Adsorption behavior of Nickel (II) and cobalt (II) onto hydrolyzed poly-methyl methacrylate

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ABSTRACT

In this research work hydrolyzed poly-methyl methacrylate (HPMMA) was tested for removal of nickel and cobalt from aqueous solution. Effect of various parameters such as pH, adsorbent dose, initial metal ion concentration, contact time and temperature on adsorption of Ni (II) and Co (II) onto HPMMA was investigated. Equilibrium studies show that the adsorption follows both Langmuir and Freundlich isotherm model. Kinetic studies show that the adsorption follows pseudo-second order kinetics.

Key words: Adsorption; Equilibrium; Nickel; Cobalt; Hydrolyzed poly-methyl methacrylate.

INTRODUCTION

The heavy metal pollution is of great concern among the kinds of environmental pollution because of their high toxicity and other adverse effects on human health. Nickel (Ni) and cobalt (Co) are toxic heavy metals found in the environment as a result of various natural and industrial activities. The higher concentration of Ni causes headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis and extreme weakness. The higher concentration of Co causes vomiting, nausea, vision problem, heart problem and thyroid damage. Hence it is necessary to remove Ni and Co ions from water at least below the regulatory level.

Various processes have been proposed for the removal of metal ions from aqueous solution. The important ones are adsorption [1], ion exchange [2], photocatalysis [3], ion floatation [4], hyperfiltration, chemical precipitation, reverse osmosis. Among these the adsorption process is found to be quite suitable, cheap and effective for the removal of metal ions from aqueous solution. A considerable amount of work has also been published in the literatures regarding the adsorption
of metal ions on various adsorbent surfaces such as clay [5], zeolite [6], bio-sorbents [7-9], agricultural wastes [10], organic/inorganic composite [11], alumina [12].

Poly-methyl methacrylate (PMMA) is a transparent thermoplastic and synthetic polymer of methyl methacrylate. It is a low cost material used for several purposes such as in medical, optics, semiconductor, paints etc. This paper presents results on the ability of hydrolyzed Poly-methyl methacrylate (HPMMA) to remove Ni (II) and Co (II) from aqueous solutions by adsorption.

EXPERIMENTAL SECTION

Adsorbent

Poly-methyl methacrylate (PMMA) was obtained from Sigma Aldrich, India (average Mol.wt. 15000, powder) and was hydrolysed by procedure reported by Brown et al. [13]. PMMA was sonicated for 10 min in a 50% aqueous 2-propanol solution and dried under a stream of nitrogen to clean and hydrate the polymer surface. The PMMA was then submerged in 3 M sulphuric acid at 60 °C for 20 min (Figure 1). The resulting material was rinsed with copious amounts of water, followed by rinsing with 2-propanol and dried in oven at 50 °C. The final material (HPMMA) was kept in dessicator to use as an adsorbent.

![Scheme for acid hydrolysis of PMMA surface.](image)

Adsorption experiment

Stock solution (1000 mg/L) of Ni and Co was prepared from Ni(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O and was subsequently diluted to 5, 10, 15, 20, and 25 mgL⁻¹. pH of the solution was maintained by adding 0.1 M HNO₃ or 0.1 M NaOH. 50 mL of metal ion solution was taken in 150 mL conical flask and required amount of adsorbent was added into that, resultant solution was stirred on magnetic stirrer (Remi) at the speed of 200 rpm. The adsorption was monitored by determining the concentration of metal ion in solution by atomic absorption spectrophotometer (ECIL-4141).

Percentage of metal ion adsorption and quantity of metal ion adsorbed on adsorbent at the time of equilibrium (qₑ) was calculated by Eq. 1 and 2 respectively.

\[
\text{% metal ion adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100
\]  
\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where C₀ and Cₑ are the initial and the equilibrium concentrations (mg/L) of metal ion in solution, qₑ is quantity of metal ion adsorbed on the adsorbent at the time of equilibrium (mg/g), V is volume (L) of solution and W is mass of adsorbent (g) taken for experiment.

Batch experiments were carried out to determine the effects of pH, adsorbent dose, initial metal ion concentration, contact time and temperature by varying the parameter under study and keeping other parameters constant. Each experiment was carried at constant pH (6), adsorbent
dose (5 g/L), temperature (303 K), initial metal ion concentration (10 mg/L) and contact time (60 min) unless mentioned.

RESULTS AND DISCUSSION

FTIR study

The FT-IR spectra of PMMA and HPMMA were recorded by FTLA2000 spectrophotometer using KBr disc method. Spectra of PMMA shows a band at 1739 cm\(^{-1}\) is due to C=O stretching of ester group. An overtone band at 3440 cm\(^{-1}\) is due to stretching of C=O group (frequency twice than that of C=O stretching). A band at 1242 cm\(^{-1}\) is due to C-O-C stretching. The band at 2951 and 2994 cm\(^{-1}\) are due to C-H stretching and corresponding bending peak occurs at 1449 cm\(^{-1}\). Spectra of HPMMA shows a band at 1720 cm\(^{-1}\) is due to C=O stretching of carboxylic group. The broad band at 3100-3400 cm\(^{-1}\) is assigned to O-H stretching. The shifting of C=O stretching band from 1739 cm\(^{-1}\) to 1720 cm\(^{-1}\) confirms hydrolysis of ester group of PMMA.

Influence of pH

The influence of pH on adsorption of metal ions was studied over the range of pH 2-6. As shown in Fig. 2, adsorption of Ni (II) and Co (II) on HPMMA was increased from 21 to 59 % and 25 to 66 % respectively with increasing pH from 2 to 6. At lower pH values, hydrogen ion competes with metal ions and most of the carboxyl of adsorbent exists in the form of –COOH, which reduce the adsorbed amounts for Ni (II) and Co (II) ions. At higher pH values, more –COO\(^-\) occur, which may enhance electrostatic attraction and the adsorption capacity of adsorbent for metal ions. However, further increase in pH causes precipitation of Ni (II) and Co (II) due to formation of hydroxyl complexes, therefore, the pH higher than 6 was avoided.

![Graph showing influence of pH on adsorption](image)

**Fig. 2. Influence of pH on adsorption of Ni (II) and Co (II) on HPMMA**

Effect of temperature

To observe the effect of temperature on the adsorption of metal ions on HPMMA, experiments were conducted at three different temperatures 303, 313 and 323 K. It was observed that the adsorption decreases with increasing temperature (Fig. 3), which indicates a low temperature favours Ni (II) and Co (II) removal by sorption onto the HPMMA. This may be due to a tendency for the Ni (II) and Co (II) ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. A similar observation was also reported in the study on the sorption of Pb onto modified and unmodified kaolinite clay [14].
The effect of adsorbent dose on adsorption was studied using different amount of dosage in the range of 1-6 g/L. Fig. 4 shows that as increasing adsorbent dose frequently from 1 to 5 g/L adsorption of Ni (II) and Co (II) on HPMMA increased from 20 to 59 % and 28 to 66 % respectively, due to the greater availability of the adsorption binding sites. Further increase of adsorbent dose of HPMMA did not cause any significant change because equilibrium was achieved between solid and solution phase.

Effect of Initial metal ion concentration
To observe the effect of initial metal ion concentration on adsorption, experiments were conducted over the wide range of initial metal ion concentration (5-25 mg/L). Fig. 5 shows that the % removal of Ni (II) and Co (II) ions decreases from 65 to 46 % and 72 to 54 % respectively.
with increasing initial metal ion concentration from 5 to 25 mg/L. The decrease in % adsorption of metal ions is due to lesser availability of adsorption site.

![Graph showing the influence of initial metal ion concentration on adsorption of Ni (II) and Co (II) on HPMMA.](image1)

**Fig. 5.** Influence of initial metal ion concentration on adsorption of Ni (II) and Co (II) on HPMMA.

**Adsorption kinetics**

Adsorption kinetics study shows that the rates of sorption decreases with increase of time and after 60 min equilibrium were achieved (Fig. 6).

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto an adsorbent. The rate constant of adsorption was determined from the pseudo-first order rate expression [15] (Eq.3) given by Lagergren:

\[
\ln(q_e - q_t) = \ln q_e - k_{ad}t
\]

(3)

where \( q_e \) and \( q_t \) are the amount of metal ion adsorbed at equilibrium and at time \( t \) (mg/g) respectively and \( k_{ad} \) (min\(^{-1}\)) is rate constant of adsorption. It was observed from the plots of Eq. 3 that the pseudo-first order model was not suitable to describe the kinetic profile of the adsorption.

![Graph showing sorption kinetics of Ni (II) and Co (II) on HPMMA.](image2)

**Fig. 6.** Sorption kinetics of Ni (II) and Co (II) on HPMMA.
The pseudo-second order sorption kinetics [15] may be written as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

(4)

where \( k_2 \) is the rate constant of sorption (g/mg/min). The values of \( k_2 \) and \( q_e^{cal} \) were calculated from intercepts \( (1/k_2q_e^2) \) and slopes \( (1/q_e) \) of the plots of \( t/q_t \) vs. \( t \) (Fig. 7) respectively and are reported in Table 1. Results shows that values of regression correlation coefficient \( (R^2) \) are close to unity and the values of \( q_e^{cal} \) and \( q_e^{exp} \) are almost equal which confirm that adsorption of metal ions on HPMMA follows pseudo-second order kinetic model.

![Fig. 7. Pseudo-second order kinetics plots for adsorption of Ni (II) and Co (II) on HPMMA.](image)

Table 1: Pseudo second order kinetic parameters for Ni(II) and Co(II) adsorption on HPMMA

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>( q_e^{exp} )</th>
<th>( q_e^{cal} )</th>
<th>( k_2 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (II)</td>
<td>1.18</td>
<td>1.24</td>
<td>0.191</td>
<td>0.988</td>
</tr>
<tr>
<td>Co (II)</td>
<td>1.32</td>
<td>1.37</td>
<td>0.161</td>
<td>0.986</td>
</tr>
</tbody>
</table>

**Adsorption isotherm**

The analysis of the sorption process requires the relevant adsorption equilibria for better understanding the adsorption process. Sorption equilibrium describes the nature of adsorbate-adsorbent interaction. In the present study the equilibrium data were analyzed using the Langmuir and Freundlich isotherms.

**Langmuir isotherm model**

The saturated monolayer isotherm can be represented by Eq. 5

\[
q_e = \frac{Q_m b C_e}{(1 + bC_e)}
\]

(5)

The linearized forms of Langmuir can be written as follows [16]:

\[
\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}
\]

(6)

where \( q_e \) is the adsorption density (mg/g) at equilibrium of metal ion, \( C_e \) is the equilibrium concentration (mg/L) of the metal ion in solution, \( Q_m \) is the monolayer adsorption capacity.
(mg/g) and b is the Langmuir constant related to the free energy of adsorption (L mg⁻¹). The values of Qₘ and b were calculated from the slope (1/Qₘ) and intercept (1/bQₘ) of the linear plots of Cₑ/qₑ vs. Cₑ (Fig. 8) and are given in Table 2. Linear plots of Cₑ/qₑ vs. Cₑ shows that adsorption isotherm of adsorption of metal ions on HPMMA follows the Langmuir isotherm model.

Fig. 8. The Langmuir plots for the adsorption of Ni (II) and Co (II) on HPMMA.

**Freundlich isotherm model**
Freundlich isotherm can be expressed as follows [17]:

\[
q_e = K_f C_e^{1/n} \tag{7}
\]

The linearized forms of Freundlich equations can be written as follows:

\[
\ln q_e = \ln K_f + (1/n)\ln C_e \tag{8}
\]

where Kₖ and n are Freundlich constants related to sorption capacity [mg g⁻¹ (mg L⁻¹)⁻¹/n] and sorption intensity of adsorbents. The values of Kₖ and n were calculated from the intercept (lnKₖ) and slope (1/n) of the plots ln qₑ vs. ln Cₑ (Fig. 9) and results are presented in Table 2. Linear plots of ln qₑ vs. ln Cₑ show that the adsorption isotherm of metal ions on HPMMA also fitted well in the Freundlich isotherm model. The values of n > 1 indicate favourable adsorption conditions [18].

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir isotherm parameters</th>
<th>Freundlich isotherm Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Qₘₐₓ b R²</td>
<td>Kₖ n R²</td>
</tr>
<tr>
<td>Ni</td>
<td>3.69 0.11 0.998</td>
<td>0.475 1.63 0.996</td>
</tr>
<tr>
<td>Co</td>
<td>4.40 0.13 0.990</td>
<td>0.596 1.59 0.998</td>
</tr>
</tbody>
</table>
This study shows that HPMMA is an effective adsorbent for removal of Ni (II) and Co (II) from aqueous solution. The pH 6 and temperature 303 K was found to be optimum for the adsorption. The adsorbent dose of 5 gL\textsuperscript{-1} was able to remove 59\% of Ni (II) and 66\% of Co (II) within 60 min of contact time. Adsorption processes follow pseudo-second order kinetics. The adsorption of metal ions onto the HPMMA follows both, Langmuir and Freundlich isotherm models.

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