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ADSORPTION OF HEAVY METALS FROM IGBETI MARBLE MINING WASTEWATER USING CRAB CHITOSAN.

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Abstract

The need to treat wastewater before being discharged into the environment brought about the use of crustacean Crab chitosan adsorbents in removing selected heavy metals (Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) from Igbeti Marble Mining Wastewater (IMMW). Adsorbent dosage (g), agitation rate(rpm), contact time(min), pH and temperature(°c) parameters were used. Treatment's Initial and final concentrations of the metal ions present in the wastewater were estimated using Atomic Absorption Spectrometer (AAS). The results obtained showed that optimum adsorption was achieved for both adsorbents at 0.1 dosage; 150 rpm Crab Chitosan (CrC) and 50 rpm for Activated Crab Chitosan (ACrC); 15 to 30 minutes at pH of 4 at room temperature (i.e. 25 ℃) with 98.9 to 100% removal efficiencies of the selected heavy metals from IMMW. The Freundlich isotherm models was found to be most appropriate in descending order Pb^{2+} (0.9980) > Cu^{2+} (0.9902) > Cd^{2+} (0.9651) for CrC, while ACrC was Cu^{2+} (0.9986) > Zn^{2+} (0.9695) > Cd^{2+} (0.9657) > Pb^{2+} (0.8944). All selected heavy metals' data also best suited Langmuir and Temkin isotherms; then followed the orders of kinetics of pseudo- second order and intra-particle diffusion. Therefore, the adsorbents could be used for sequestration of heavy metals from real wastewater.

Keywords: Adsorption, IMMW, metal ions, removal efficiency, isotherm, kinetics.

1 Introduction

Water, a fundamental component of life, constitutes around 70 to 80 percent of the Earth's surface. According to An et al. (2015), a mere 2.78% of the Earth's total water supply is classified as fresh water, serving as a vital resource for human consumption, wildlife sustenance, and agricultural cultivation. Contaminated water exerts a substantial influence on the existence of living organisms and the ecosystems reliant on water for their sustenance. The significance of water in the context of existence is well acknowledged due to its universal characteristics (Jayalekshmi*et al* 2021). The wastewater that is generated is released into the natural watercourse. Discharge of untreated wastewater leads to unpleasant situations such as negative effects on human health, sludge and scum accumulation and oxygen depletion and odour production in the streams (Jayalekshmi*et al* 2021). Wastewater contains many pathogenic bacteria, microorganisms, suspended solids, nutrients, minerals, toxic metals etc. Presence of various contaminates in water bodies has posed several challenges to the disposal, recycling and re-usage of the wastewater.

Heavy metal contamination in wastewater is a worldwide problem. The persistent presence of these metals in water even in small quantities may become toxic through natural processes such as bio-magnification (Ayeni et al., 2022; Ojoawo et al., 2022).Water bodies have been contaminated with heavy metal ions due to the discharge of these ions by various businesses, including electroplating, electronic equipment production, and chemical processing factories. The toxicity of various heavy metal ions, such as Chromium (Cr), Cadmium (Cd), Lead (Pb), Mercury (Hg), Zinc (Zn), Nickel (Ni), and Iron (Fe), and their corresponding complexes, has been seen in aquatic creatures inhabiting water bodies that have been exposed to wastewater (Mojiri and Bashir, 2022).Heavy metal pollution is an important issue with human health and of major concern and has serious environmental consequences. It is therefore important to remove heavy metals from water and wastewater (Mojiri and Bashir, 2022).

Adsorption technique has several values over other techniques such as ease of application in field conditions, possible regeneration ability, and high metal ion removal performance (Ojoawo *et al.*, 2022, Mojiri and Bashir, 2022). Natural polymers, such as chitin and chitosan, which possess a cellulose-like structure, have the potential to serve as effective adsorbents, coagulants, and flocculent aids in the treatment of wastewater contaminated with heavy metals. Previous studies conducted by Agarwal et al. (2018), Rizzi et al. (2018), Boudouaia et al. (2019), Casadidio et al. (2019), Machodi and Daramola (2019), Nakayama et al. (2020), and other researchers have explored the potential applications of chitosan adsorbents in the field of wastewater treatment. The objective of this research is to investigate the efficacy of chitosan adsorbents derived from specific crustacean shell (crab) in the remediation of targeted heavy metals ((Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) present in mine effluent.

However, literature is scarce onthe utilization of crab chitosan and its activation with HCl in remediating heavy metals from a real life wastewater of Igbeti marble mining wastewater (IMMW).

2 Materials and Methods

2.1 Materials, equipment and apparatus

The materials used was raw Crab Shell (CRS) (Plate 1) and Igbeti Marble Mining Wastewater(IMMW). The reagents used were Hydrochloric acid (HCl), Sodium Hydroxide (NaOH), Sodium Hypochlorite (NaOCl) and distilled water. Equipment used include Atomic Absorption Spectrometer (AAS) machine, muffle furnace, oven, mechanical grinding machine, mechanical sieve shaker, sieve, and weighing balance. Apparatuses used include beaker, conical flask, dropper, funnel, heating bottle, heating mantle, measuring bottle, paper tape, volumetric flask, test tubes, thermometer, Whatman filter paper (12.5 cm) and pH litmus paper.

Plate 1: Crab shell

2.2 Methods

The methods of analysis used consist of collection of the crustacean shells, oven-dryingand grinding to powder, Atomic Absorption Spectrophotometry (AAS) analyses of the selected heavy metals concentrations in IMMW, production of chitosan adsorbents, batch adsorption experiments, best fitted adsorption isotherm and kinetics model.

2.2.1 Preparation of chitosan adsorbents

1. Collection and preparation of chitosan from crab crustacean's shells

The crustacean shells samples were collected from riverine area Makoko fish market at Oyingbo Lagos State, Nigeria. These shells were washed with distilled water and air-dried for 48 h to get rid of all moisture content. Thereafter, pulverized and sieved to 300 µm size. The prepared powders were subjected to demineralization, deproteinization a*nd deacetylation* processes based on modified method of Rayane et al. (2017).

2. Demineralization process

The demineralization procedure was performed on the crab crustacean shells with the purpose of eliminating the calcium carbonate ($CaCO_3$) content. The experimental procedure involved the introduction of 500 mL of hydrochloric acid (HCl) with a concentration of 0.1M to 50 g of the crab shell powder. Following this, the combination underwent agitation for a period of one hour at room temperature, resulting in the release of carbon dioxide gas as a byproduct of the reaction. Subsequently, the mixture was kept undisturbed for a duration of twenty-four hours in order to facilitate the process of settlement. Furthermore, the shells powder that had undergone demineralization were subjected to filtering and subsequent washing using distilled water until a neutral pH of 7 was attained. The materials were subjected to oven drying at a temperature of 70°C for a period of one night, following the methodology outlined by Jadhav and Diwan in their 2018 publication.

3. Deproteinization process

The demineralized crustacean shell powders were deproteinized in order to remove protein. NaOH (1.25 M) was added to each of the demineralized crustacean shells at a solid liquid ratio of 1:15 (g/mL) and the mixtures agitated at 60 °C for 1 h before being left for 24 h. Thereafter, the mixture was filtrated using 300 µm sieve and washed with distilled water until it achieved pH of 7. The product was then immersed in 100 mL of NaOCl for 30 mins to further bleach it in order to eliminate pigments and then oven - dried at 70 °C overnight. The dried residue obtained is chitin powder according to Jadhav and Diwan (2018).

4. Deacetylation process

A solution of NaOH (50 g) was prepared by dissolving it in 100 mL of distilled water. This concentrated NaOH solution was then utilised for the treatment of chitin in crustacean shells and allowed to react for a duration of 1 hour at ambient temperature. The chitosan powder for the chosen crustacean shell was produced by subjecting it to a pH of 7 and subsequently drying in an oven at a temperature of 60 °C overnight. The specimen was placed in desiccator to ensure their preservation and preparedness for subsequent procedures and utilisation, following the methodology outlined by Jadhav and Diwan (2018).

5. Production of activated chitosan

The crab chitosan powders (50 g each) was soaked in 0.1 M of HCl acid for 24 h. Thereafter, washed to pH of 7 and oven dried at 60 °C overnight before being stored in desiccator in readiness for use (Adetoro and Ojoawo, 2020).

2.2.2 Analysis of concentrations of metals present in the IMMW- initial concentrations of the metals (Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}) present in the wastewater before treatment were estimated using AAS analysis in the department of Chemical Engineering, AfeBabalola University Ado Ekiti, Nigeria. The IMMW sample (10 mL) was measured and poured into a test tube and mixed with nitric acid (HNO_3) for digestion. Another test tube was provided with 10 mL of a blank sample. The test tubes were placed on heating mantles and their contents heated at 100 ℃for about 10 mins. The equipment was adjusted in each time to the wavelengths of metals to be analyzed while its mono-chromator measured the quantities of the absorbed metals. The flame that was in the analysis is air-acetylene. (Adetoro *et al*., 2022).

2.2.3 Treatment of IMMW with CRAB CHITOSAN (CRC) and ACTIVATED CRAB CHITOSAN (ACRC)–Twelve conical flasks of 100 mL volume were labelled A to L, and then 50 mL of the untreated IMMW were put in each flask. After this 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6g of both CRC and ACRC was added to the twelve respective conical flasks. The flasks were placed in rotary shaker and agitated at a speed of 150 rpm for 1 hour at a room temperature of 26°C. The filtrate from each flask was subjected to AAS analysis.

2.2.4 Investigation of effects of adsorption parameters

The batch adsorption experiments of the selected heavy metals were performed using adsorption parameters such as: adsorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g), agitation rate (50, 75, 100, 125 and 150 rpm), contact time (15, 30, 45, 60, 75 and 90 mins.), pH (4, 6, 8, and 10), and temperature (25, 35, 45, 55 and 65 ℃). OFAT analyses were performed for all the adsorption parameters. The Removal Efficiency (RE) were carried out using Equation 1 according to Adetoro and Ojoawo (2021).

$$RE = \frac{(C_O - C_e)}{C_O} \text{ x } 100\% \qquad 1$$

Where C_0 and Ce is the initial and equilibrium concentration in the solution (mg/L).

2.2.5 Adsorption isotherm studies

The appropriateness of the adsorption data behavior was assessed by employing three selected isotherms, Freundlich, Langmuir and Temkin.Equations 2 was utilized for linear analyses of the Freundlich isotherm. Langmuir isotherm suitability was established using Equation 3 (linear) and 4 (separation factor).Temkin isotherm was established using Equation 5

$$Log q_e = Log K_f + \frac{1}{n} Log C_e \qquad 2$$

Irreversible, non-optimum and optimum adsorption processes were represented by *1/n* = 0, *1/n* > 1 and 0 <*1/n* < 1, respectively (after Bello et al., 2019; Adetoro and Ojoawo, 2021).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{b}{q_m} \qquad 3$$

$$R_L = \frac{1}{1 + K.C_o} \qquad 4$$

Where C_e (mg/L) is the equilibrium concentration; q_e(mg/g) is the amount of ion adsorbed at equilibrium, q_m and b (i.e. b = 1/K) are Langmuir constants related to capacity and energy of adsorption respectively. Non-optimum, linear, irreversible and optimum adsorption requires that R_L> 1, 1, 0 and 0 <R_L< 1 respectively (Bello et al., 2019; Adetoro and Ojoawo, 2021).

$$qe = B \ln A + B \ln Ce \qquad 5$$

where B = RT/b, T is the absolute temperature in K and R is the universal gas constant 8.3143j/mol K. The constant b is related to the heat of adsorption qe (mg/g) and Ce (mg/l) and the equilibrium concentration respectively. A and B are constants related to adsorption capacity and intensity of adsorption (Adetoro and Ojoawo, 2020).

2.2.6 Adsorption kinetic studies

The batch adsorption data were compared with two selected adsorption kinetics models: pseudo-second-order and intra-particle diffusion. Equations 6 was used for linear analyses of the pseudo-second-order kinetic model, while intra-particle diffusion analysis was carried out using Equation 7 (after Bello et al., 2019; Adetoro and Ojoawo, 2021).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad 6$$

where K_2= pseudo-second-order rate constant, q_t and q_e = adsorption capacity at time *t* and equilibrium respectively, $K_{diff}$is the intra-particle diffusion rate constant (mg/(gmin)) and *C* is the intercept (Bello et al., 2019; Adetoro and Ojoawo, 2021).

$$q_t = K_{diff} (t^{1/2}) + C \qquad 7$$

3 Results and Discussions

3.1 Concentrations of heavy metal ions in the IMMW sample

The results of concentrations of heavy metals in the IMMW sample before and after treatment using AAS analyses was shown in Table 1. The presence of the selected heavy metals in the IMMW were 103.60, 133.43, 160.57 and 56.70 mg/L for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. All the heavy metals' concentrations were higher than the permissible limits as stipulated by WHO (2022), which portray possible contamination of soil, water and surroundings of the study area by the mining wastewater.

Cd^{2+} and Zn^{2+} were totally removed by CrC, while Cu^{2+} and Pb^{2+} were drastically reduced. ACrC reduced Cu^{2+} and Pb^{2+} further, though Pb^{2+} concentration is still above the permissible limit of WHO (2022).

Table 1: Concentration of heavy metals in the IMMW sample

Heavy metal	Concentration (mg/L)			WHO (2022) Standards
	Before Treatment	After Treatment		
	IMMW	Crab chitosan	Activated Crab chitosan	
Cu^{2+}	103.6	0.132	0.089	1
Cd^{2+}	133.43	ND	ND	0.003
Pb^{2+}	160.57	1.479	0.438	0.01
Zn^{2+}	56.7	ND	ND	3

*ND – Not Detected

3.2 Effects of adsorbent dosage

Removal Efficiencies (REs) of the selected heavy metals with adsorbent dosages ofCrC and ACrC are shown in Figures 1 and 2 respectively. The REs of Cu^{2+}, Cd^{2+} and Pb^{2+} decreased with increase in adsorbent dosage, while Zn^{2+} remained constant for CrC. Moreover, theACrC has REs of Cu^{2+}, Cd^{2+} and Zn^{2+} decreased, while Pb^{2+} increased as the adsorbent dosage increases. Both adsorbents dosages attained optimum at 0.1 g, which resulted in CrC having REs of 99.87,100, 99.72 and 100 %; while ACrC has REs of 99.92, 100, 99.07 and 100 % for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. Both adsorbents were able to remove two heavy metals (Cd^{2+} and Zn^{2+}) completely and drastically reduced the remaining two heavy metals (Cu^{2+} and Pb^{2+}); though the ACrCis better than the other one.

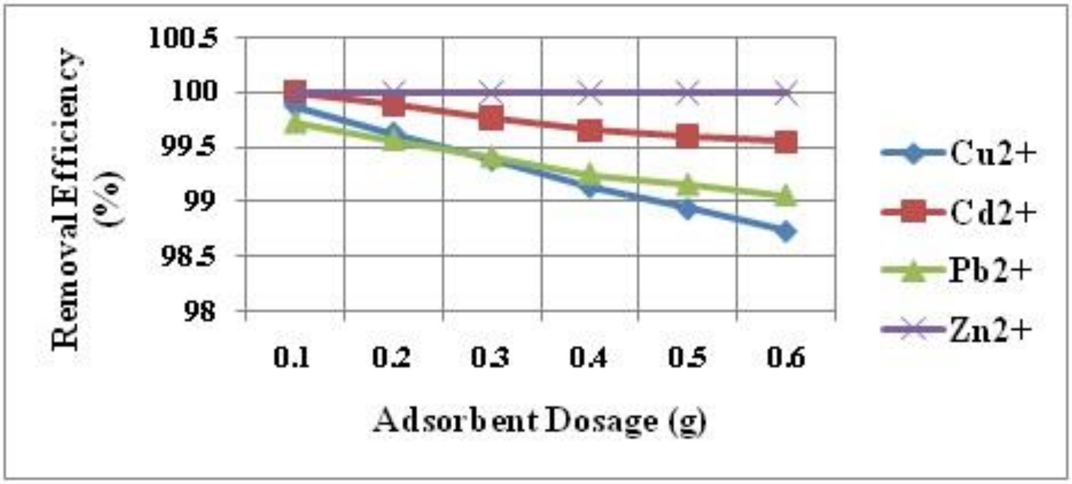

Figure 1: Removal Efficiency Trend with Crab Chitosan Adsorbent Dosage

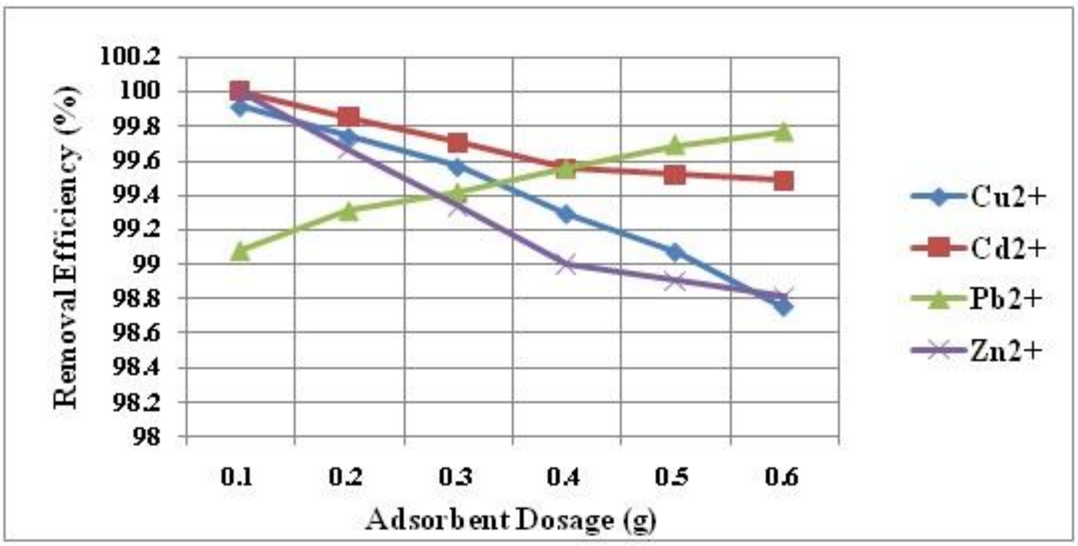

Figure 2: Removal Efficiency Trend with Activated Crab Chitosan Adsorbent Dosage

3.3 Effects of agitation rate

REs of the selected heavy metals with agitation rate of CrCand ACrC are shown in Figures 3 and 4 respectively. The REs of Cu^{2+}, Cd^{2+} and Pb^{2+} decreased with increase in agitation rate, while Zn^{2+} remained constant for crab chitosan. Moreover, the crab activated chitosan has REs of Cu^{2+}, Pb^{2+} and Zn^{2+} decreased, while Cd^{2+} increased as the agitation rate increases. CrC agitation rate reached optimum at 150 rpm, which resulted in CrC having REs of 99.90, 100, 99.21 and 100 %; while ACrCoptimum at 50 rpm with REs of 100, 99.60, 99.83 and 100 % for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. Both adsorbents were able to remove two different heavy metals (CrC- Cd^{2+} and Zn^{2+}; ACRC - Cu^{2+} and Zn^{2+}) completely and drastically reduced the remaining two heavy metals.

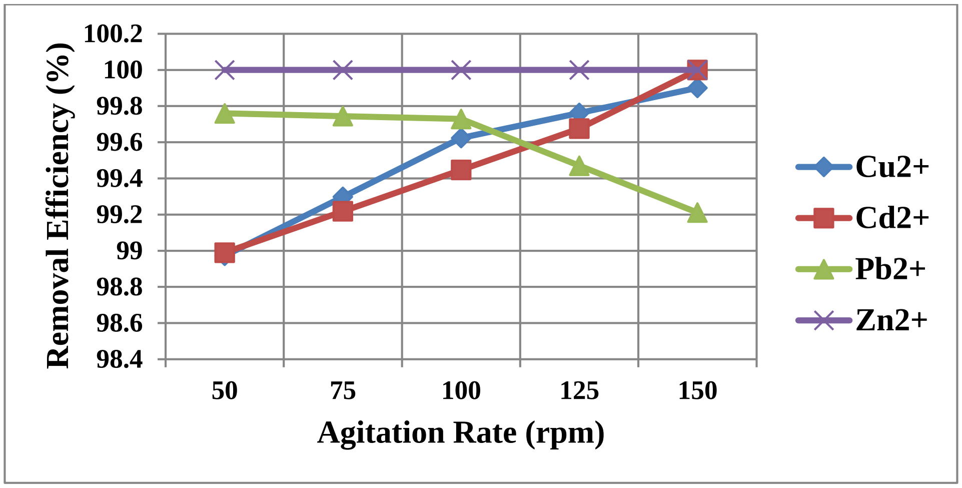

Figure 3: Removal Efficiency Trend with Crab Chitosan Agitation Rate

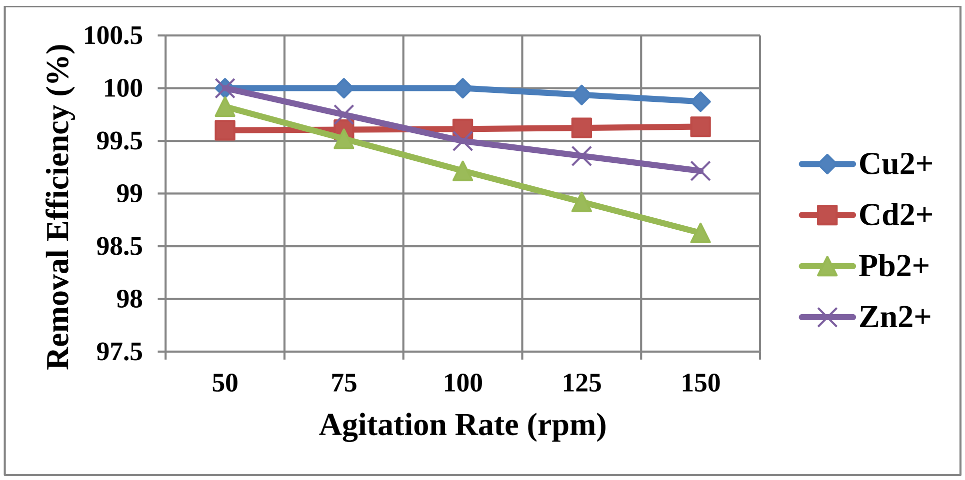

Figure 4: Removal Efficiency Trend with Activated Crab Chitosan Agitation Rate

3.4 Effects of contact time

REs of the selected heavy metals with agitation rate of CrCand ACrC are shown in Figures 5 and 6 respectively. The REs of Cu^{2+}, Cd^{2+} and Zn^{2+} decreased with increase in contact time, while Pb^{2+} increased for CrC. Moreover, the ACrC has REs of Cu^{2+} and Cd^{2+} being decreased, while Pb^{2+} and Zn^{2+} increased as the contact time increases. CrC reached optimum at 15 minutes, which resulted in REs of 99.87, 99.66, 98.98 and 100 %; while ACrC also attained optimum at 15 minutes with REs of 100, 99.90, 99.31 and 98.91 % for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. Both adsorbents were able to remove one different heavy metal (CrC - Zn^{2+}; ACrC - Cu^{2+}) completely and drastically reduced the remaining three heavy metals.

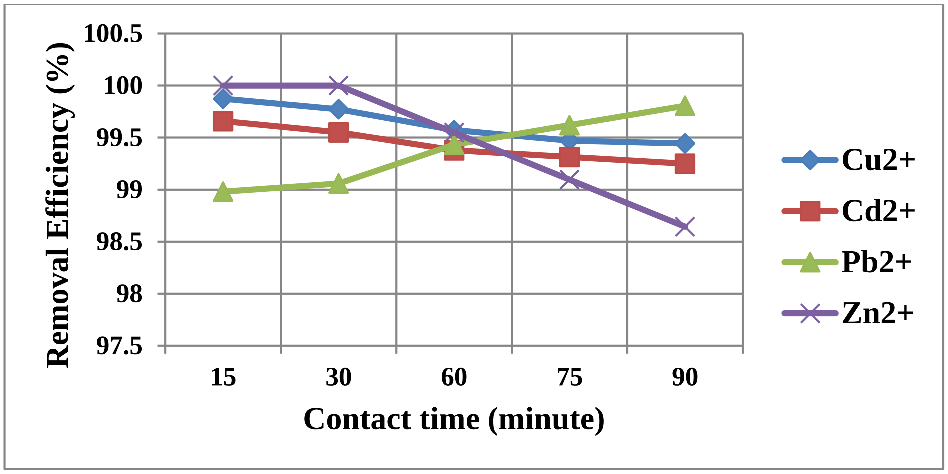

Figure 5: Removal Efficiency Trend with Crab Chitosan Contact Time

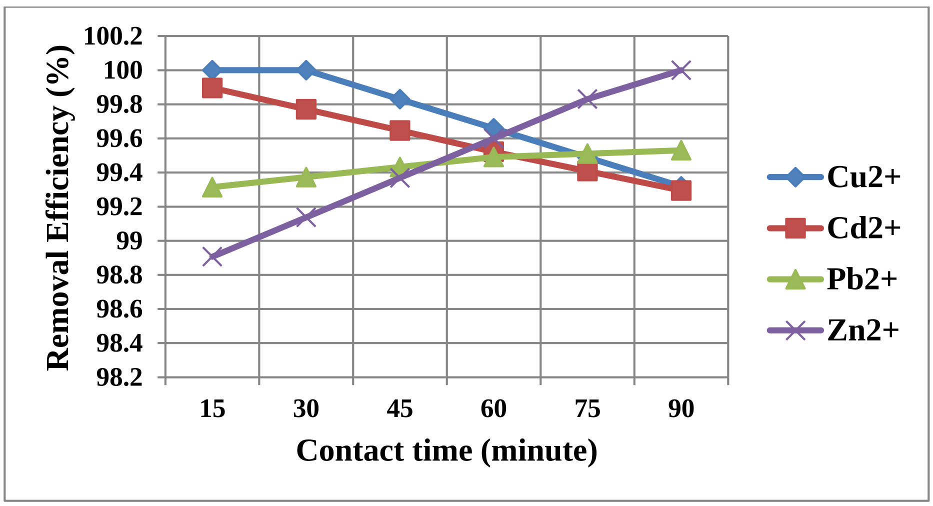

Figure 6: Removal Efficiency Trend with Activated Crab Chitosan Contact Time

3.5 Effects of pH

REs of the selected heavy metals with pH of CrC and ACrC are shown in Figures 7 and 8 respectively. The RE of Cu^{2+} decreased, Cd^{2+} and Pb^{2+} increased with increase in pH, while Zn^{2+} remained constant for CrC. Moreover, the REs of Cu^{2+}, Cd^{2+} and Zn^{2+} decreased with increase in pH, while Pb^{2+} reduced forACrC. The RE of both adsorbents reached optimum at pH of 4, which resulted in RE values of 100, 99.65, 98.49 and 100 %; while that of ACrC were 100, 99.82, 98.93 and 100 % for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. Both adsorbents were able to remove the same two heavy metals (Cu^{2+} and Zn^{2+}) completely and drastically reduced the remaining two heavy metals; though there was improvement with the activated one.

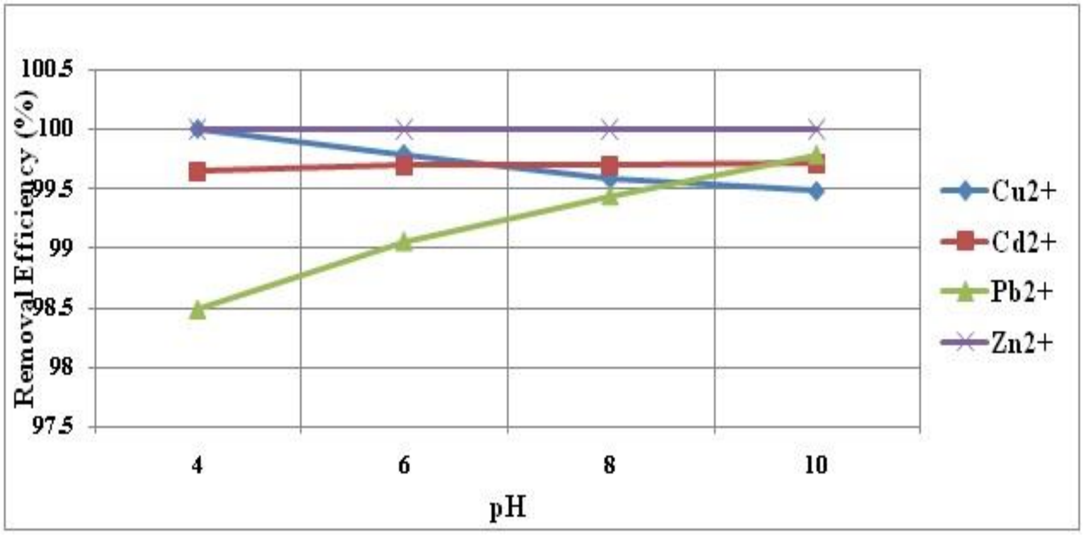

Figure 7: Removal Efficiency Trend with pH for Crab Chitosan

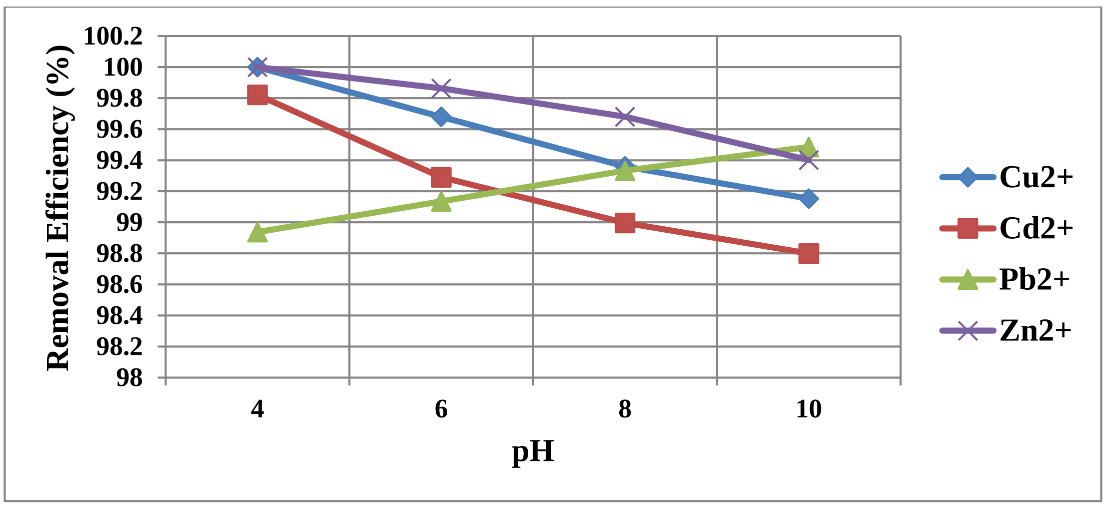

Figure 8: Removal Efficiency Trend with pH for Activated Crab Chitosan

3.6 Effects of temperature

REs of the selected heavy metals with temperature of CrC andACrCare shown in Figures 9 and 10 respectively. The REs of all the selected heavy metals decreased except Zn^{2+}, which remained constant as the temperature increases for CrC. Moreover, the REs of Cu^{2+}, Cd^{2+} and Zn^{2+} increased with increase in temperature, while Pb^{2+} decreased for ACrC. The RE of CrC reached optimum at 25 °C, which resulted in RE values of 100, 99.40, 99.83 and 100 % for Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. While ACrCattained maximum RE at 65 °C. The CrC removed two heavy metals completely, while it reduced to one with ACrC. These results portrayed that there was no improvement in the adsorbent efficacy as regards temperature or there was negative influence of temperature on the ACrC.

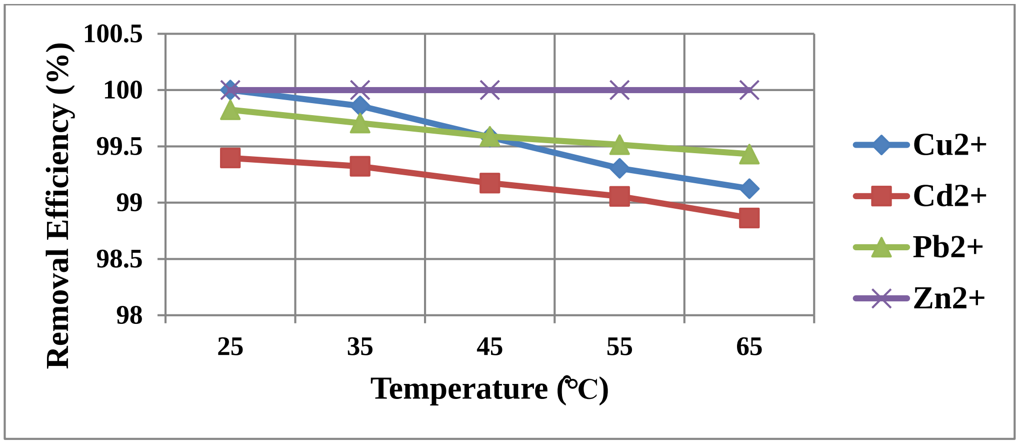

Figure 9: Removal Efficiency Trend with Temperature for Crab Chitosan

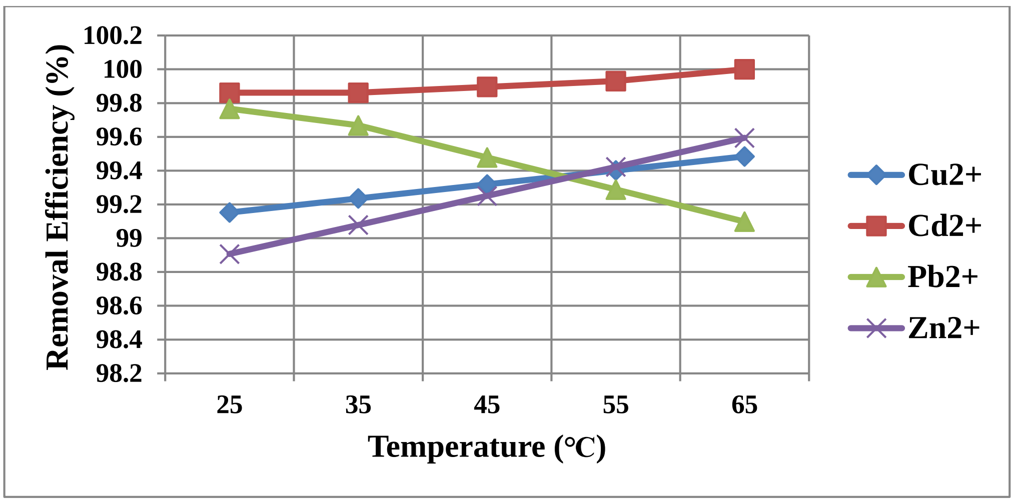

Figure 10: Removal Efficiency Trend with Temperature for Activated Crab Chitosan

3.7 Adsorption isotherms

The Freundlich isotherm for the heavy metals under consideration was shown in Table 2. The experimental findings of 1/n indicated that the concentrations of Pb^{2+} ions in activated crab chitosan was found to exceed unity, suggesting suboptimal adsorption. On the other hand, the remaining heavy metals in the crab adsorbents displayed a value of zero or negative, suggesting that they undergo irreversible adsorption. The reactions observed can be classified as chemisorption reactions, as described by Adetoro and Ojoawo (2020). The Freundlich isotherm is the most appropriate adsorption model for $Cu^{2+,}$ Cd^{2+}, and Pb^{2+} ions, with R^2 values indicating a strong fit to the data. The descending order of R^2 values for the adsorption of these ions onto crab chitosan is as follows: Pb^{2+} (0.9980) > Cu^{2+} (0.9902) > Cd^{2+} (0.9651). The Freundlich isotherm was found to be best matched by the adsorption models of activated

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crab chitosan in the following order: Cu^{2+} (0.9986) > Zn^{2+} (0.9695) > Cd^{2+} (0.9657) > Pb^{2+} (0.8944).

Table 2: Isotherm values for the adsorption of the heavy metals

Model parameter	Adsorbents							
	Crab Chitosan				Activated Crab Chitosan			
	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}
Freundlich								
1/n	-0.7797	-1.0182	-1.4203	0	-0.6789	-1.1646	1.2177	-1.1419
K	1.0556	0.9769	1.3887	1	1.009	1.0179	1.5644	0.6362
R^2	0.9902	0.9651	0.998	0	0.9986	0.9657	0.8944	0.9695
Langmuir								
q_{max}	7.8616	11.5207	10.1215	0	7.9872	11.8343	-65.3595	4.9579
K	-4.198	-1.8046	-15.6825	0	-5.5644	-11.9014	0.3592	-12.0778
R_L	-0.0023	-0.0042	-0.0004	1	-0.0017	-0.0006	0.017	-0.0015
R^2	0.9431	0.9123	0.9453	0	0.9666	0.8945	0.9599	0.8987
Temkin								
B	-18.87	26.87	-51.954	0	-16.133	28.304	41.113	11.92
K_T	0.5566	6.3536	0.5667	0	0.5838	5.0063	2.8676	5.1895
R^2	0.9775	0.6775	0.9359	0	0.9485	0.5752	0.7171	0.5929

The Langmuir isotherm for the heavy metals selected for the adsorbents was presented in Table 2. The findings revealed that the adsorption capacities (R_L) of Zn^{2+} in crab chitosan was equal to one, indicating a linear adsorption behavior. The Pb^{2+} ions present in activated crab chitosan, exhibited values ranging from zero to one, indicating an optimal level of adsorption. Conversely, the remaining heavy metals had negative values, suggesting irreversible adsorption (Adetoro et al., 2022). The Langmuir isotherm was shown to be the most suitable model for describing the adsorption behavior of the selected heavy metals on the adsorbents, with the exception of Zn^{2+} on crab chitosan. Table 2 present the results of Temkin isotherm for the selected heavy metals of the adsorbents. The adsorption models of all the selected heavy metals except $Zn^{2+}$of crab chitosan, all the selected heavy metals of activated crab chitosan best suited Temkin isotherm with their R^2 ranged between 0.5752 and 0.9775.

3.7 Adsorption kinetics

The results fitting of pseudo-second-order and intra-particle diffusion models to the data for metal adsorption by both adsorbents are presented in Table 3. The actual and estimated adsorption capabilities, denoted as qe (expt.) and qe (cal.) respectively, were found to be nearly identical across all cases and for each of the selected heavy metals and adsorbents. The findings indicate that the adsorption processes for all heavy metals adhered closely to the pseudo-second-order kinetic model, as evidenced by a high correlation coefficient approaching unity (R^2 = 1) in all instances. Adetoro et al. (2022) have shown that the rate of adsorption is typically regulated by chemical adsorption, as described by the pseudo-second-order kinetic model.

Table 3: Kinetic values for the adsorption of the heavy metals

Model	Kinetic parameter	Adsorbents							
		Crab chitosan				Activated Crab chitosan			
		Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}
Pseudo- second order	R^2	0.9992	1	0.9992	1	0.9998	1	0.9998	1
	q_e expt.(mg/g)	80.066	66.715	80.066	28.35	79.546	66.715	79.546	28.35
	$q_e$cal (mg/g)	80	66.711	80	28.345	80	66.707	80	28.353
	K_2 (/min)	0.049	-0.14	0.049	-0.073	0.223	-0.09	0.223	0.114
Intra-particle	R^2	0.9514	0.9999	0.9514	0.9593	0.9843	0.9891	0.9843	0.9902
	C	78.922	66.676	78.922	28.603	79.61	66.944	79.61	27.807
	K_{diff}	0.1211	-0.0486	0.1211	-0.0635	0.0325	-0.0719	0.0325	0.0564

The results of the intra-particle kinetic model for the selected heavy metals showed that the determinant factor C varied from 27.807 (in the case of Zn^{2+}adsorption on activated crab chitosan) to 79.61 (in the case of Cu^{2+} and Pb^{2+} adsorption on activated crab chitosan) across both adsorbents. Based on the findings of Bello et al. (2015) and Adetoro et al. (2022), it can be observed that there exists a positive correlation between the intercept C and the extent of surface adsorption in the rate controlling step. This observation demonstrated a higher level of involvement of surface adsorption in the rate-determining processes of the chosen heavy metals.

4 Conclusion

Both chitosan adsorbents were effective at 0.1 dosage; 150 rpm (for CRC) and 50 rpm for ACRC; 15 to 30 minutes at pH of 4. Temperature has no effect on them as CRC was able to remove two heavy metals at room temperature (i.e. 25 °C), while the ACRC did not remove any heavy metal. The result also indicated that the activation process on the crab chitosan has effect on the agitation rate as it was reduced from 150 rpm (for raw crab chitosan) to 50 rpm (for activated crab chitosan). CrC and ACrC was effective in removing completelytwo heavy metals from IMMW and this makes the water suitable for reuse without any adverse effect on human at lower cost. All the selected parameters (dosage, agitation rate, contact time and pH) played significant roles in the biosorption process of remediating the selected heavy metals from IMMW. The majority of the chosen heavy metals across the adsorbents demonstrated compatibility with the adsorption isotherms. However, it should be noted that Zn^{2+} in crab chitosan exhibited exceptions to this trend. All data points were found to be most accurately described by the pseudo-second-order kinetic model since the calculated q_e and experimental q_e are almost similar.

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