ADSORPTION STUDIES OF POMEGRANATE PEEL ACTIVATED CHARCOAL FOR NICKEL (II) ION

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ABSTRACT

Presence of toxic heavy metals in air, soil, and water are growing threats to the environment. In this study, removal of divalent nickel from aqueous solutions has been investigated by utilizing a low cost pomegranate peel activated charcoal (PPAC) adsorbent. Adsorption capacity of the prepared charcoal at various parameters such as pH, contact time, metal ion concentration and adsorbent dose has been studied. Batch equilibrium experiments showed that maximum nickel adsorption takes place at neutral pH, while the maximum adsorption capacity for PPAC was 10.82 mg g^{-1} . It was also found that percentage removal of nickel is directly proportional to the adsorbent dose with maximum adsorption at an adsorbent dose of $0.5\text{g}/50 \text{ ml}$ for various concentrations (10-150 ppm) and contact time of 50 minutes. Experimental equilibrium data was verified for *Langmuir* and *Freundlich* isotherm models to establish the adsorbate-adsorbent interaction phenomena. The values of regression coefficient for *Langmuir* and *Freundlich* isotherm are found to be 0.942 and 0.931 respectively which showed that data fitted well in both models.

Keywords: Pomegranate peels; solid waste management; nickel adsorption; activated charcoal.

1. INTRODUCTION

Management of hazardous waste is an emerging problem of the world these days. Heavy metals are being discharged to nature in various forms due to industrial advancement, especially in the areas of electroplating, glass production, battery & paint manufacturing, tannery and mining. These heavy metals are the cause of various diseases and are non-biodegradable in nature having tendency of bioaccumulation in living tissues¹⁻⁴.

Among heavy metals, nickel has been frequently reported in waste water discharges from non-ferrous metal processing, mineral processing, porcelain enameling and metal cleaning industries causing serious damage to water resources⁵. Its input in the environmental degradation has increased tremendously in recent years due to inadvertent discharge of industrial residues in waste streams. Inappropriate agricultural use of fertilizers, pesticides and bio-solid sources is also a major source for nickel contamination in nature. Health issues concerning with the exposure of nickel are dizziness, vomiting, lungs and kidney malfunctioning, cyanosis and renal edema⁶. Excessive concentration of nickel in body may have carcinogenic effect⁷.

Due to vast range of hazards associated with nickel pollution, a systematic study for its removal from wastewaters is of considerable significance. Technologies such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption have been reported in the literature for the removal of nickel ions from aqueous solutions^{8,9,10}. However, the most frequently applied method in industries for the waste water treatment is adsorption processes and in this regard, a number of adsorbents like peanut and almond husk¹¹⁻¹², baggase¹³, automobile tires¹⁴, gypsum¹⁵, soya cake¹⁶, blast furnace slag¹⁷ and fly ash¹⁸ have been studied for the removal of different heavy metals.

However, a need still exists to develop a low cost and more effective adsorbents for the removal of nickel from wastewater as these processes are not now commonly being used due to their high costs, need of possible secondary treatments and low efficiency¹⁹. Pomegranate is used as a fruit throughout the world in juices, jams, wines and other products while its peels are not being used at large, causing a problem for solid waste management. In this paper, potential of pomegranate peels as a low cost and effective adsorbent for the removal of nickel ions has explored. During the course of this work, charcoal from pomegranate peels has been prepared and used as adsorbent for nickel (II). Various factors affecting the adsorption process like metal ion concentration, adsorbent dose, contact time and pH were studied. Equilibrium studies of adsorption data has also been analyzed by using *Langmuir* and *Freundlich* isotherm models.

2. MATERIALS AND METHODS

2.1 Preparation of pomegranate peel charcoal

Pomegranate peels were collected from fresh juice vendors of local

market (Lahore, Pakistan). The peels were washed and sun dried for 48 hrs. A medium sized modified mud earthenware vessel was used for the process of charcoal preparation. Dried pomegranate peels (300g) were taken in the mud vessel. Two tiny holes were drilled in its lid to pass nitrogen gas during the charcoal formation. From one hole, nitrogen gas was introduced and the second one was left open to expel the air present inside the vessel (Figure 1). After approximately 10 mins., nitrogen flow was stopped and lid along with its both holes were sealed with wet mud. The vessel was placed on a medium flame for a period of 10 hrs. After cooling, the obtained charcoal (114.6g) was ground to attain 0.6 mm mesh size.

Fig. 1: Schematic diagram of the assembly used for the preparation of Charcoal.

2.2 Activation of adsorbent

Freshly prepared charcoal was activated with concentrated hydrochloric

acid by mixing in 1:4 ratio. After 24 hrs. , the mixture was filtered and the residue was washed with distilled water to remove the residual acid completely (neutral to phenolphthalein). The washed charcoal was dried at 110°C for 2 hrs and stored in an air tight container.

2.3 Preparation of nickel stock solution

Nickel stock solution (1000 ppm) was prepared by dissolving nickel acetate tetra-hydrate (4.231g) in de-ionized water (1000 ml). It was further diluted in order to attain the required concentration of nickel in solutions.

2.4 Procedure for batch adsorption studies

Batch adsorption experiments were carried out to determine the effect of physical parameters like pH, adsorbent dose, contact time and initial metal ion concentration on nickel uptake from aqueous solutions by PPAC.

2.4.1 Effect of pH

The pH of the system is varied from 3-11 by using 0.1N HCl and 0.1N NaOH. The initial concentration of nickel (20mg/l) and adsorbent dose (0.5g) was kept constant for all the experiments. The mixture is stirred for 50 mins. and filtered. Nickel concentration at equilibrium was analyzed by Atomic Absorption Spectrometer. From the nickel ion concentration in filtrate, percentage removal of nickel by adsorbent was calculated by using the formula:

$$\% \text{ Removal of Ni (II)} = (C_i - C_e) * 100 / C_i \quad (1)$$

Where, C_i is the initial metal ion concentration in mg l^{-1} and C_e is the metal ion concentration at equilibrium.

2.4.2 Effect of adsorbent dose

The effect of PPAC dose on adsorption of nickel (II) from aqueous solutions was investigated by using four different adsorbent concentration and five different initial nickel (II) concentrations. Amount of charcoal varied from 0.1g to 0.75g/50 ml and metal concentrations from 10 to 150 mg l^{-1} . Concentration of nickel (II) at equilibrium was analyzed by atomic absorption spectroscopy.

2.4.3 Effect of contact time and initial metal concentration

This parameter was used to determine the adsorption efficiency of PPAC at different contact time. The experiments were carried out on initial concentrations of nickel solutions in range of 10-130 mg l^{-1} and the time varied between 30-60 mins PPAC (0.5g) was added in 50 ml of each solution. The solutions were agitated at room temperature and filtered. The equilibrium concentration of metal was determined in the solution through Atomic absorption spectrometry. The metal adsorbed on the adsorbent (Q_e) was calculated by the formula:

$$Q_e = C_i - C_e * V / m \quad (2)$$

Where C_i is the initial metal concentration, C_e is the equilibrium metal concentration, V is the volume of the solution in liter. and m is the mass of adsorbent in grams added.

2.5 Thermodynamic studies

Modeling of the adsorption data helped in its application on industrial scale. In this work data is analyzed using *Langmuir* and *Freundlich* isotherms models. For this study nickel (II) concentration was ranged from (10-200 mg l^{-1}) while the adsorbent dose was set to 0.5g/50ml. The solution is stirred for 50 mins at pH 7.

The linear form of *Langmuir* isotherm is:

$$C_e / q_e = 1 / q_{\max} b + C_e / q_{\max} \quad (3)$$

Where $q_{\max}$ is the capacity of adsorbent (mg/g) and b is the adsorption constant.

A plot of C_e / q_e vs C_e is drawn which resulted in straight line. The slope is $1/q_{\max}$ and intercept is $1/q_{\max} b$.²⁰

The *Freundlich* equation was expressed as:

$$Q_e = K C_e^{1/n} \quad (4)$$

For linearization of the data, the *Freundlich* equation was written in their logarithmic forms:

$$\log Q_e = \log K + 1/n \log C_e \quad (5)$$

Where, ($Q_e = x/m$)

Plotting $\log Q_e$ against, $\log C_e$, a straight line, slope was $1/n$ and intercept was $\log K$.

2.6 Desorption studies

Reusability of adsorbent was investigated by desorption-adsorption experiments. Metal ion loaded biosorbent material was taken in the beaker and treated with 25ml of 0.05 mol/lit HCl solution for 30 mins. It was filtered again and desorbed metal ions were determined in the filtrate. The adsorbent is washed several times with distilled water to remove excess acid. This regenerated biosorbent was used in further adsorption steps. Regeneration of adsorbent material is important in determining the potential for economical usage of the selected material²¹. All desorption studies were carried out in triplicate and showed average of 85% recovery for nickel metal from PPAC.

3. RESULTS AND DISCUSSION

The process of metal adsorption is a surface phenomenon which is affected by physical and chemical characteristic of adsorbent and the adsorbate. The adsorption studies of nickel (II) on PPAC were carried out by optimizing various parameters like agitation time, pH, nickel (II) concentration and amount of PPAC added.

3.1 Effect of pH

pH of the solution has a significant impact on the uptake of heavy metals from aqueous media by specific adsorbent. The variations in percentage removal of nickel (II) on different initial pH (3-11) are demonstrated in Figure 2. The trend showed gradual increase in nickel (II) uptake from 27.1% to 68.9 % with the increase in pH from 3-7. No considerable change has been observed at pH above 7.0. This is due to change on the charge of the adsorbent and degree of ionization as pH varied.²² At lower pH value the hydrogen ions are in higher concentration and compete for sorption site present on adsorbent surface with metal ions but with the increase in pH, presence of hydroxyl ions in solution provide more sorption sites for metal ions by deprotonating the adsorbent surface²³ hence more metal ion get adsorbed.

Fig. 2 Effect of system pH on adsorption of nickel (II) (20 mg/L) onto PPAC (0.5g/50ml) at $30 \pm 1^\circ\text{C}$ temperature and a contact time of 50 minutes.

3.2 Effect of adsorbent dose

The effect of adsorbent dose on nickel uptake is shown in Figure 3. The results show an increase in percentage removal of nickel ions with the increase of adsorbent dose from 27.7% to 69%. This is attributed to the fact that the extent of adsorption is proportional to specific areas and higher sorbent doses provide more surface area and pore volume for nickel (II) adsorption²⁴ to certain extent.

Fig. 3: Effect of adsorbent dose on adsorption of nickel (II) 10-150mg/L with pH 7.0 at $30 \pm 1^\circ\text{C}$ temperature and contact time of 50 minutes.

3.3 Effect of contact time and initial metal concentration

The effect of initial metal concentrations of nickel (II) ions from 10-130 mg/L was studied at 30-60 mins time intervals with 0.5g/50 ml adsorbent dose. The results are presented in Figure 4.

Fig. 4: Effect of contact time (30-60mins) and initial nickel concentration (10-130mg/L) onto PPAC (0.5g/50ml) at $30 \pm 1^\circ\text{C}$ temperature.

Data showed a fast rate of sorption during 30-50 mins of the sorbate-sorbent contact and the rate of percentage removal of nickel (II) becomes almost insignificant above this contact time. This rapid adsorption in the beginning by the PPAC is due to the availability of the larger surface area for the adsorption of the nickel ions but this decreases with the exhaustion of the adsorption sites with nickel ions and no further considerable change is observed. Removal efficiency also significantly affected by the initial concentration of metal ion in aqueous solutions. Metal adsorption is dependent on the concentration of nickel in the solution, by increasing the nickel ion concentration the resistance between aqueous and solid phase for mass transfer of nickel ion decreases. The adsorption of nickel ions by PPAC (Q_e) increased from 3.1 to 7.78 with increase in the initial metal ion concentration and hence increased the removal efficiency by increasing adsorption sites^{25,26}.

3.4 Adsorption isotherms

Studies were carried out to explain the relationship between the adsorbent and adsorbate interaction to establish equilibrium. Two well-known adsorption isotherms, *Langmuir* (Figure 5.) and *Freundlich* (Figure 6) were chosen to analyze the experimental data. These equilibrium modeling provides important information for industrial design of adsorption systems. *Langmuir* model describes that the interaction of metal ion is maximum at the homogenous monolayer of the adsorbent surface. The values of the monolayer adsorption capacity of the adsorbent $q_{\max}$ and the *Langmuir* constant b were calculated for nickel adsorption by plotting the graph between C_e and Q_e and are reported in table 1. The $q_{\max}$ value for nickel (II) ions was 10.82 mg/g which is higher from the other adsorbents previously studied for nickel adsorption from aqueous medium²⁷⁻³²; for detailed comparison of $q_{\max}$, please see Table 2. According to *Freundlich* model, value of constants, K and n , are found to be 0.446 and

1.47 respectively which indicate that experimental data of nickel adsorption is fitting well in both adsorption models.

Table 1 Parameters of Langmuir and Freundlich isotherms.

Langmuir Model			Freundlich Model		
$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K	N	R^2
10.82	0.028	0.942	0.446	1.47	0.931

Table 2. Comparison of adsorption capacities of various nickel adsorbents.

Biosorbent	$Q_{\max}$
Activated sludge ²⁷	7.78
Baggass fly ash ²⁸	6.49
Sugar beet pulp ²⁹	5.52
Orange Peel ¹⁸	9.82
<i>Aspergillus niger</i> ³⁰	6.63
Cross-linked chitosan ³¹	6.40
Lignin ³²	5.99
PPAC (This work)	10.82

Fig. 5: *Langmuir* Isotherm for Nickel (II) 10-200mg/L onto PPAC (0.5g/50ml).

Fig. 6 *Freundlich* Isotherm for Nickel (II) 10-200mg/L onto PPAC (0.5g/50ml).

4. CONCLUSIONS

The present study shows that the activated carbon prepared from waste peels of pomegranate is an effective adsorbent for the removal of nickel ions from aqueous solutions. The adsorptions process is a function of adsorbent and adsorbate concentrations, pH, and time of agitation, the effective pH for

nickel adsorption was found to be neutral. Maximum adsorption occurred at 50 mins of contact time and sorbent dose of 0.5g/ 50ml. Equilibrium data are well correlated with *Langmuir* and *Freundlich* adsorption equations. The maximum monolayer adsorption capacity of the adsorbent is 10.82mg/g. This study provides a cost effective and useful design of wastewater treatment plants for the removal of nickel that uses waste as a resource and helps to get rid of waste disposal expenses.

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