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NPP-modified bentonite for adsorption of Ni (II) from aqueous solution and electroplating wastewater

Sandeep B.N, Suresha. S
Department of Environmental Science, Yuvaraja's College, University of Mysore, Mysore-570 005, Karnataka, India
sureshakumar12@yahoo.com
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ABSTRACT

Application of sodium pyrophosphate modified bentonite (NPP-bentonite) for adsorption of Ni (II) from aqueous solution and electroplating wastewater was investigated. Batch experiments were carried out to find the effect of pH, adsorbent dose, contact time and initial metal ion concentration. Maximum Ni (II) adsorption of 87.30 % was achieved at pH 6.0 with adsorbent dose of 2 g/L with contact time of 120 min and initial metal ion concentration of 50 mg/L. The equilibrium adsorption data fitted well to Langmuir and Freundlich isotherm models with Langmuir monolayer adsorption capacity of 30.30 mg/g and Freundlich adsorption capacity of 3.98 $(mg/g)/(mg/L)^{1/n}$. The practical applicability of NPP-bentonite as potential adsorbent for Ni (II) removal from electroplating wastewater has been proved.

Keywords: NPP-bentonite, Adsorption, Nickel, Isotherm, Electroplating wastewater.

1. Introduction

Nickel is one of the toxic heavy metals released into the environment at an exceedingly high level through the discharge of wastewater from electroplating, mining and battery industries (Parab et al., 2006). The persistent nature and non biodegradability of the metal causes disposal problems in the environment. Its presence above the permissible limit results in several health effects including gastrointestinal distress, lung and kidney damage, pulmonary fibrosis and dermatitis (Borba et al., 2006).

Several techniques such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis and ultrafiltration have been reported for removal of heavy metals from wastewater. The disadvantages of these methods include inefficiency, high operational cost and sludge disposal problems (Ahalya et al., 2003). Therefore, an effective and simple technique is essentially required for the removal of heavy metals from wastewater. Adsorption technique, of late has received attention due to its simple and cost effective nature. Various low cost adsorbents have been employed for removal of the heavy metals from wastewater which include bentonite (Suresh et al., 2009), coir pith (Parab et al., 2006), expanded pertlite (Mostaedi et al., 2010), fly ash (Agarwal et al., 2013), maghnite (Zenasni et al., 2013), montmorillonite (Gupta and Bhattacharyya, 2008 'b'), oak sawdust (Argun et al., 2007), peat moss (Gupta et al., 2009) and smectite (Ketcha et al., 2012).

Bentonite is having large surface area and high cation exchange capacity (Donat et al., 2005) which allows it to act as an effective adsorbent for heavy metal removal from wastewater. The modified clays employed as adsorbent showed higher removal efficiency as reported earlier examples of which include Pb (II) and Cd (II) on sodium tetraborate (NTB) modified

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kaolinite (Unuabonah et al., 2008), Fe (III), Co (II) and Ni (II) on zirconium oxychloride (ZrO) modified kaolinite and montmorillonite (Bhattacharyya and Gupta, 2008 'a').

This paper reports the application of NPP-bentonite for adsorption of Ni (II) from aqueous solution. The adsorption process will be studied with several parameters such as pH, adsorbent dose, contact time and initial metal ion concentration. Langmuir and Freundlich isotherm models are going to be employed for analyzing the equilibrium adsorption data. The practical performance of NPP-bentonite will be assessed with electroplating wastewater containing Ni (II).

2. Material and methods

2.1 Preparation and modification of adsorbent

Natural bentonite was procured from S.B. Patil Minerals Limited, Gulbarga (Karnataka), India. The powdered sample was washed with deionised water and dried at room temperature. The dried sample was treated with 0.01% sodium pyrophosphate solution for 24 h. The resulting NPP-bentonite was centrifuged and washed several times with deionised water, oven dried at 110°C for 24 h, cooled and stored in air tight container for further use.

2.2 Preparation of adsorbate

A known amount of $NiSO_4.6H_2O$ (Merck, A.R grade, India) was dissolved in deionised water to obtain Ni (II) stock solution of 1000 mg/L, which was further diluted to get working solutions of lower concentration. The pH adjustment of the solutions was done by using 0.01N HCl and 0.01N NaOH.

2.3 Electroplating wastewater

The wastewater was collected from electroplating industry located in Bangalore, Karnataka, India. The physico-chemical parameters were analyzed using standard methods (Clesceri et al., 1998). The physico-chemical characteristics are presented in Table 1.

Table 1: Physico-chemical characteristics of electroplating wastewater

Parameters	Contents (mg/L)
pH	2.70
Conductivity (µs/cm)	1863
Total Dissolved Solids	1018
Calcium	107.12
Magnesium	46.89
Chloride	208.51
Sulphate	82.64
Sodium	70.36
Potassium	2.52
Nickel (II)	43.00
Chromium (VI)	12.30

Note: Except pH and conductivity all other parameters are expressed in mg/L.

2.4 Batch experiments

Batch experiments were carried out at room temperature. For experimental run 100 ml of solution containing 50 mg/L of Ni (II) at required pH level were taken in 250 ml Erlenmeyer flasks. Known amount of adsorbent was added and the mixture was shaken at 200 rpm using a mechanical shaker (KEMI KRS 110, India) for a fixed length of time. The mixture was centrifuged (Eltek TC 450, India) at 5000 rpm for 10 min and concentration of Ni (II) ions remaining in the supernatant solution was determined by atomic absorption spectrophotometer (Perkin Elmer AAnalyst 800, USA). All determinations were done in triplicate and average values were considered. Percentage adsorption was calculated by the following equation

$$\% A = [(C_i - C_e) / C_i] \times 100 \qquad (1)$$

Where, C_i and C_e are initial and final Ni (II) concentrations (mg/L) respectively.

2.5 Effect of pH

Hundred ml of solution containing 50 mg/L of Ni (II) was taken in a 250 ml Erlenmeyer flask. To this, 2 g/L of adsorbent were added and the determinations were done at solution pH of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 by using either 0.01N HCl or 0.01N NaOH solutions as required. After 120 min of shaking, the solution was centrifuged and Ni (II) concentration was estimated by AAS.

2.6 Effect of adsorbent dose

Adsorbent at varying levels of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 g/L were taken separately in 250 ml Erlenmeyer flasks and each was added 100 ml of solution containing 50 mg/L of Ni (II). The pH was adjusted to 6.0 and resulting solution was agitated for 120 min. The concentration of unabsorbed Ni (II) ions in filtrate was determined by AAS.

2.7 Effect of contact time

Adsorbent at 2 g/L level was added to each 250 ml Erlenmeyer flasks containing Ni (II) solution (100 ml of 50 mg/L) and pH was adjusted to 6.0. The mixture was shaken on a mechanical shaker for different time intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170 and 180 min. The residual concentration of Ni (II) in the filtrate of each was determined by AAS.

2.8 Effect of initial metal ion concentration

Hundred ml of Ni (II) solution in 10, 20, 30, 40 and 50 mg/L concentrations were taken in separate Erlenmeyer flasks. Adsorbent (2 g/L) was added and pH was adjusted to 6.0 and the contact time allowed was 120 min. The unabsorbed Ni (II) concentration in supernatant solution was determined by AAS.

3. Results and discussion

3.1 Effect of pH

The initial pH of solution is one of the significant parameters for Ni (II) adsorption. From Figure 1 it is clear that percentage Ni (II) adsorption increased with increase in pH from 1.0 to 6.0 with adsorption rate increasing from 14.50 to 87.30 %, respectively. Further increase in pH from 6.0 to 8.0 showed marginal increase. Above pH 8.0 rapid Ni (II) adsorption was evident which indicates the precipitation of Ni^{2+} and $NiOH^{+}$ as $Ni(OH)_2$ (Bayat, 2002). At lower pH, adsorption of Ni (II) is less due to complete coverage of H_3O^{+} ions on clay surface and this poses difficulty for Ni (II) ions to compete for adsorption sites. When pH increases number of H_3O^{+} ions decreases and as a result Ni (II) ions get adsorbed onto free available sites of adsorbents (Gupta and Bhattacharyya, 2006). Similar observations were reported by Gupta and Bhattacharyya, (2008 'b') and Mostaedi et al., (2010) for Ni (II) adsorption on montmorillonite and expanded perlite, respectively.

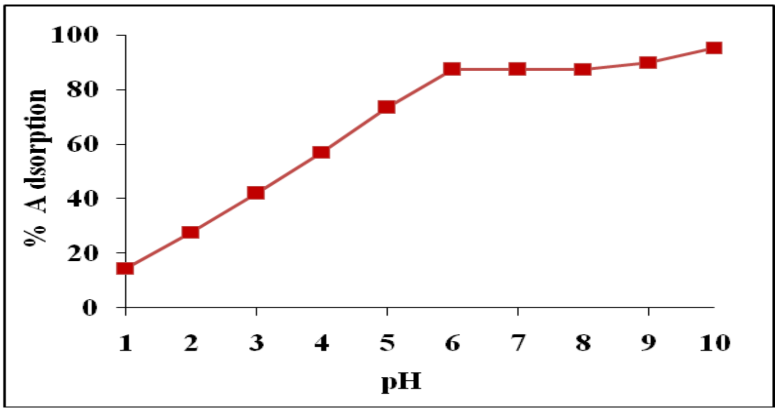

Figure 1: Ni (II) adsorption by NPP-bentonite at various pH levels

3.2 Effect of adsorbent dose

The effect of varying adsorbent doses on Ni (II) adsorption by NPP-bentonite is depicted in Figure 2. The results demonstrate that Ni (II) adsorption by NPP-bentonite increases with increase in adsorbent dose from 1.0 to 2.0 g/L (72.60 to 87.30 %). This is due to the increase in surface area which in turn increases the availability of exchangeable sites on NPP-bentonite for adsorption of Ni (II) (Donat et al., 2005; Gupta and Bhattacharyya, 2006). Further increase in adsorbent dose beyond 2 g/L keeps Ni (II) adsorption static which may be attributed to attainment of equilibrium between liquid and solid phases. Similar trend was reported for Ni (II) adsorption on bentonite (Alandis et al., 2010; Suresh et al., 2009).

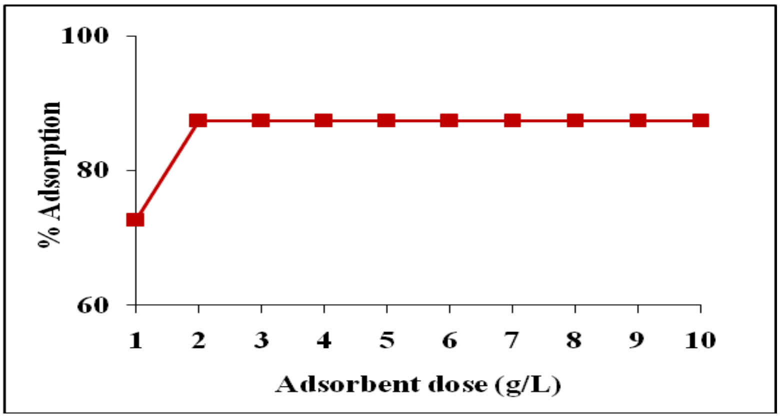

Figure 2: Ni (II) adsorption by NPP-bentonite at different adsorbent doses

3.3 Effect of contact time

Figure 3 shows the results of different contact times on Ni (II) adsorption by NPP-bentonite. It is clear that maximum Ni (II) adsorption (87.30 %) on NPP-bentonite was achieved at 120 min. A rapid Ni (II) adsorption of 80.52 % took place in the initial 60 min and thereafter it proceeded at a slower rate until equilibrium was reached. The reason being that, at initial stage more number of vacant adsorption sites are available on NPP-bentonite which gets occupied at later stages by Ni (II) ions as a result the number of vacant adsorption sites decrease. Zenasni et al., (2013) have reported that equilibrium was attained within 10 min for Ni (II) adsorption on maghnite. Similar results were reported by other workers for Ni (II) adsorption on different adsorbents like expanded pertlite (Mostaedi et al., 2010), fly ash (Agarwal et al., 2013), oak sawdust (Argun et al., 2007) and smectite (Ketcha et al., 2012).

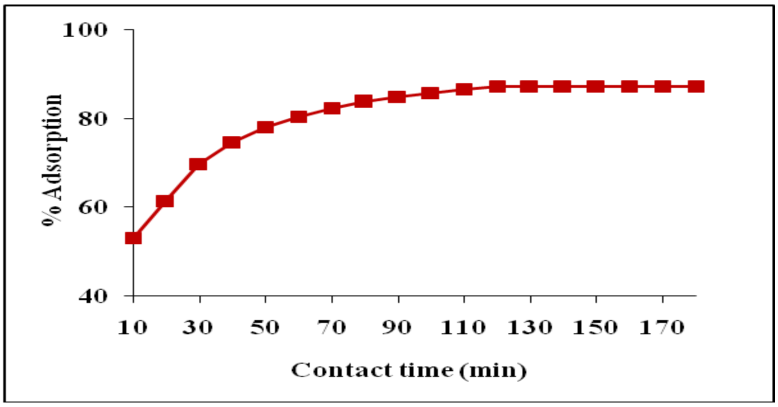

Figure 3: Ni (II) adsorption by NPP-bentonite for varying contact time

3.4 Effect of initial metal ion concentration

The initial metal ion concentration on Ni (II) adsorption by NPP-bentonite as shown in Figure 4 illustrates that percent adsorption decreases from 97.90 to 87.30 % with increase in initial Ni (II) concentration from 10 to 50 mg/L. This is due to the fact that increase in metal ion concentration causes saturation of adsorption sites on NPP-bentonite and this blocks further Ni (II) adsorption on adsorption sites and as a result the adsorption efficiency decreases (Jiang et al., 2010). The results of Ni (II) adsorption are similar to that reported by Prabakaran and Arivoli, (2012) on thespesia populnea bark, Argun et al., (2007) on oak sawdust and Donat et al., (2005) on bentonite.

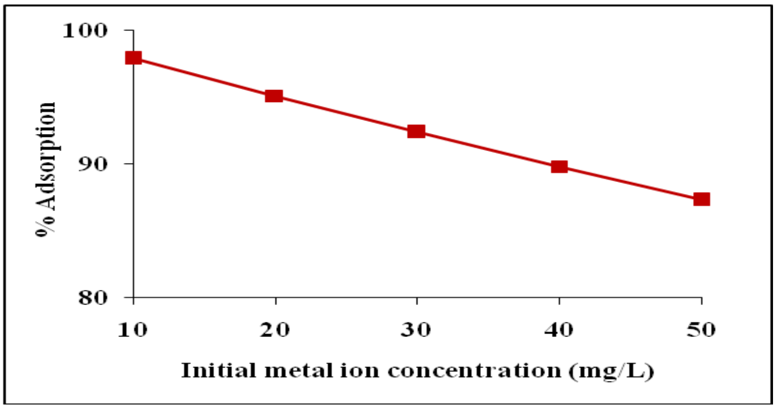

Figure 4: Ni (II) adsorption by NPP-bentonite for varying initial metal ion concentration

3.5 Adsorption isotherm

Adsorption isotherms such as Langmuir and Freundlich effectively describe the mechanism of adsorption process and the interactions between adsorbate and adsorbent

3.5.1 Langmuir isotherm

The Langmuir isotherm model is applicable to monolayer adsorption whose adsorbent surface consists of equal number of identical sites. The Langmuir isotherm (Langmuir, 1918) is given by

$$C_e / q_e = 1 / (b\, q_m) + C_e / q_m \qquad (2)$$

Where, q_e is the equilibrium concentration of adsorbate in solid phase (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), q_m (mg/g) and b (L/g) are Langmuir constants.

Figure 5 shows the linear plot obtained by plotting C_e/q_e versus C_e. The Langmuir model parameters q_m (mg/g) and b (L/g) statistically fits the adsorption data which are presented in Table 2. The Langmuir model effectively describes the adsorption data with R^2 value of 0.999. This behavior indicates a monolayer adsorption. Higher values of b (89.20 L/g) and q_m (30.30 mg/g) indicate maximum interaction and greater affinity of Ni (II) with NPP-bentonite (Gupta and Bhattacharyya, 2008 'b'). Similar results were also recorded earlier for Ni (II) adsorption on bentonite (Alandis et al., 2010), chitosan immobilized bentonite (Futalan et al., 2011), and montmorillonite (Gupta and Bhattacharyya, 2008 'b') and thespesia populnea bark (Prabakaran and Arivoli, 2012).

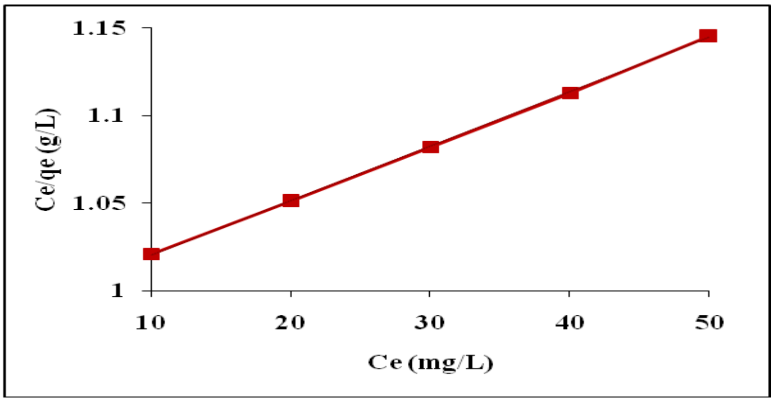

Figure 5: Langmuir isotherm plots for Ni (II) adsorption by NPP-bentonite

3.5.2 Freundlich isotherm

The Freundlich isotherm model is applicable for adsorption on heterogeneous surface. Freundlich isotherm (Freundlich, 1906) is given by

$$q_e = K_f\, C_e^{\,n} \qquad (3)$$

Where, q_e is the equilibrium concentration of adsorbate in solid phase (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), K_f [$(mg/g)/(mg/L)^{1/n}$] and n are Freundlich constants. Figure 6 shows the linear plot obtained by plotting log q_e versus log C_e. The Freundlich model parameters K_f $(mg/g)/(mg/L)^{1/n}$ and n are given in Table 2. The R^2 value of 0.999 obtained indicates Ni (II) adsorption also takes place on heterogeneous surface of NPP-bentonite. The K_f value of 3.98 $(mg/g)/(mg/L)^{1/n}$ indicates higher adsorption capacity and n value of 0.90 indicates favorable adsorption. Therefore, it can be concluded that Ni (II) adsorption on NPP-bentonite showed good representation with both Langmuir and Freundlich isotherm models and these suggest homogeneous and heterogeneous adsorption of Ni (II) on NPP-bentonite.

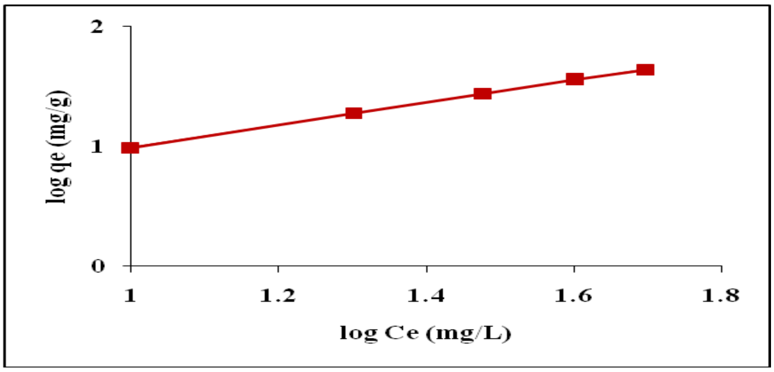

Figure 6: Freundlich isotherm plots for Ni (II) adsorption by NPP-bentonite

Table 2: Isotherm constants for Ni (II) adsorption by NPP-bentonite

Metal ion	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	b (L/g)	R^2	K_f (mg/g)/(mg/L)$^{1/n}$	n	R^2
Ni (II)	30.30	89.20	0.999	3.98	0.90	0.999

Table 3: Comparison of sorption capacity of various adsorbents for Ni (II) adsorption

Adsorbent	Langmuir sorption capacity (mg/g)	Reference
Chitosan immobilized bentonite	15.82	Futalan et al., 2011
Maghnite	18.95	Zenasni et al., 2013
Montmorillonite	21.10	Gupta and Bhattacharyya, 2008 ‘b’
NPP-bentonite	30.30	Present study
Smectite	6.68	Ketcha et al., 2012
Thespesia populnea bark	54.34	Prabakaran and Arivoli, 2012
Zeolite-bentonite mixture	33.00	Dwairi and Rawajfeh, 2012
ZrO-montmorillonite	22.00	Bhattacharyya and Gupta, 2008 ‘a’

4. Application to electroplating wastewater

The efficiency of NPP-bentonite for Ni (II) adsorption from electroplating wastewater was tested. Experiment was performed in an Erlenmeyer flask containing 100 ml of wastewater sample. To this 2 g/L of NPP-bentonite was added and pH was adjusted to 6.0. After 120 min of agitation, the wastewater sample was centrifuged and Ni (II) concentration was determined by AAS. The result showed that Ni (II) adsorption from electroplating wastewater was

88.74 % which was slightly less compared to that of aqueous solution. This may be due to competition between Ni (II) ions and interfering ions for adsorption sites on NPP-bentonite.

5. Conclusion

The application of NPP-bentonite as adsorbent for adsorption of Ni (II) from aqueous solution and electroplating wastewater showed encouraging results. Several parameters such as pH, adsorbent dose, contact time and initial metal ion concentration influenced the adsorption process. The adsorption equilibrium was attained at 120 min and adsorption efficiency reached a maximum of 87.30 % at optimal pH of 6.0, adsorbent dose of 2 g/L and initial metal ion concentration of 50 mg/L. The equilibrium adsorption data showed good fitting to both Langmuir and Freundlich isotherm models. The results of the study conclusively proved the effectiveness of NPP-bentonite as an adsorbent for Ni (II) removal from electroplating wastewater.

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