REMOVAL OF Cr (VI) AND Ni (II) IONS FROM AN AQUEOUS SOLUTION USING MODIFIED POMEGRANATE PEEL

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ABSTRACT

Heavy metals are very toxic and pose a threat to man and the environment. Removal of heavy metals from wastewater has received greater attention in recent years. The objective of study was to investigate the possibility of using modified pomegranate peel as an alternative adsorbent for the removal of Cr (VI) and Ni (II) ions from aqueous solution. The effect of temperature, contact time and initial ion concentration was investigated on the adsorption of Cr (VI) and Ni (II) ions by modified pomegranate peel using batch adsorption experiment. The adsorption increased with rise in temperature. Thermodynamic parameters like adsorption distribution coefficient (K), change of Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) during the adsorption were determined. The results show that adsorption process of Cr (VI) and Ni (II) ions by modified pomegranate peel is fissile, spontaneous and endothermic under studied condition.

INTRODUCTION

The adsorption of toxic metals onto the agricultural waste and waste materials provides economical and eco-friendly technique for their removal from aqueous solutions. However, decontamination of heavy metal ions from water and wastewater had received considerable attention by using various techniques such as activated carbon adsorption (Koby et al. 2005), chemical precipitation (Ahalya et al. 2003), reverse osmosis (Volesky 2003), electro-dialysis (Xia and Liyuan 2002) and ion exchange (Rengaraj et al. 2001). Recently much attention has been spent on successfully using biological materials and wastes for the removal of heavy metals from water and wastewater such as microbial biomass (Nwuche and Ugoji 2008, Ge et al. 2009, Chatterjee et al. 2012, Rajendran et al. 2014) and biological wastes (Khafia and Surchi 2011 and Muthusamy et al. 2012, Kumar et al. 2013, Mohammed et al. 2014). The characteristics of biosorbent materials are less expensive, high bio-removal capacity, metal selective, non sludge generation, possible ion recovery (Reddad et al. 2002) and environmentally sound methodology (Volesky 2001). The technique of plant residues heavy metal ions adsorption was worldwide used for wastewater treatment (Helal et al. 2014) such as peat and nut shells, coconut shells, rice husk, tea waste, peanut hulls, almond shells, peach stones, citrus peels, and many others (Ahmed 2010, Khafia and Surchi 2011, Muthusamy et al. 2012, Kumar et al. 2013, Mohammed et al. 2014).

Pomegranate peel is rich in ellagitanins (ETs) such as punicalagin and its isomers, as well as lesser amounts of punicalin (4, 6-gallagyglucose), gallagic acid, ellagic acid (EA) and EA-glycosides (Seeram et al. 2005). Moghadam et al. (2013) have used pomegranate peel carbon for removal of Fe (II) while Deosarkar (2012) for removal of lead and cadmium from aqueous solutions. El-Ashtoukhly et al. (2008) also used pomegranate peel (raw), activated carbon prepared from pomegranate peel for removal of lead (II) and copper (II) from aqueous solutions. Similar trend was observed for removal of heavy metal ions from industrial wastewater by using raw pomegranate peel (Shartooh et al. 2013).

Therefore, we thought pomegranate peel as modified form can be used as adsorbent for Cr (VI) and Ni (II) ions as it is a material composed of several constituents, including polyphenols, ellagic tannis and gallic and ellagic acids (Ben
Nasr et al. 1996). The objective of this work was to study the feasibility of using modified pomegranate peel as new adsorbents for the removal of Cr (VI) and Ni (II) ions from aqueous solution. In this work batch adsorption experiments were carried out to evaluate the adsorption characteristics for different contact time and for different temperature.

**MATERIALS AND METHODS**

**Preparation of solutions:** All chemicals used in the present work were of analytical grades. The stock solution of Cr (VI) and Ni (II) was prepared in 1.0 g/L concentration using \( K_2CrO_4 \) and \( NiSO_4 \) respectively and then diluted to appropriate concentration for study. Before mixing the adsorbent, the pH of each test solution was adjusted to required value with diluted HCl and NaOH solution respectively.

**Biosorbent preparation:** Pomegranate peels were collected from different local markets, washed thoroughly by de-ionised water and dried in dark at atmospheric temperature then milled and sieved to particle size of 500 µm. It was shaken with distilled water for overnight then filtered, this process was repeated for about ten times or until we get rid off all soluble colored materials or until we get constant weight. It was observed that more than 40% of pomegranate peel was soluble in water. The yield was dried in an hot air oven at 80°C for overnight and then milled to 150 µm particle size, this was named as modified pomegranate peel (MPGP).

**Experimental Procedure:** In the present investigation the batch mode of operation was selected to measure the progress of adsorption. To determine the adsorption effect 100 ml each of the metal ion solution of 3 mg/L initial concentration was placed in a conical flask containing 200 mg of modified pomegranate peel at different temperatures (15°C, 25°C, 35°C). The pH of mixtures was maintained at 6 by manually adding 0.1 M HCl or 0.1 M NaOH using a pH meter. Flasks were corked and placed in shaker for desired time (25, 50, 100, 150, 180, and 200 min). After 25, 50, 100, 150, 180 and 200 minutes the mixtures were filtered using Whatman (No.40) filter paper and filtrates were analyzed for equilibrium metal ion concentration by Atomic Absorption Spectrophotometer.

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<th>Cr (IV) (mg/l)</th>
<th>Ni (II) (mg/l)</th>
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<th>Ni (II)</th>
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RESULTS AND DISCUSSION

Adsorption studies

The percent removal of Cr(VI) and Ni(II) ions from aqueous solution was calculated by the following equation (1).

\[
\text{% removal } (X) = \frac{C_0 - C_e}{C_0} \times 100
\]

(1)

Where, \(C_0\) and \(C_e\) are initial and equilibrium concentration of metal ion solution (mg/L). The values of equilibrium concentration and percent metal ion removal for different temperatures are reported in Table 1. The adsorption of metal ions onto modified pomegranate peel was studied at different temperatures for different shaking times (contact time between adsorbate and adsorbent) and variation of percent adsorption with temperature and shaking times for Cr(VI) and Ni(II) is as shown in Fig. 1(a and b).

3.2. Effect of contact time: Fig. 1(a & b) shows the effect of contact time on the extent of adsorption of Cr (IV) and Ni (II). It has been observed that the removal of Cr (IV) and Ni (II) ions increases with time and attains saturation in about 150 min. However, the experimental data were measured for 200 minutes to ensure that full equilibrium was achieved. The adsorption rate increased from 40% to 90% in case of Cr (VI) and 36.67% to 87.33% in case of Ni(II) with increased in contact time from 25 to 200 min. Maximum Cr (VI) and Ni(II) ion removal was achieved within 150 min after which metal ions concentration in the test solution became constant. It may be explained by the facts that initially for adsorption large number of vacant sites was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecules and bulk phase (Bansal et al. 2009). Similar trend was observed for adsorption of lead onto agricultural waste by Khafia and Surchi (2011) and by using waste tire rubber ash by Mousavi et al. (2010). The two stage adsorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature (Saeed et al. 2005).

Effect of temperature: Fig. 2(a and b) shows the effect of temperature on the adsorption of Cr (VI) and Ni (II). From the results it is evident that there is gradual increase in the percentage removal of chromium and nickel from 73.33% to 90% and 70.67% to 87.33% respectively. The above results also showed that the adsorption was endothermic in nature. Since adsorbent is porous in nature and possibilities of diffusion of adsorbate cannot be ruled out therefore, increase in the adsorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e. the rise of temperatures favors the adsorbate transport within the pores of adsorbent (El-Shafeey 2005).

Fig. 2(a & b) Plots of % metal removal versus temperature for Cr (VI) and Ni (II) ions at constant time (150 min)

Thermodynamic parameters

![Cr (VI) ion](image1)

![Ni (II) ion](image2)

![Cr (VI) ion](image3)
Equilibrium constant (Adsorption distribution coefficient) of adsorption process was calculated by using following Nernst distribution equation [2].

\[ K_d = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \cdot \frac{C_{\text{liquid}}}{C_{\text{solid}}} \]  

(2)

Where, \( K_d \) is equilibrium constant (Adsorption distribution coefficient); \( C_{\text{solid}} \) and \( C_{\text{liquid}} \) are solid phase and liquid phase concentration (mg/l) of metal ion at equilibrium. The values of log \( K_d \) are reported in Table 1.

The standard Gibbs energy change (\( \Delta G^0 \)) associated with adsorption was calculated using following Gibbs Helmholtz equations [3].

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

(3)

Where, (\( \Delta S^0 \)) is standard entropy change; (\( \Delta H^0 \)) is standard enthalpy change; \( T \) is temperature in Kelvin.

Standard Gibbs energy change (\( \Delta G^0 \)) is related with \( K_d \) as equation (4).

\[ \Delta G^0 = -2.303RT \log_{10} K_d \]  

(4)

Where, \( R \) is gas constant (8.314 J/mol K) and \( T \) is temperature (K).

Therefore, entropy change (\( \Delta S^0 \)) and enthalpy change (\( \Delta H^0 \)) are related with \( K_d \) by following [5].

\[ \log_{10} K_d = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \]  

(5)

From the plot of \( \log_{10} K_d \) versus \( 1/T \), Fig. 3a (a & b) (Vant Hoff plots), \( \Delta S^0 \) was determined from intercept (\( \Delta S^0 = \text{intercept} \times 2.303 \text{ R} \)) and \( \Delta H^0 \) was determined from slope (\( \Delta H^0 = -\text{slope} \times 2.303 \text{ R} \)) of curve. The values of thermodynamic parameters are listed in Table 2.

Enthalpy change (\( \Delta H^0 \)): The positive value of enthalpy change, \( \Delta H^0 \) (Table 2) for Cr (IV) and Ni (II) ion is 43.23 KJ/mole and 38.33 KJ/mole respectively indicate endothermic nature of the adsorption onto modified pomegranate peel. The positive values of \( \Delta H^0 \) indicate the endothermic nature of adsorption and it also supports the possibility of physical adsorption (Najim and Yassin 2009). Arival et al. (2008a) found that the values of \( \Delta H^0 \) are within the range of 1 to 93 KJ mol\(^{-1}\), indicates the physisorption. From the results it is clear that the extent of chromium and nickel ions adsorption increases with increase of temperature, this rule out the possibility of chemisorptions (Najim and Yassin 2009).
Table 2. Thermodynamic parameters like $\Delta G^0$, $\Delta S^0$ and $\Delta H^0$ for optimized contact time

<table>
<thead>
<tr>
<th>T (K)</th>
<th>time (min.)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/K mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
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**Entropy change ("$S^0$")**: The positive value of entropy, "$S^0$" (Table 2) corresponds to an increase in the degree of freedom of the adsorbed species. The positive value of "$S^0" also reflects that some changes occur in the internal structure of modified pomegranate peel during the adsorption process. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system (Arivoli et al. 2008b). Similar types of observation were reported by other researchers for removal of lead (Choudhary et al. 2011) and chromium (Najim and Yassin 2009) from waste water.

**Gibbs energy ("$G^0$")**: The Gibbs energy indicates the degree of spontaneity of the adsorption and higher negative value reflects more energetically favorable adsorption (Hengpang et al. 2012). The negative values of Gibbs energy, "$G^0$" (Table 2), show that the adsorption is highly favorable and spontaneous. Gibbs energy change ($\Delta G^0$) is negative for all temperature indicating spontaneity of the adsorption and these values become more negative as temperature rises which is due to increase in spontaneity of the adsorption with rise in temperature.

**REFERENCES**

**CONCLUSION**
The modified pomegranate peel (MPGP) proved to be effective adsorption material for Cr (VI) and Ni (II) metal ions. For given temperature the adsorption has increased with shaking time. Rise in the temperature favored the adsorption of both the metal ions indicating it is an endothermic process.

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