Studies on the Removal of Ni (II) from Aqueous Solutions Using Powder of Mosambi Fruit Peelings as a Low Cost Sorbent

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Abstract

In the present investigation, the powder of mosambi fruit peelings (PMFP) was used as an inexpensive and efficient adsorbent for Ni (II) removal from aqueous solutions. The influence of physico-chemical key parameters such as the initial metal ion concentration, pH, agitation time, particle size and adsorbent dosage has been considered in batch tests. Sorbent ability to adsorb Ni (II) ions was examined and the mechanism involved in the process investigated. The optimum results were determined at an initial metal ion concentration of 50 (mg L^{-1}), pH=4, agitation time – 90 min, an adsorbent dose (125 mg/50 ml) and the particle size (0.6 mm). The % adsorption, Langmuir constants [Q_0=29.41(mg/g) and b=0.4789(L/mg)], Freundlich constant K_f= 23.92(mg/g) and n=2.24(L/mg), Lagergren rate constants [K_{ad} (min^{-1}) = 4.37 x 10^{-2}] for [Ni (II)] 50 (mg L^{-1}), were determined for the adsorption system as a function of sorbate concentration. The equilibrium data obtained were tested using Langmuir, Freundlich adsorption isotherm models, and the kinetic data obtained were fitted to pseudo first order model.

Keywords: Adsorption; Ni (II) ions; Powder of Mosambi Fruit Peelings (PMFP); adsorption kinetics; adsorption isotherms.

1. Introduction

Heavy metals have a great tendency to bio-accumulate and end up as permanent additions to the environment. The removal of heavy metals from waste water has recently become the subject of considerable interest owing to strict legislations introduced to control water pollution. Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method. The development of low-cost adsorbents has led to the rapid growth of research interests in this field [1]. One of the important toxic metals, Nickel (II) finds its way into the 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 jewellery. Skin contact with nickel causes a painful disease called "nickel itch" which is fatal [2]. Heavy metals have a tendency to bio-accumulate and end up as permanent destructive elements in environment [3]. Heavy metals like Zn, Cu, Ni, and As are known to have toxic effects at very low concentrations [4] as well as very high concentration [5]. Nickel is a toxic heavy metal found in the environment as a result of various natural and industrial activities. Nickel has been implicated as an embryotoxin and teratogen [6]. The higher concentration of Ni causes poisoning effects like headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness [8].

These harmful effects of Ni (II) necessitate its removal from waste water before release in to streams. Nickel is well known heavy metal pollutant, which is present in effluents of electroplating industries to the tune of 20–200 ppm [9]. Studies of human cell cultures have indicated that nickel is a possible carcinogen, creating a need for the cleanup of nickel pollution. So it is very much essential to remove Ni from soil, industrial wastewater and effluents. The conventional methods which are commonly used for the removal of nickel from the industrial effluents are physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical

treatment, evaporative recovery, filtration, ion exchange, and membrane technologies. These processes may be ineffective or expensive, especially when the heavy metal ions in the contaminated media are high i.e. in order of 1-100 mg dissolved heavy metal ions per liter [8]. Secondly the operational problems and the high cost of treatment necessitate research for some newer methods. Biological methods such as biosorption/ bioaccumulation may provide an attractive alternative to physico-chemical methods for the removal of heavy metal ions [10]. In this context it may be noted that few non-conventional and less expensive adsorbents have been investigated for removal of Ni(II) such as sphagnum peat [11], blast furnace slag [12], apple waste [13], soybean and cottonseed husk [14], peat nut husk carbon [15], straw [16], treated saw dust and activated alumina [17] and silica gel. The acceptable limit of Ni in drinking water is 0.01mg/L and the industrial discharge limit in wastewater is 2mg/L [18]. Microorganisms uptake metal either actively (bioaccumulation) or passively (biosorption) [19-23]. In recent years, much attention has been focused on the removal of heavy metals using industrial wastes, agricultural wastes, etc. Many authors used natural adsorbents like activated carbon prepared from activated rice husk [24], agricultural solid waste [25], peanut hull [26] and fly ash [27]. In an effort to evolve a useful user-friendly, eco-friendly and economical process, the present study was taken up. The present study includes the adsorption studies on Nickel (II) using powder of mosambi fruit peelings. The efficiency of this adsorbent was studied and maximum adsorption and lowest equilibrium time for this adsorbent was recorded.

2. Methods

2.1. Adsorbent

Easy availability, economical to use and proven potential for other metals, have been the reasons for selection of this adsorbent Powder of Mosambi Fruit Peelings (PMFP) were used to adsorb Nickel (II).

2.2. Powder of Mosambi Fruit Peelings (PMFP)

Mosambi fruits are very famous in India. They belong to citrus family and are popularly called as sweet limes. It is the first choice of many Indians as fruit juice. The peelings of the fruits were collected from the shops, dried and chopped, cleaned and soaked in distilled water for 24 hrs. The soaked pieces of peelings were sun-dried and powdered. Size of the particles selected for the study was 0.6 mm.

2.3. Measurement of pH of the adsorbent

Five grams of adsorbent powder was taken into a 1000 ml beaker. To this 150 ml of freshly boiled and cooled water was added and then heated till boiling point. The contents were digested for ten minutes and kept aside for ten minutes. The solution was filtered and pH was measured. The metal ion solutions for standard solutions and further dilutions were prepared following the procedures described [28].

2.4. Preparation of metal ion solutions

The Nickel (II) was estimated using standard methods. AR grade chemicals and double distilled water were used for all the analyses. The concentrations of the metal ions were estimated using UV-visible spectrophotometer (ELICO SL 150).

Standard Nickel Solution: Nickel (II) solution was prepared by using AR Grade nickel ammonium sulphate; 6.7280 g of nickel ammonium sulphate was taken into a 1000 ml volumetric flask. 5 ml of 1% HNO_3 was added to it immediately. Then the contents were made up to 1000 ml with double distilled water.

2.5. Analysis of nickel (II)

Spectrophotometric analysis was adopted to estimate Nickel (II), by using dimethylglyoxime (DMG). Different standard solutions containing less than 100 mg/l of Nickel (II) were prepared and 2 ml of 20% w/v sodium tartarate solution 10 ml of 4% w/v potassium persulphate 2.5 ml of 5 M sodium hydroxide solutions and 15 ml of (1+30) HCl solutions were added. Again 0.6 ml of 1% DMG solutions were added to this mixture. The contents were made

upto 50 ml. The absorbance was measured after 30 minutes using UV–visible spectrophotometer at 465 nm. A reagent blank was also prepared for Nickel (II) solution. The amount of Nickel present in the sample was obtained from the calibration curve. The results for a heavy metal concentrations were expressed in mg L^{-1} while those of the concentration equilibrium, equilibrium time, and adsorption capacity etc., were compared with the Langmuir and Freundlich isotherms.

2.6. Batch Equilibrium Method

All experiments were carried out at 27^{0}C in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were carried out of taking 50 ml metal ion sample and known amount of the adsorbent in a 100 ml Stoppard conical flask. The flasks were agitated at 160 rpm for predetermined time intervals using a mechanical shaker at room temperature (27^{0}C). Control experiments were conducted without absorbent to given correction for metal ion adsorption on the walls of the container.

3. Results and Discussion

3.1. Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions, concentration of counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. To find out optimum pH for the removal of Nickel (II), 125 mg of the PMFP adsorbent in 50 ml solution of 50 mgL^{-1} of nickel (II) concentration are adjusted to different pH values ranging from 2.0 to 9.0. They were equilibrated for 120 minutes and centrifuged. The filtrates were tested for Ni (II) concentrations spectrophotometrically. Figure 1 shows the effect of pH on adsorption of Ni (II) ion.
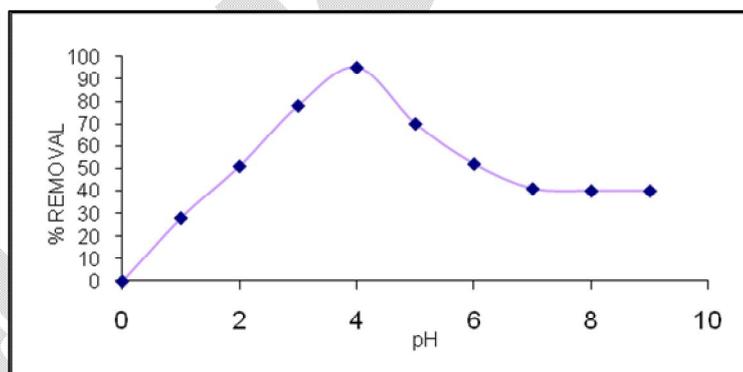

Figure 1: Effect of pH on the % removal of Ni (II).

Maximum 92.56% removal was observed at pH 4. The percentage of adsorption increased with increase in initial pH and decreased with increase in initial pH up to 6. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and species of the metals. At lower pH values, Nickel removal was inhibited, possibly because of the competition between hydrogen and nickel ions in the sorption site. With apparent preponderances of hydrogen ions, it restricts the approach of metal cations as a consequence of the repulsive force. At pH > 6 precipitations started and hence, higher pH was not selected for the present study. Biosorption of nickel Ni^{+2} was maximum at pH=4, as the pH exceeded, the biosorption began to decrease. This is possibly due to the precipitations of Ni (II) ions as a result of hydroxide anions forming nickel hydroxide precipitate. The adsorption of Ni (II) ion is reported to be highly pH dependent. Adsorption of Ni (II) on activated carbon is found to be efficient at

pH less than 4.5 [29]. And adsorption of Ni (II) on waste tea (*Camellia sinensis*) materials is also found to be efficient at pH less than 5 [30].

3.2. Effect of equilibrium time and initial metal ion concentration

To investigate the optimum equilibrium time, batch experiments were carried out by agitating 50 ml of different concentrations of nickel (II) solutions ranging from 50 mgL^{-1}, 75 mgL^{-1}, 100 mgL^{-1} which are maintained at pH 4.0 and with 125 mg of adsorbent. After equilibrating for different time periods from 15-120 min, the solutions were centrifuged and analyzed for Ni (II) content and the percent adsorption in each case was determined. Equilibrium time from the Table 1 was found to be 90 min. At this equilibrium time, the amounts adsorbed were 18.51; 24.80; and 29.52 mg/g for Ni (II) concentrations of 50, 75 and 100 mgL^{-1}, respectively. The increase in initial Ni (II) concentration decreased the percentage of adsorption and increased the amount of metal uptake per unit mass of the adsorbent in mg/g.

Table 1: Adsorption of Ni (II) at different concentrations and equilibrium time.

| Agitation time in minutes | Concentration of Nickel (II) in mg/lit | | | | | | | | |
| | 50   mg/lit | | | 75 mg/lit | | | 100 mg/lit | | |
	Amount of Nickel (II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Nickel (II) adsorbed q (mg/lit)	qe-q	% Removal
15	8.28	10.22	41.44	10.21	14.59	34.04	10.70	18.82	26.77
30	12.54	5.97	62.70	15.94	8.86	53.13	17.43	12.09	43.58
45	15.08	3.43	75.40	19.60	5.20	65.36	22.24	7.28	55.62
60	16.81	1.70	84.08	22.15	2.65	73.84	25.73	3.79	64.33
75	17.83	0.68	89.16	23.83	0.97	79.44	28.12	1.40	70.32
90	18.51	-	92.56	24.80	-	82.66	29.52	-	73.82
105	18.51	-	92.56	24.80	-	82.66	29.52	-	73.82
120	18.51	-	92.56	24.80	-	82.66	29.52	-	73.82

From Table 1, it was evident that the equilibrium time was independent of initial Ni (II) concentrations. The per cent adsorption vs time plot in Figure 2 was smooth and continuous leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. Similar results have been reported for the adsorbents like treated GAC and carbon aerogel [31]. In case of PMFP, per cent removal increased sharply leading to 98% removal of Nickel (II).
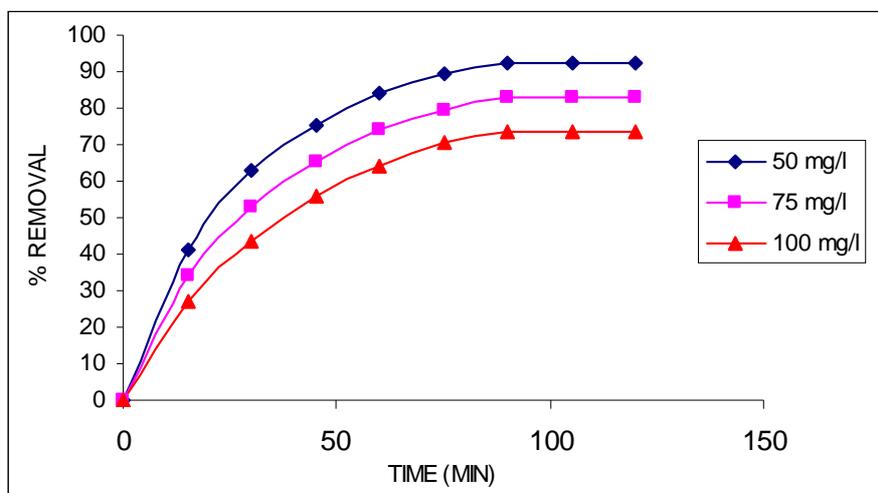
Figure 2. Effect of time on the % removal of Ni (II) for different concentrations.

3.3. Effect of adsorbent dosage

The effect of dosage on the adsorption was studied by varying the amount of adsorbent from 25 to 200 mg. The adsorbent was added to 50 ml of Nickel (II) solution of 50 mgL^{-1} concentrations and equilibrated for 90 min. After the equilibrium time, the solutions were centrifuged and analyzed for the amount of Nickel (II) and the per cent adsorption was estimated. The data in Table 2 indicate that complete removal was possible with a dose of 200 mg.

Table 2: Percent removal at different adsorbent doses.

Adsorbent dose mg/50ml	% Removal	Equilibrium Concentration Ce(mg/lit)	Amount Adsorbed mg/g
25	28.70	35.64	28.72
50	51.48	24.26	25.74
75	67.84	16.08	22.61
100	82.50	8.75	20.62
125	92.48	3.76	18.49
150	97.16	1.42	16.19
175	99.04	0.48	14.14
200	100.00	0.00	12.50

The results in Figure 3 indicated that adsorption increased with increase in adsorbent dosage. This increase in percent adsorption with the increase in adsorbent dosage was due to the availability of more surface area of the adsorbent [32].
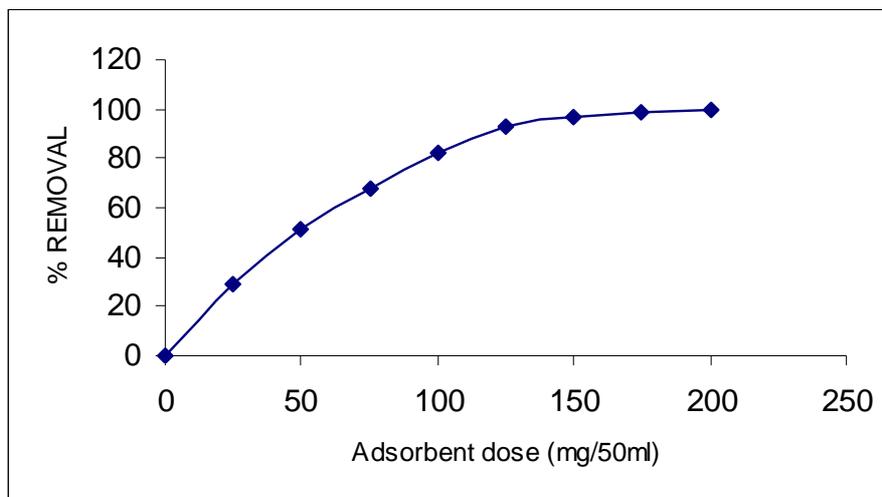
Figure 3: Effect of adsorbent dose on % removal of Ni (II).

3.4. Effect of particle size

To study the effect of particle size, adsorbent particles of sizes 0.6 mm, 0.8 mm and 1.7 mm were used. In each study 125 mg of adsorbent in 50 ml of 10 mgL^{-1} of Ni(II) solution was agitated to equilibrium time of 60 min, the adsorbent was separated and the supernatant solution was analyzed for chromium concentration and the values are noted in Table 3, the amounts adsorbed for 0.6 mm, 0.8 mm and 1.7 mm particle size were 3.01, 2.66 and 2.34 mg/g, respectively.

Table 3: Adsorption of Ni (II) ions on different particle sizes (mm) of the adsorbent.

Agitation time in minutes	Particle size in mm								
	0.6 mm			0.8 mm			1.7 mm		
	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	%Removal	Amount of Ni(II) adsorbed q (mg/lit)	qe-q	% Removal
10	1.33	1.68	40.18	1.13	1.53	34.20	0.94	1.40	28.40
20	2.09	0.92	62.75	1.75	0.91	52.50	1.47	0.87	44.22
30	2.48	0.53	74.69	2.12	0.54	63.85	1.82	0.52	54.74
40	2.77	0.24	83.11	2.43	0.23	72.95	2.08	0.26	62.50
50	2.94	0.07	78.02	2.60	0.06	78.02	2.21	0.13	66.46
60	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
70	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
80	3.01	-	90.58	2.66	-	80.05	2.34	-	70.13
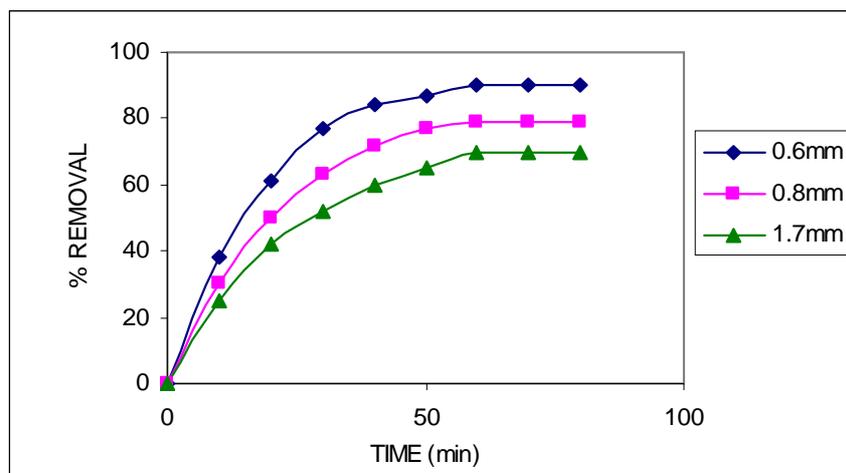
Figure 4: Relationship between particle size, % removal at different times.

It is evident from figure 4 that increase in particle size decreased the percentage of removal. At a fixed adsorbent dosage, the decrease in particle size increases the metal uptake. The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar trend had been observed on removal of Ni(II) by using *Pitchellobium dulce* Benth – a kinetic study [33].

3.5. Adsorption isotherms

Isotherms relate metal uptake per unit weight of adsorbent to equilibrium adsorbate concentration in the bulk fluid phase. The Langmuir isotherm was based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm was expressed in the following formula:

$$\frac{Ce}{qe} = \frac{1}{Q_o b} + \frac{Ce}{Q_0} \qquad ----1$$

where Ce is the equilibrium Concentration (mgL^{-1}), qe is the amount adsorbed at equilibrium time (mg/g) , Qo and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. Data for Langmuir plot are given in Table 4. Regression analysis of the Langmuir data resulted in high correlation coefficient.

Table 4: Effect of initial concentration on the equilibrium concentrations.

Initial Concentration C_i (mg/lit)	Equilibrium Concentration Ce (mg/lit)	qe (mg/g)	Ce/qe (g/lit)
50	3.72	18.51	0.20
75	13.00	24.80	0.52
100	26.18	29.52	0.88
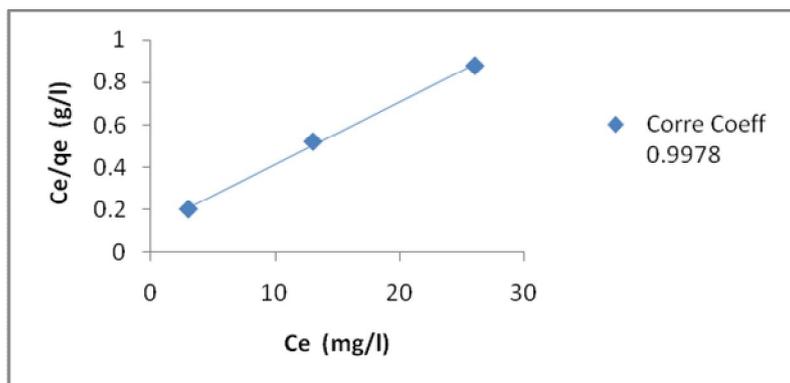
Figure 5: Langmuir isotherm showing initial concentration vs. equilibrium concentration.

Figure 5 indicates the applicability of Langmuir isotherm. The Langmuir constants Q_0 and b evaluated from the slope and intercept are 29.41 mg/g and 0.4789 L/mg, respectively. Q_0 value is less than the value of adsorption capacity of bagasse studied [34]. The essential characteristics of Langmuir are expressed in terms of a dimensionless constant separation factor R_L (Equilibrium Parameters) that is given by:

$$R_L = \frac{1}{1+bc_i} \qquad ----2$$

where C_i was the initial concentration (mgL^{-1}) and b was the Langmuir constant. The values of R_L in Table 5 indicate the nature of isotherm.

Table 5: The ranges of R_L values for comparison.

R_L	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present investigation, R_L values were 0.040, 0.027 and 0.020 for Ni(II) concentration of 50, 75 and 100 mgL^{-1}, respectively which were less than unity showing that the adsorption of metal ion onto sweet lime peelings powder was favorable. The Freundlich isotherm is generally used for mathematical description of adsorption in aqueous system and describes heterogeneous surface energies. The equation is expressed in logarithmic form as:

$$\log x/m = \log k_f + \frac{1}{n}\log Ce \qquad ----3$$

where x/m is the amount adsorbed in mgL^{-1}, Ce is the equilibrium concentration (mgL^{-1}), K_f and n were Freundlich constants. K_f [mg/g, L/mg] was the capacity of the adsorbent and n indicated the favorability of adsorption.

This isotherm was applied for the adsorption of Ni(II) on powder of Mosambi fruit peelings adsorbent and plot of log x/m vs log Ce is shown in Figure 6. The linearity of the plot shows that adsorption followed Freundlich isotherm and the constants K_f and n calculated from the intercept and slope are 23.92 and 2.24, respectively.
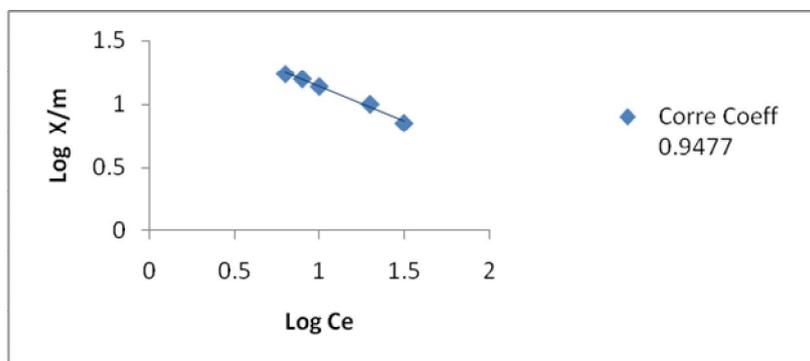
**Figure 6:** Freundlich adsorption isotherm for the equilibrium concentration and adsorption rate.

The results indicated that the adsorbent has several different types of adsorption sites. According to [35], the n values between 2 and 10 represent good adsorption. The calculated n value of 2.24 indicates good adsorption of Ni (II) on PMFP.

3.6. Adsorption kinetics: Effects of Ni (II) concentration on Lagergren Rate Constant

The kinetics of Ni (II) adsorption followed the first order rate. Equation given by Lagergren was:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t \qquad ----4$$

where q and qe were the amounts of metal ion adsorbed (mg/g) at time t (min) and at equilibrium time, respectively and K_{ad} was the rate constant of adsorption (min^{-1}). From the Figure 7, it was evident that the linear plots of log (qe-q) vs time at different concentrations show the applicability of the Lagergren equation.
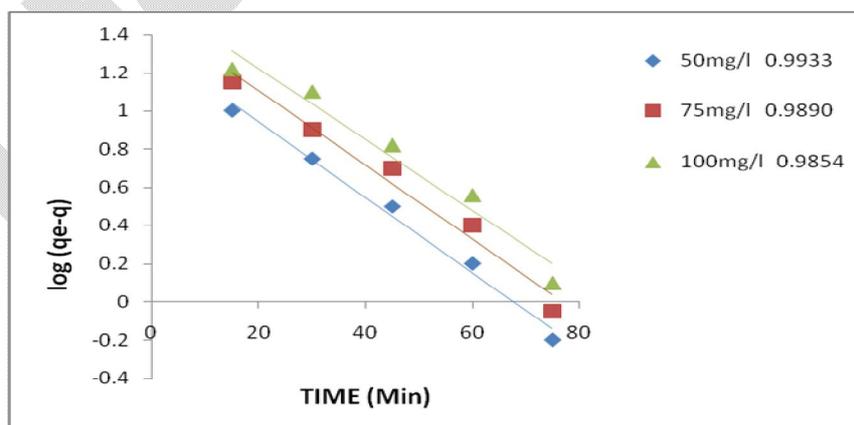
Figure 7: Relationship between the time in minutes and log concentrations of Ni (II) for various known concentrations.

The K_{ad} values calculated from the slopes of the linear plots are presented in Table 6.

**Table 6:** Calculated values for the rate constants for different concentrations of Ni (II).

Ni (II) mg/lit	Rate Constant K_{ad} (min^{-1})
50	4.37 x 10^{-2}
75	4.37 x 10^{-2}
100	4.23 x 10^{-2}

These results indicated that the metal ion concentration has no significant effect on the rate. The values were comparable with the results obtained by [36].

3.7. Effect of particle size on Lagergren Rate Constant

Table 7: Lagergren rate constants calculated for different particle sizes (mm).

Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.6	6.01 x 10^{-2}
0.8	5.21 x 10^{-2}
1.7	4.37 x 10^{-2}
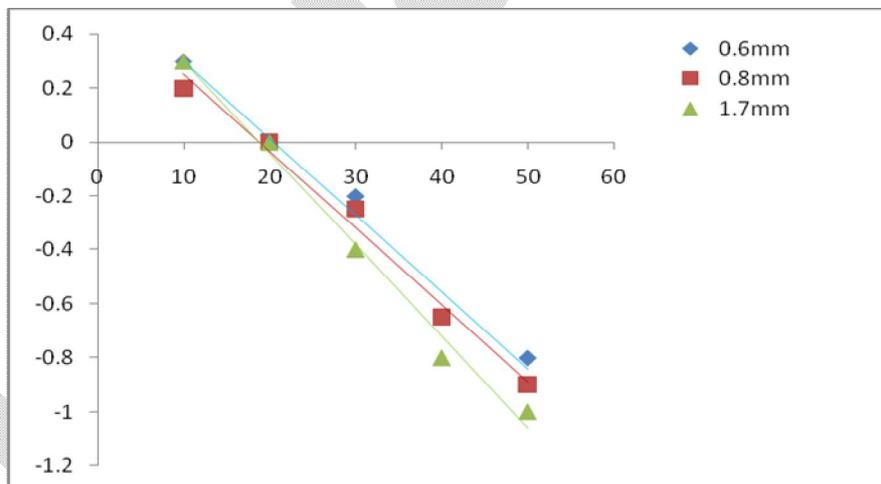
Figure 8: Relationship between different particle sizes and time of adsorption.

The effect of particle size on the rate of adsorption is shown in Figure 8 and the rate constant K_{ad} values are given in Table 7. For the adsorption of Ni (II), increase in particle size from 0.6 mm to 1.7 mm decreased the rate of adsorption from 6.01 x 10^{-2} to 4.37 x 10^{-2} min^{-1}. The higher rate of metal uptake by smaller particles was due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent have stated that the breaking up of larger particles to form smaller ones opens some tiny sealed channels that will be available for adsorption and therefore the rate of uptake by smaller particles was higher than that larger particle.

4. Conclusion

A) In this study the heavy metal, namely, Nickel (II) was selected for removal from aqueous solutions using adsorption technique. Batch experiments were conducted to study the impacts of particle size, pH, agitation time, adsorbent dose and initial metal ion concentrations. A particle size of 0.6 mm was observed to be highly efficient for nickel (II). A decrease in the size of the particle increased the adsorption, as a decrease in size of the particle increased the availability of the number of active sites. The increase of pH showed a negative impact on the adsorption of nickel (II). Maximum adsorption was recorded at pH 4.0 for Ni (II). An increase in the adsorbent dosage gave increased adsorptions for nickel, whereas the adsorption decreased with increase of initial metal ion concentrations.

B) The adsorbent selected for the present study proved to be good adsorbent which was evident with the adsorption data obeying the Langmuir and Freundlich isotherms. The equilibrium parameter R_L in Langmuir isotherm, the Langmuir constants for nickel (II) are Q= 29.41 mg/g and b= 0.4787 L/mg, by PMFP and Freundlich adsorption constants K_f for nickel (II) is 23.92, and n=2.24 by PMFP indicated that the adsorption of Ni (II) on PMFP was favorable. The kinetics of the adsorption of the metal ions also obeyed Lagergren equation. This results shows that PMFP has a considerable potential as an adsorbent for the removal of nickel (II) from aqueous solutions.

C) If low cost adsorbents perform well in removing heavy metals at low cost, they can be adopted and widely used in industries not only to minimize cost inefficiency, but also to improve profitability. In addition to this, the alternative adsorbents are found highly efficient for heavy metal removal, not only in the industries, but also in the living organisms. The surrounding environment will be also benefited from decrease or elimination of potential toxicity due to the heavy metal. Thus, the use of low cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly, low cost adsorbents offer a lot of promising benefits for commercial purpose in the future. Heavy metal removal with the above adsorbent appears to be technically feasible, eco-friendly and has high efficacy. Also, it helps in reduction of waste generation.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

A.V.V.S.S. and R.H.K. made the plan, explained data, and dissected the results involved in the preparation of manuscript. R.H.K. carried out experimental work and reviewed the scientific background.

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