms of coefficient of determination (R^2) than pseudo first order in all the four cases of adsorbate i.e. Cr, Ni, Pb and Cd. The first-order rate constant, K_1 , the correlation coefficients, R^2 and the theoretical and experimental equilibrium adsorption capacity q_e are given in Table 3. The plot of $\ln(q_e - q_t)$ versus t shown Figure 1 was nonlinear with R^2 values 0.714, 0.753, 0.814 and 0.8673 for Cr, Ni, Pb and Cd respectively. Moreover, the theoretical and experimental equilibrium adsorption capacity q_e obtained from the plot did not agree (i.e., varied widely), suggesting the inadequacy of the pseudo-first-order model for describing the

adsorption kinetics of Cr, Ni, Pb and Cd onto cactus ash residue. However, the kinetic data was fitted well to the pseudo-second-order model. The pseudo-second order rate constant K_2 , the initial adsorption rate, H and the theoretical and experimental equilibrium adsorption capacity are given in Table 3. The plot of t/q_t against t is depicted in Figure 2. Contrary to the pseudo-first-order model, the fitting of the kinetic data in the pseudo-second-order model showed excellent linearity with high correlation coefficients, R^2 for both the adsorbate. In addition, there was a good agreement between the calculated q_e and the experimental q_e values (i.e., the q_e values were very much close with both the theoretical and experimental values) indicating that the adsorption of Cr, Ni, Pb and Cd by cactus ash residue followed the pseudo-second-order kinetics. Hence the adsorption process is controlled by chemisorptions (Neelaveni et al., 2019). This suggests that the forming of interaction between the adsorbate and the adsorbent on the external surface of the adsorbent (film diffusion) is the rate determining step (Gupta et al., 2013). Suitability of pseudo-second-order model suggests chemisorptions as the rate limiting step. This chemical adsorption can be explained by the valence forces through sharing electrons between adsorbent and the adsorbate molecules. The power function constants, a , b and the correlation coefficients, R^2 are given in Table 3. The plot of $\log qt$ versus $\log t$ Figure 3 was nonlinear with low R^2 suggesting that the power function model was not appropriate for describing the adsorption of Cd and Pb onto Cactus ash residue.

Table 3: Kinetic Models Parameters for Cr, Ni, Pb and Cd Removal

Kinetic Model	Parameters	Cr	Ni	Pb	Cd
Pseudo First Order	$q_{e, cal}$ (mg/g)	5.09214	20.393	15.345	16.99297
	$q_{e, exp}$ (mg/g)	987.633	997.300	975.667	982.267
	K_1	0.0174	0.02	0.0158	0.0201
	R^2	0.714	0.7526	0.8148	0.8673
Pseudo Second Order	h (mg/g.min)	0.1	0.01089	0.01089	0.01089
	$q_{e, cal}$ (mg/g)	1000	1000	1000	1000
	$q_{e, exp}$ (mg/g)	987.633	997.300	975.667	982.267
	K_2 (g/mg.min)	0.01	0.0033	0.0033	0.0033
	R^2	1	1	1	1
Power Function	A	19.89960	19.86	19.62	19.73
	B	0.0018	0.004	0.0057	0.0043
	R^2	0.9104	0.7054	0.9407	0.892

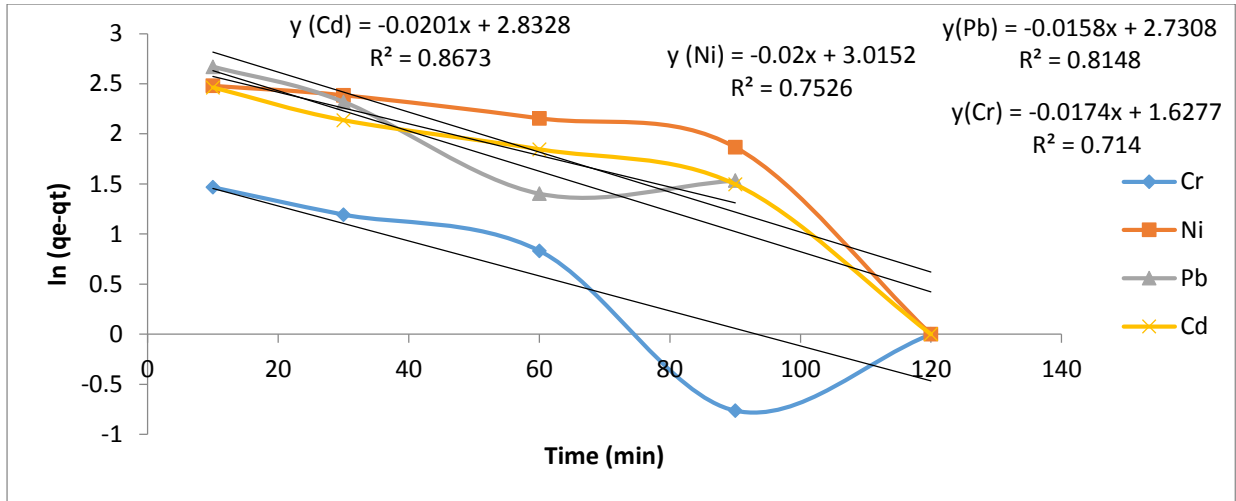


Figure 1: Pseudo First Order Kinetic Model for Cr, Ni, Pb and Cd Removal

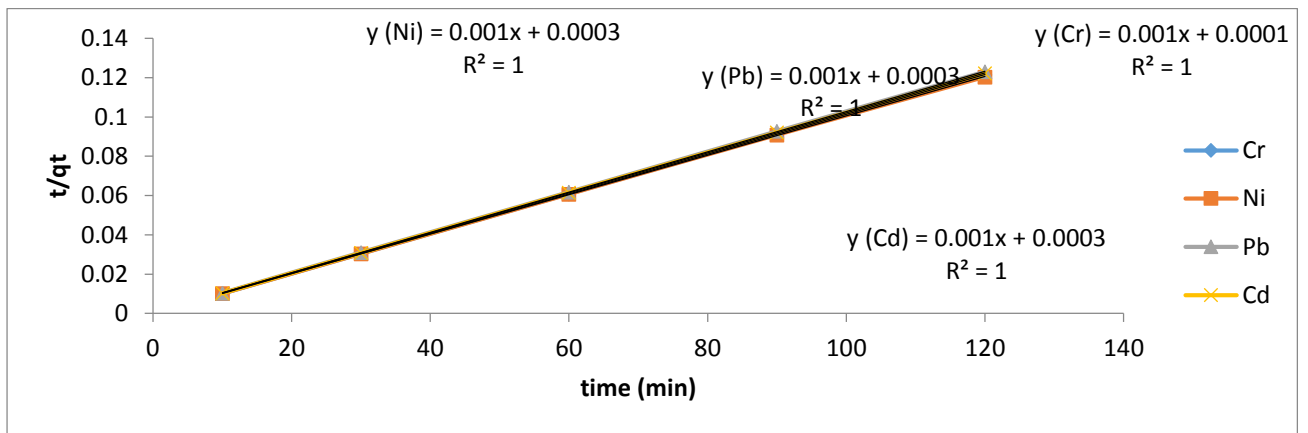


Figure 2: Pseudo Second Order Kinetic Model for Cr, Ni, Pb and Cd Removal

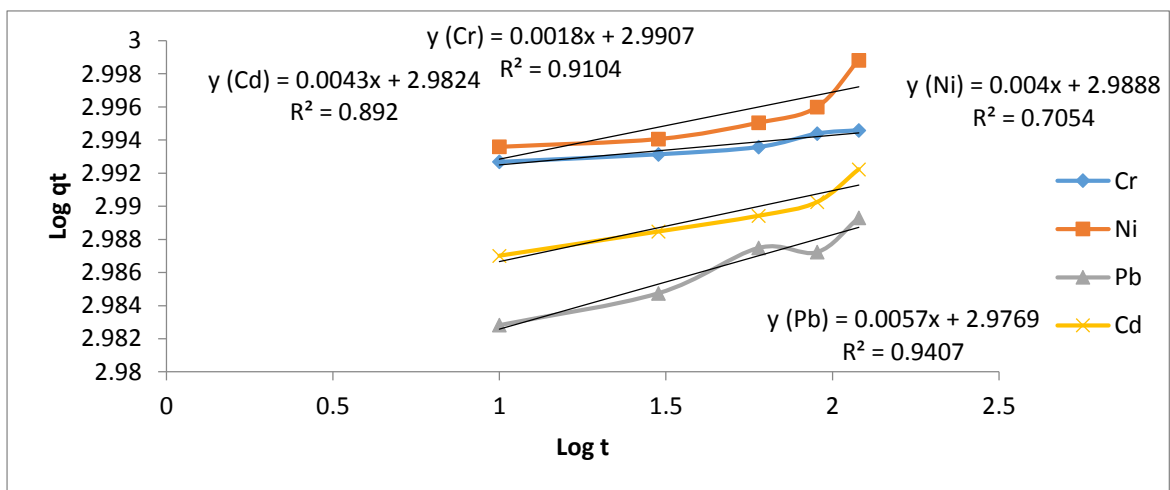


Figure 3: Power Function Kinetic Model for Cr, Ni, Pb and Cd Removal

Conclusion

In this work, the use of agricultural combusted product to address the problem of metal ions loaded wastewater was exploited. For this purpose, cactus ash residue was used successfully as an adsorbent for the removal of Cr, Ni, Pb and Cd ion from aqueous solutions. From the batch experiments, it was found that the adsorption of Cr, Ni,

Pb and Cd ions onto cactus ash residue adsorbent was best fitted in the pseudo second order model for the evaluation of kinetic parameters of the adsorption process, which R² values on the ions is approximately equals 1.

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Conflict of Interest

The author declares no conflict of interest.

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