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Kinetic modeling of Cu2+, Cd2+ and Pb2+ ions adsorption onto raw and modified Artocarpus heterophyllus L. seeds from a model solution (AbstractView.aspx?PID=2021-14-4-1)

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Kinetic modeling of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption onto raw and modified *Artocarpus heterophyllus* L. seeds from a model solution

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ABSTRACT:
Heavy metals contaminated water has detrimental health effects to human beings and animals not limited to hypertension, kidney damage, cancer and eventual death. Available water treatment methods have proved to not only function at high operation costs and ineffective but also yielded insignificant results to a local ordinary Kenyan citizens. The present study investigates the use of Jackfruit seeds wastes as a low cost adsorbent in adsorption water treatment technique. Raw and modified Jackfruit seeds adsorbent were applied to study kinetic studies of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption from an aqueous solution under batch conditions. The adsorption behavior of the three metal ions onto raw and modified adsorbents was monitored spectrophotometrically and analysed with Pseudo-first-order and Pseudo-second-order kinetic models. Correlation coefficients (R^2) confirmed that all experimental data fitted Pseudo-second-order with $R^2 > 0.984$ which implied a chemisorption process. Experimental and calculated adsorption capacities was higher for modified adsorbent with Pb^{2+} ions registering higher values. The rate constants (k_2) was higher in modified adsorbent than in raw adsorbent with Pb^{2+} ions registering highest value of rate of 4.54×10^{-1} (mg $g^{-1}min^{-1}$). Adsorption capacities was in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The results showed viability of the adsorbents for the removal of the heavy metals from waste solution in an economical and environmental friendly manner.

KEYWORDS: Adsorption, kinetics, *Artocarpus heterophyllus* L. seeds, chemisorption, pseudo-first-order, pseudo-second-order.

INTRODUCTION:

In the modern society, industrialization and mining activities among others have led to constant discharge of heavy metal pollutants to the environment[1]. Heavy metals have toxic effects on animals and human body[2]; hence, it is crucial to remove them pollutants to the environment . Heavy metals have toxic effects on animals and human body , hence, it is crucial to remove them from industrial wastewaters before discharging them into the surface water[3].

They accumulate in the body tissues causing life-threatening health effects to human beings such as kidney damage, emphysema, hypertension, neurological effects, and even cancer[4].

Disposal of wastewater loaded with heavy metals has been a challenge to many environmentalists and industrialists because cost-effective treatment alternatives are not available[5]. Techniques such as ion exchange, precipitation, electrochemical techniques, coagulation and adsorption have been employed in heavy metals wastewater remediation[6]. However, adsorption technique have emerged the most used technique due to its cost effectiveness in operation, availability of the adsorbent materials in large quantities and easy in design[7,8]. Recent studies have reported utilization of adsorbents from agricultural wastes such as *Acacia nilotica* bark[9], mango bark[10], Jackfruit peels and seeds[11, 12] among others in heavy metal ions elimination from contaminated water.

Jackfruit seeds are disposed as a waste from Jackfruit produced by Jackfruit plant (*Artocarpus heterophyllus* L.). The plant species is believed to originate from India and produces the largest fruit in the whole world[13]. It has been an orphan fruit in African continent but it is gaining demand in recent years especially in Kenya where it's now being grown in many parts of the country due to its non-seasonal nature and its increased consumer demand. The fleshy yellow pulp is eaten while the seeds, which are about 15% of the total fruit weight are discarded as a waste[14]. The waste has been utilized in the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions heavy metals from water[11,15,12]. The study aimed at applying an ion exchange raw and modified adsorbent material from Jackfruit seeds to assess kinetics of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption from wastewater.

MATERIALS AND METHODS:

Research design:
The focus of the study was to apply a synthesized cheaper, non-toxic and environmental friendly adsorbent material from Jackfruit seeds to study kinetics of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption. Optimized parameters of pH, contact time, agitation speed, adsorbent dosage and initial concentration were used.

Chemicals:
Lead Nitrate, Copper Nitrate, Cadmium Nitrate, Sodium acetate, Potassium hydroxide and Hydrochloric acid chemicals were all of analytical grade and purchased from Sigma Aldrich (Kobian, Nairobi Kenya).

Preparation of stock and working solutions:
Stock solutions of Cu^{2+}, Cd^{2+} and Pb^{2+} metal solutions (1000 ppm) were prepared by dissolving fixed weighed amounts of $Cu(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ salts in sodium acetate buffer agent. The pH of the metal solutions was adjusted by 0.1 M HCl and 0.1 M KOH solutions.

Adsorption batch studies:
Batch kinetic experiments were performed at optimal parameters of pH, agitation speed, adsorbent dosage and initial concentration previously discussed[11]. Experiments were carried out by putting optimal dose of 15mg and 10 mg; 13mg and 10mg; and 15mg (raw and modified) to 20mL of 30ppm solutions of Cu^{2+}, Cd^{2+} and Pb^{2+} at pH of 4.2 and 5.7; 5.0 and 6.4 and 5.6 and 6.0 (raw and modified) respectively. The mixtures were agitated at varying agitation times (10-80 minutes) at optimal agitation speeds of 150rpm for Cu^{2+} ions; 175rpm (raw) and 150rpm (modified) for Cd^{2+} and 150rpm for Pb^{2+} metal solutions. The mixtures were then filtered and the amount of metal ions in the supernatant solution determined by AAS.

The amount of metal ion adsorbed was calculated by equation 1:

Where is the amount of metal ions adsorbed at equilibrium, is initial adsorbate concentration and is adsorbate final concentration at equilibrium (mg/L), V is the total volume of the solution and M is the adsorbent dosage mass[11].

Kinetic modeling:
The adsorption kinetics provides information on reaction rates and the residence time of adsorbate uptake at adsorbent-solution interface[16, 17]. This is achieved by the use of pseudo-first-order and pseudo-second-order kinetic models[18] where the best-fit model is the one having the highest coefficient of correlation (R^2) values[19].

Pseudo-first-order model:
Pseudo-first-order kinetic model is based on the assumption that physisorption is the rate determining step. Linearized form of pseudo first-order equation is given by equation 2:

Where is the amount of solute ions adsorbed at equilibrium and is the amount of solute adsorbed at time (t). is the rate constant for pseudo-first order sorption[20].

Pseudo-first-order plot of ln (-) against time (t) results in a straight line with - as the slope and the ln as the intercept and can be used to obtain (pseudo-first-order constant) and calculated value.

Pseudo-second-order model

Pseudo-second-order kinetic model is based on the assumption that chemisorption is the rate-determining step. Linearized form for pseudo-second-order equation is given in equation 3:

and is the rate constant for pseudo-second order sorption[21]. Pseudo-second-order plot of against time (t) yields a linear relationship with as the slope and as the intercept which can be used to calculate (calculated) value and (pseudo-second-order constant).

Table 1: Kinetic parameters for Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption

Metal ion	Sorbent	, cal (mg g^{-1})	, exp (mg g^{-1})	(min^{-1})	R^2	, cal (mg g^{-1})	(mg $g^{-1}min^{-1}$)	R^2	Comment
Cu^{2+}	Raw	4.7726	7.95	5.70×10^{-2}	0.6449	6.8729	3.96×10^{-2}	0.9948	Pseudo-second-order
	Modified	2.6538	14.24	1.89×10^{-2}	0.2949	12.4224	1.01×10^{-1}	0.9899	Pseudo-second-order
Cd^{2+}	Raw	2.7574	6.67	2.50×10^{-3}	0.0247	4.4583	3.28×10^{-2}	0.9126	Pseudo-second-order
	Modified	3.9650	10.43	4.50×10^{-3}	0.0681	6.8634	3.18×10^{-1}	0.9925	Pseudo-second-order
Pb^{2+}	Raw	2.0647	9.71	7.29×10^{-2}	0.1820	7.8064	4.35×10^{-2}	0.9844	Pseudo-second-order
	Modified	2.6653	17.25	3.60×10^{-3}	0.0497	14.6199	4.54×10^{-1}	0.9933	Pseudo-second-order

RESULTS AND DISCUSSIONS:

Kinetic adsorption studies:

In order to evaluate kinetic parameters, experimental kinetic data of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption on raw and modified Jackfruit seeds was analysed using Pseudo-first-order and Pseudo-second-order models and results are recorded in table 1.

Pseudo-second-order model plots showed a better fitting of experimental data compared to pseudo-first-order kinetic model as shown in figures (1 and 2). Poor pseudo-first-order R^2 values were obtained for the three metal ions. Also, calculated and experimental values were not close to each other and this shows that the complexation did not fit the model. Therefore, the adsorption was described by pseudo-second-order kinetics with $R^2 > 0.984$ which suggested a chemisorption process[22] attributed to valence forces through sharing or ion exchange of electrons between the electron-rich surface sites and electron-deficient metal ions[23].

The rates of adsorption was also higher in modified form comparatively with the raw form with Pb^{2+} ions registering the highest rate of 4.54×10^{-1}mg/g/min in modified form as compared to 4.35×10^{-2}mg/g/min in raw form. The adsorption capacity values of q_e, cal were higher in modified adsorbent as compared to the raw form with that of Pb^{2+} ions registering the highest value of 14.6199mg g^{-1} in modified form compared to 7.8064 mg g^{-1} in raw form. This showed that chemical modification of the material not only improved the adsorption capacity but also the rate of adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} ions making the process to adsorb more of the metal ions within a shorter period of time. This is attributed by a change in adsorbent surface charge and the structure after chemical modification with EDA[23]. The results are similar to those reported in the study[24,25,26].

Figure 1: Linearized plot of Pseudo-first-order model plot of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions respectively

Figure 2: Linearized plot of Pseudo-second-order model plot of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions respectively

CONCLUSION:

In this work, raw and modified Jackfruit seeds were used as highly efficient metal ion chelator in studying kinetic adsorption studies for Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorption. Kinetic studies showed that the adsorption of the three metal ions on both raw and modified Jackfruit seeds was pseudo-second-order showing chemisorption process with higher rate of 4.54×10^{-1} for Pb^{2+} ions in modified adsorbent.

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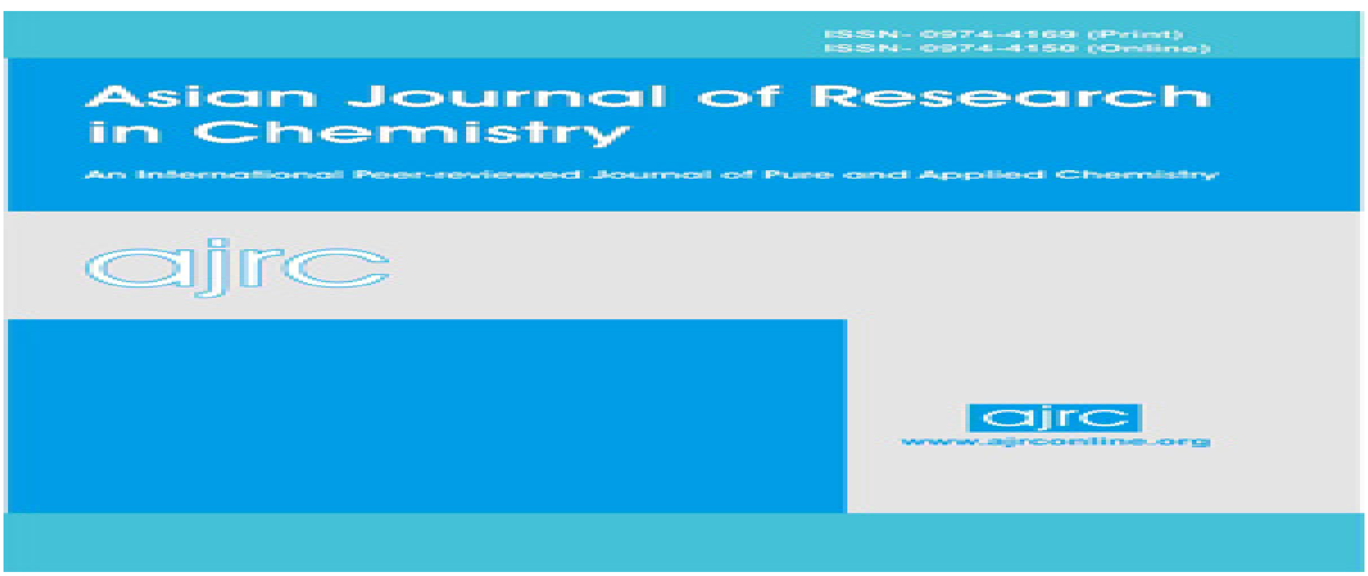

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