



ISOTHERM AND KINETIC STUDIES OF CO(II) AND NI(II) IONS REMOVAL FROM SIMULATED WASTEWATER BY SPINES OF *Bombaxbuonopozense*

*Mustapha S¹., Dauda B.E.N¹., Ndamitso M. M¹., Abdullahi Z¹., Gbajabiamila A.T².,
Mathew, J.T¹.

¹Department of Chemistry, Federal University of Technology, P.M.B. 65, Minna, Nigeria

²Department of Chemical Sciences, Federal University Otuoke, P.M.B. 126, Yenagoa, Nigeria

*Corresponding author E-mail: saheedmustapha09@gmail.com

ABSTRACT

Adsorption studies of heavy metals (Co and Ni) from aqueous solution were performed using spines of *Bombax buonopozense* (raw), carbon prepared from *Bombax buonopozense* (AC₁) and activated carbon prepared from modification of spines of cotton silk tree (AC₂). Batch experiments were performed as function of contact time, initial concentration, pH and dosage. The respective optimum contact times required for adsorption Co and Ni were 90 min. The experimental equilibrium adsorption data were tested for the Freundlich and Langmuir equations. The adsorption kinetic data were treated with pseudo-first-order and pseudo-second-order. The results indicated that second order model better described the adsorption kinetic data. This could be as a result of ion exchange involved in the removal of the metal ions by the adsorbents. Therefore, sorption using spines of *Bombax buonopozense* has been adjudged as one of the best tools for replacing conventional methods for the removal of heavy metals because of its cost effectiveness, efficiency and availability of the materials used as biosorbents.

Keywords: Adsorption, Heavy metals, Modification, Conventional methods

1. INTRODUCTION

Potentially toxic elements are individual metals and metal compounds that affect human when present in the environment at low levels. The ever-growing population, unplanned urbanization, rapid industrialization and unskilled utilization of natural water resources have led to deterioration in water quality of many parts of the world. Thus, discharge of these metal pollutants into the aquatic environment could damage the quality of the ecosystem thereby rendering water bodies unsuitable for their intended uses. This in effect, poses serious health threat to the immediate population since, most of them are toxic to living organisms due to their non-degradable nature (Abowei and Sikoki 2005). Therefore, in industrial activities such as discharge of industrial effluents, mining and metallurgical operations have intensified environmental pollution problems with deterioration of several ecosystems (Lalitagauri *et al.*, 2000). The immense environmental impact of heavy metal pollution has been reported by Zouboulis *et al.* (2007) that these metals are capable of causing both ecological and health damages. Due to their accumulation and transportation down the food chain, these metals have caused problems such as dysfunction in the renal, reproductive and central nervous system (Manaham, 2004). They are also known for their ability to cause diseases and disorder such as headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness (Ozer and Pirincci, 2006).

Removal and recovery of heavy metals are very important with respect to environmental and economical considerations (Nourbakhsh *et al.*, 2002). Various methods have been developed to remove these potentially toxic elements from industrial wastewater and these include precipitation, electro dialysis, membrane processes, ionic exchange and floatation (Xiaomin *et al.*, 2004). Adsorption, on the other hand, has emerged as a potential alternative to conventional physicochemical technologies in waste-treatment facilities. It is an effective separation process that has advantages in terms of cost, flexibility, simplicity of design and ease of operation. It also does not result in the formation of harmful substances (Rafatullah *et al.*, 2010). However, biosorption mechanisms remain unclear and hence required further studies (Vieira *et al.*, 2008).

It was on this basis that this readily available and affordable agricultural waste known as the spine of *Bombaxbuonopozense* was used to treat wastewater containing potentially toxic element (Ni and Co), in order to remedy our environment from the effect of these metals as well as improve the quality of water. In an effort to evolve a useful user-friendly, eco-friendly and low cost-effective, the present study was taken up. This study examined the adsorption of Co(II) and Ni(II) ions using spines of this plant.

2. MATERIALS AND METHODS

Preparation and Characterization of Biosorbent

The low cost adsorbents used in this study were derived from spine of *Bombaxbuonopozense* (cotton silk tree). The samples obtained from farms in Bosso Local Government, Niger State, Nigeria, where they are



generated as primary agricultural waste. These were extensively washed to remove dirt and other particulate matter that might interact with sorbed metal ions. They were then into chip, washed with distilled water, sun dried, ground and then sieved to particle size of 200 μ m. The materials after sieving were divided into three parts: The first part was labeled 'Raw'. The second portion was placed in crucibles and positioned at the center of a muffle furnace for 15 min at 500°C and carbonized (AC₁). This was cooled and washed with deionized water. The third portion was activated as mentioned above (AC₂) and then washed with benzoic acid. The percentage yield of the adsorbent was calculated using:

$$\% \text{ Yield} = \frac{W_o - W_c}{W_o} \times 100 \quad (1)$$

Where W_o is the mass of material before carbonization and W_c is the mass of material after carbonization. The physicochemical characteristics of the adsorbents were measured using standard procedures.

Preparation of Metal Ion concentration

Stock solution of 1000 mg/dm³ concentration were prepared by dissolving appropriate amounts of CoCl₂.6H₂O and NiSO₄.6H₂O in distilled water to obtain standard Co and Ni respectively. Standard solutions concentration were prepared by successive dilution of the respective stock solutions.

Batch Adsorption Studied

Effect of four parameters on the adsorption of the metal ions in solutions were considered and these were contact time, metal ion concentration, pH and dosage. All experiments were carried out with constant shaking for uniform distribution of the optimum time. The solutions were filtered and the filtrates were analyzed by atomic absorption spectroscopy (AAS) for residual metal concentrations. Removal efficiency and adsorption capacity were calculated by using the relationship:

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

$$q_e = \frac{C_i - C_e}{M} \times 100 \quad (3)$$

Where C_i is initial concentration of metal ions in the solution (mg/dm³), C_e is the equilibrium concentration or initial concentration of metal ions in the solution (mg/dm³), V is the initial volume of metal ion solution used (dm³) and M is the mass of adsorbent (g).

Adsorption Isotherms

Adsorption isotherm were used to describe the equilibrium adsorptive behaviours and to investigate the adsorption mechanism. Langmuir and Freundlich isotherm equations were investigated to fit the experimental data

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (4)$$

$$\text{Freundlich: } \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where C_e is the equilibrium concentration (mg/dm³), q_e is the amount (mg/g) adsorbed at equilibrium time, Q_m and K_L are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg) respectively. K_F and n are Freundlich constants representing the adsorbent and favourability of adsorption respectively.

Adsorption Kinetics

The pseudo-first and pseudo-second order adsorption kinetic model were applied for the adsorption of the adsorbent of the adsorbents in this study using equation given below:

$$\text{Pseudo - first - order: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

$$\text{Pseudo - second - order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q_e and q_t are the amount adsorbed at equilibrium at time, t , while k_1 and k_2 are the pseudo-first-order rate constant (min⁻¹) and the second-order reaction rate equilibrium constant (g/mgmin) respectively.



3. DISCUSSION of RESULTS

Effect of Contact Time

The rate of adsorption is important when designing batch adsorption experiments. Therefore, it is significant to establish the time dependence of such system under various conditions. In this study, the adsorption of cobalt and nickel increased with contact time until it attained the maximum adsorption equilibrium at 90 min for the raw, carbonized and activated adsorbents as shown in Figure 1 and 2. These results showed that the adsorption process was fast due to large amounts of metal ions attached to the adsorbents within the first 90 min. The initial fast adsorption rate could be attributed to the sufficient surface binding sites on the substrates. The optimum time for cobalt and nickel obtained in this study are in accordance with the findings of Muthusamy et al. (2012). The higher percentage removal of metal ions could be due to the availability of large surface area of the adsorbents while the decrease in the removal of metal ions below the optimum time could be due to the exhaustion of the remaining surface sites and repulsive forces between the solute molecules and the bulk phase (Saravanane et al., 2012). Furthermore, increase in the residence time resulted in the desorption of the metal ions from the adsorbent surfaces. The rate of adsorption of these ions decreased probably due to the slow pore diffusion of the solute ions into the bulk of the adsorbents or due to the longer diffusion process of these ions into the inner cavities of the solutions (Li et al., 2010).

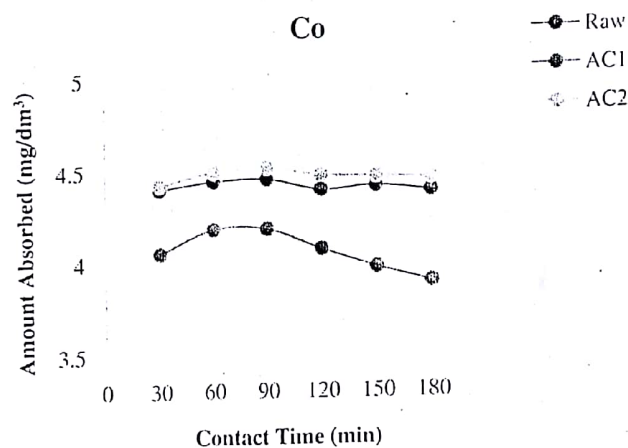


Fig. 1: Effect of contact time on the removal of cobalt ions using 0.5 g adsorbent's weight, pH 6 at temperature $28^{\circ}\text{C} \pm 1$ and a 5 mg/dm^3 cobalt solution

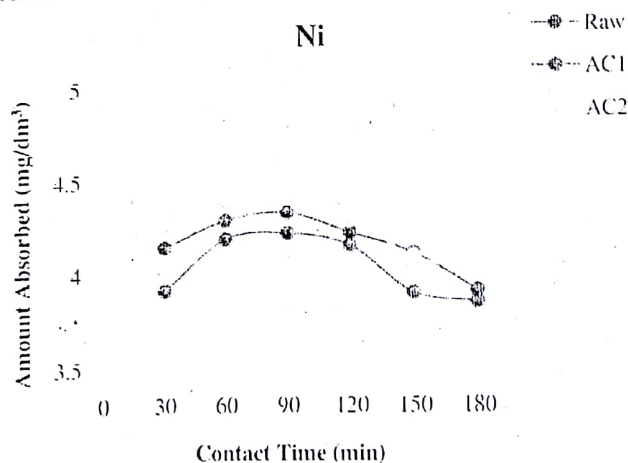


Fig. 2: Effect of contact time on the removal of nickel ions using 0.5 g adsorbent's weight, pH 6.9 at temperature $28^{\circ}\text{C} \pm 1$ and a nickel standard solution of 5 mg/dm^3 cobalt

Effect of Initial Concentration

Studies were performed with cobalt and nickel concentrations ranging from 10 to 50 mg/dm^3 . Figure 3 and 4 show that the removal of cobalt and nickel initially depended on the initial concentrations of metal ions



which decreased with increase in the initial concentration. According to Arief et al. (2008), the initial concentration acts as driving force that tries to overcome mass transfer resistance to metal ions transport between the solution and the surface of the adsorbents. Therefore, at higher concentration, the metal ions are left unabsorbed due to saturation of adsorption site which leaves the amount of adsorbate concentration constant (Bhatti et al., 2007). This is as a result of an increase in amount of ions competing for the available binding site or inadequate availability of adsorption sites on the adsorbent at high concentrations. This means that there are more adsorption sites on the adsorbent at low concentration of the metal ion than at higher concentration. As the surface of adsorption to metal ion concentration decrease with an increase in metal ion concentration, the amount of metal ion removed is reduced and this is what was observed in this study.

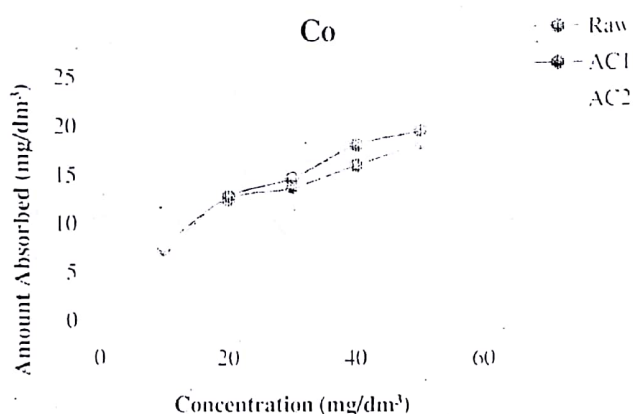


Fig. 3: Effect of metal ion concentrations on the removal of cobalt ions at 90 min contact time, pH 6.9 and adsorbent dosage of 0.5 g

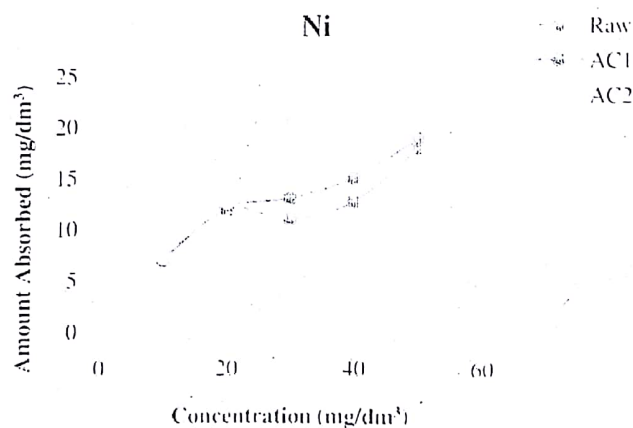


Fig. 4: Effect of variation of initial concentrations on the removal of nickel using contact time of 90 min at pH 6.9 and adsorbent weight of 0.5 g

Effect of pH

The effect of solution pH on Co(II) and Ni(II) ions removal are shown in Figures 5 and 6. The pH of aqueous solution is an important controlling parameter in adsorption process. This is due to the fact that hydrogen ion (H^+) are strong competing ions and the solution pH influences the chemical speciation of the functional groups onto adsorbent surface. Low degree of adsorption at low pH values could be due to high concentration of H^+ ions which compete with the metal cations for the surface sites since at low pH the metal ions are present in aqueous solution as free cations. The strong function of the pH is as a result of surface charges on the adsorbents. Therefore, heavy metal cations are completely released in acidic conditions. There is a decrease in positive surface charges since deprotonation of the adsorbents functional groups occurs as a result of low electrostatic repulsion between the positively charged metal ions and the surface of adsorbents (El-Said, 2010). The high sorption levels at high pH values (high percentage removal) indicated that a high affinity for metal ions is predominant in this pH region. The removal of the positively charged metal ions increase as a result of the availability of more ligands having negative charges. Similar trends have been reported by Rozaini



et al. (2010) who stated that rise in pH usually results in increased metal ions sorption and decrease in their solubilities.

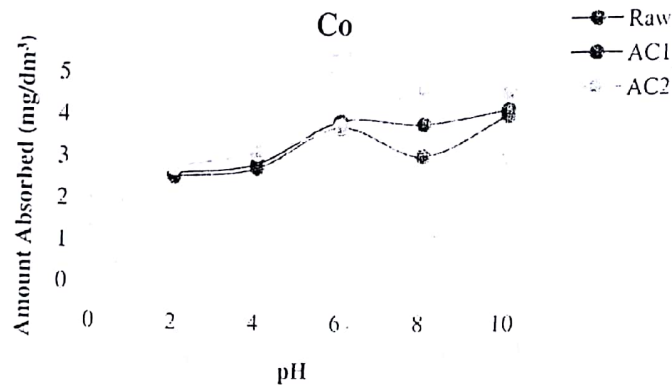


Fig. 5: Effect of pH on the removal of cobalt ions from 5 mg/dm³ standard solution and 0.5g adsorbent's weight

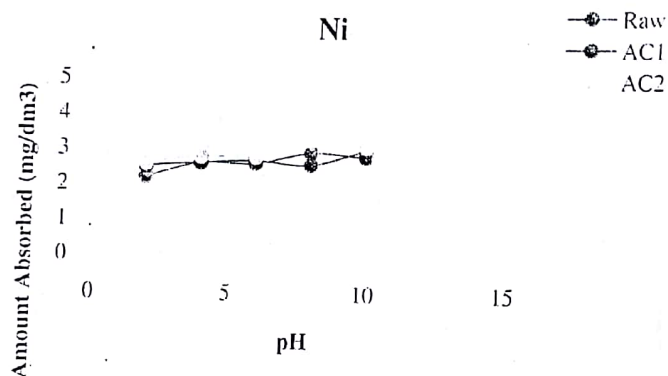


Fig. 6: Effect of pH on the removal of nickel ions from 5 mg/dm³ standard solution and 0.5g adsorbent's weight

Effect of Adsorbent Dosage

Effect of adsorbent doses on amounts of metal absorbed are shown in Figure 7 and 8. Amounts of metal ions removal increased when the adsorbent dose increase from 1 to 3.5 g. The increased adsorption with increase in sorbent dosage could be attributed to the availability of large surface areas and functional groups on the adsorbent with which the metal ions interacted. These chemical groups are significant in the formation of Vander Waals bonding since the functional groups play major roles in binding the metal ions to the adsorbents (Malik *et al.*, 2007). Aksu and Cagatay (2006) reported that lower biosorbent dosages yield higher uptake but lower percentage removal efficiencies. The adsorption capacity of the metal ions at different dosages decreased with increased adsorbent dose. The decrease in adsorption capacity with increase in dosage is as a result of increase in the remains-unsaturated as the available adsorption sites. These observations are in line with the report made by Khosravan and Lashkari (2011).

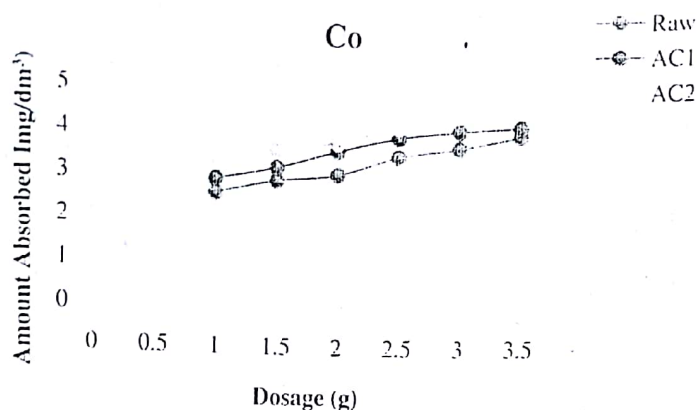


Fig. 7: Effect of adsorbent dose on the removal of cobalt ions from 5mg/dm³ standard solution at contact time 90 min and pH 6.9

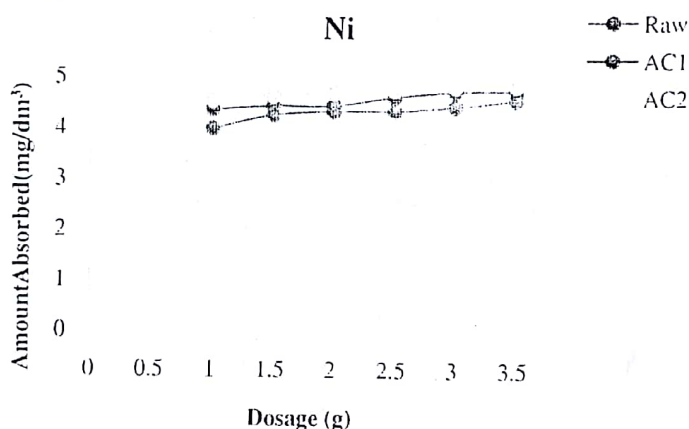


Fig. 8: Effect of adsorbent dose on the removal of nickel ions 5 mg/dm³ standard solution at contact time 90 min and pH 6.9

Adsorption Isotherms

Freundlich

Equilibrium biosorption studies were conducted for the removal of cobalt and nickel ions from solution of concentrations ranging from 10 to 50 mg/dm³ by raw, carbonized and activated adsorbents. The isotherm parameters shown in Table 1 reveals that the Freundlich isotherm coefficient and constant, n and K_F respectively. The plot of $\ln q_e$ against $\ln C_e$ were linear, indicated that adsorption data obeyed Freundlich adsorption isotherm. The Freundlich constant K_F for the adsorbents were in the range of 0.40 to 0.56 which are lower than the values reported by Ahalya *et al.* (2005). The biosorption intensity n is indicative of the bond energies between the metal ions and the adsorbents which showed a possibility of physisorption and slight chemisorption. The values of n were between 2 and 10 which are indications of good adsorption of cobalt and nickel by the spines of *Bombaxbuonopozense* which correlates with the findings of Nasernejad *et al.* (2005). These high correlation coefficients suggest that this model is the best that describes these equilibria obtained in this study.

Langmuir

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. Thus, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Q_m values for Co(II) and Ni(II) ions were in the range of 1.90 to 2.91 mg/g which are slightly higher than the values reported by Li *et al.* (2010) for modified areca waste.



Table 1: Adsorption isotherm parameters for Co(II) and Ni(II) removal by spines of *Bombaxbuonopozense*

Isotherm	Parameter	Co(II)			Ni(II)		
		Raw	AC ₁	AC ₂	Raw	AC ₁	AC ₂
Freundlich	K _F (mg/g)	0.56	0.5	0.44	0.41	0.4	0.4
	n	2.67	2.91	2.87	3.24	2.75	2.42
	R ²	0.959	0.984	0.955	0.774	0.94	0.965
Langmuir	Q _m (mg/g)	2.26	2.56	3.18	1.9	2.3	2.91
	K _L (L/mg)	2.24	0.89	0.27	0.46	0.36	0.23
	R ²	0.979	0.985	0.917	0.775	0.915	0.946

Kinetic Studies

First-order

The values of first-order rate constant k_1 and adsorption capacity q_e for the metal ions are shown in Table 2. The correlation coefficient for the sorption of these ions ranged from 0.02-0.685 which does not fit for the adsorption pattern of Co(II) and Ni(II) ions. According to Ho and Mackay (1999) the major drawback with first-order model is that in most cases, the equations does not fit well for experimental data over the entire range of contact times.

Second-order

The rate constant, k_2 , the R^2 and q_e values for the study are given in Table 2, showing that the R^2 values from the second order kinetics for these ions are high indicating that the pseudo-second-order-kinetic model provides a good correlation for their biosorption onto the spines of *Bombaxbuonopozense* instead of the pseudo-first-order model. This corresponds to the studies of Ejikeme *et al.* (2011) on the adsorption of heavy metal onto *Gambeya albida* seed shell activated carbon.

Table 2: Kinetic parameter for Co(II) and Ni(II) adsorption onto spines of *Bombax buonopozense*

Kinetic	Parameter	Co(II)			Ni(II)		
		Raw	AC ₁	AC ₂	Raw	AC ₁	AC ₂
First-order	q_e (mg/g)	0.314	0.314	0.276	0.266	0.297	0.262
	k_1	0.0001	0.001	0.001	0.001	0.001	0.001
	R ²	0.08	0.685	0.498	0.188	0.429	0.02
Second-order	q_e (mg/g)	0.044	0.058	0.095	0.099	0.092	0.093
	k_2	5.584	1.054	0.444	0.362	0.309	0.222
	R ²	0.993	0.975	0.946	0.882	0.858	0.819

4. CONCLUSION

The ability of spines of *Bombaxbuonopozense* adsorbents to remove Co(II) and Ni(II) from aqueous solution were investigated using equilibrium and kinetics studies. The percentage removal of two ions were found to depend on pH, adsorbent dosage, contact time and concentration. The equilibrium data agreed well with Freundlich isotherm which is suitable for a highly heterogeneous surface indicating a multi-layer adsorption. The kinetic data were found to follow the pseudo-second-order model. This investigation showed that the spines of this plant are promising biosorbent for the removal of Co(II) and Ni(II) from aqueous solutions. Hence, *Bombaxbuonopozense* commonly known as silk cotton tree will be of low cost but high economic value when employed as a natural product for adsorption of pollutants from aqueous solutions.

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