Adsorption of nickel from aqueous solutions by activated carbons

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Adsorption isotherms of Ni(II) ions from aqueous solutions of nickel nitrate in the concentration range 50-1000 mg/L on two samples of granulated and two samples of fibrous activated carbons associated with varying amounts of carbon-oxygen surface groups have been determined. The adsorption isotherms are Langmuir in shape showing an initial rapid adsorption tending to be constant at higher concentrations. The adsorption of Ni(II) ions increases on oxidation, and decreases on degassing of the carbons surface. The increase in adsorption on oxidation depends upon the nature of the oxidative treatment while the decrease on degassing depends upon the temperature of degassing. The adsorption is related directly to the amount of acidic surface oxygen groups present on the carbon surface.

Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper and chromium are the three most commonly used metals, the choice depending upon the specific requirements of the article. During rinsing of the electroplated articles and washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Thus the waste water of such industries where nickel plating is one of the process, contains Ni(II) ions. It has been estimated that the amount of Ni(II) ions in the effluent when disposed off in lakes and rivers is injurious to living beings and vegetation.

Several types of adsorbents have been obtained and used by different investigators for the removal of Ni(II) ions from industrial effluents. Deokar and Tavalrides1 studied the removal of nickel and copper from dilute aqueous streams from electroplating industries by adsorption on chemically active inorganic beds and observed that the removal capacity depended upon the pH of the aqueous stream. The chemically active beds could be regenerated by stripping the adsorbed metal ions with a mineral acid. Dimitrova2, used ungranulated blast furnace slag for the removal of Ni2+, Cu2+ and Zn2+ ions from aqueous solutions in the concentration range 10^{-5}-10^{-3} mol/L.

Vishwakarma3 and Nonvinakere and Reed4 examined the influence of initial nickel concentration, residence time, temperature and pH on the feasibility of nickel removal from water by adsorption on fly ash. Increase in temperature and pH and a decrease in initial nickel concentration favoured the removal of Ni(II) ions. The maximum adsorption of Ni(II) ions was observed at pH around 7. The equilibrium data fitted the Langmuir equation and the monolayer capacity was 0.293 mg/g at 30°C. Mathur et al.5, while using blast furnace slag and flyash as adsorbents, found the removal of Ni(II) ions to be between 30-35%.

Tewari et al.6 examined the removal of Ni(II), Cu(II) and Cr(VI) ions from dilute aqueous solutions in the concentration range 5-50 mg/L by adsorption on an activated carbon in the pH range 5.5-8.0. While the adsorption of Cr(VI) ions exhibited a peak at pH 5.5 and Cu(II) ions at 8.0, the adsorption of Ni(II) ions was found to be appreciable in both acidic and basic media. However, the rate of adsorption was faster in the alkaline medium.

Singh and Rawat7, used low grade bituminous coal before and after oxidation with H2O2 and MnO2 for the removal of Ni, Cu, Zn and Cr from aqueous solutions. The rate of adsorption and the adsorption capacity of the coal enhanced significantly upon oxidation. The adsorption rate was found to follow Langmuir equation.

Above perusal of the literature shows that several types of adsorbents have been used for the removal of nickel and other metal ions from water. Active carbons, however, are the most widely used adsorbents for the removal of organics and inorganics from aqueous solution.8-10. This is due to the fact that these adsorbents have a large surface area and a high
The present work describes the removal of Ni(II) ions from aqueous solutions using different activated carbons before and after oxidation and degassing. The results have been explained in terms of the carbon-oxygen surface chemical groups.

**Experimental Procedure**

The procedures for degassing and oxidation have been described elsewhere\(^\text{4,19,21}\) but brief descriptions are given below:

*Degassing of the carbons—* About 5 g of each of the activated carbon sample was spread in thin layer about 5" long in a tube furnace. It was kept in position by means of porous copper gauge plugs. The tube furnace was connected to a Hyvac Cenco vacuum pump capable of giving a vacuum to the order of 3 x 10\(^{-3}\) mm Hg. The temperature of the furnace was raised to the required level slowly. The gases began to be evolved soon after. The temperature was allowed to rise gradually and before it was raised by another 50°C complete elimination of the gases, at the preceding temperature was ensured. After degassing at the required temperature, the sample was allowed to cool in vacuum to room temperature to avoid reformation of the carbon-oxygen surface groups and was then transferred to stoppered bottles flushed with nitrogen. These samples are referred to as "degassed samples" in the text.

*Oxidation with nitric acid—* 5 g of the activated carbon sample was heated with 150 mL of pure nitric acid in borosil beaker of 250 mL capacity in a water bath maintained at about 80°C. When all but about 10 mL of the acid had evaporated, the contents were cooled, diluted with water and transferred over a filter paper. The carbon sample was washed exhaustively with hot distilled water until the filtrate was free of nitrate ions. This oxidation and washing resulted in the loss of some carbon. Some of the oxidised carbon also passed through the filter paper. The washed carbon sample was dried first in air and then in an electric oven at 120°C outgassed at 150°C and then stored in stoppered glass bottles flushed with nitrogen.

### Table I—Freundlich equation constants for adsorption of Ni(II) ions on different as-received carbons

<table>
<thead>
<tr>
<th>Carbon Sample</th>
<th>n</th>
<th>K/m mol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-S</td>
<td>0.686</td>
<td>0.115</td>
</tr>
<tr>
<td>GAC-E</td>
<td>0.704</td>
<td>0.42</td>
</tr>
<tr>
<td>ACF-307</td>
<td>0.892</td>
<td>0.02</td>
</tr>
<tr>
<td>ACF-310</td>
<td>0.701</td>
<td>0.56</td>
</tr>
</tbody>
</table>

degree of surface reactivity. Furthermore, the surface reactivity of the activated carbons can be modified by oxidation\(^1\), degassing\(^19,21\) or by the impregnation of the carbon surfaces with organic\(^22,23\) and inorganic\(^24-28\) species.
Oxidation with gaseous oxygen—5 g of each carbon sample was spread in a platinum boat. The mouth of the platinum boat was covered with a platinum lid having holes so that oxygen gas could make contact with the carbon. The boat containing the carbon sample was placed in a resistance tube furnace. The temperature of the furnace was maintained at 350 °C. Pure and dry oxygen was passed over the sample at the rate of two litres per hour for 4 h. The sample was then cooled in oxygen gas and transferred to reagent bottles and stored under nitrogen.

Base neutralisation capacity (surface acidity)—Surface acidity of each carbon sample was determined by mixing 0.25 g of each carbon sample with 25 mL of 0.2 N NaOH solution in a borosil flask of 100 mL capacity. The suspension was heated placing the corked bottle in a water bath maintained at about 70 °C for 8 h. The amount of unused alkali was determined by titrating an aliquot of the clear supernatant liquid against a standard acid solution. A blank was run every time and the necessary corrections were applied.

Determination of pH of the carbon—0.2 g portion of the carbon sample was placed in contact with 20 mL CO₂ free distilled water in a borosil glass bottle. The suspension was shaken mechanically for 6 h and the pH of the suspension determined using a glass electrode pH meter.

Adsorption of Ni(II) ions—0.1 g of each carbon sample was placed in contact with 20 mL solution of each concentration for 24 h in a thermostat maintained at 30°C, with occasional shaking. A blank run was also placed for each solution. The amount of Ni(II) ions adsorbed was determined spectrophotometrically using a wavelength of 445 nm by making a complex with dimethyl glyoxime using standard analytical procedures. The linear calibration curves for the determination of Ni(II) spectrophotometrically was determined. The adsorption isotherms were determined at 30°C.

Result and Discussion

Adsorption isotherms of Ni(II) ions from aqueous solutions of nickel nitrate in the concentration range 50-1000 mg/L on the four activated carbon samples are presented in Fig. 1. The adsorption isotherms are Langmuirian in shape showing an initial rapid adsorption tending to be almost constant at higher concentrations. The adsorption isotherms may be described by the general Langmuir equation,

\[ x = \frac{x_m (K.C)^n}{(1 + K.C)^n} \]  

(1)

where \( x \) is the amount adsorbed at equilibrium concentration \( C \), \( x_m \) is the maximum amount of Ni(II) ions adsorbed, \( K \) is the Langmuir constant and \( n \) is the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorption surface. When \( n = 1 \), the above equation is reduced to the Classical Langmuir isotherm characteristic for homogenous surfaces.
The Langmuir equation reduces to the Freundlich equation:

This equation can be written as:

\[ \ln x = \ln x_0 + n \ln C \]  \hspace{5mm} \text{(4)}

Fig. 5—Adsorption isotherms of Ni(II) ions on HNO₃-oxidised ACF-307 before and after degassing.

At lower solution concentrations \((KC)^n\) is very small and the Langmuir equation reduces to the Freundlich equation:

\[ x = x_0 (KC)^n \]  \hspace{5mm} \text{(2)}

which is frequently used for the interpretation of adsorption from solution because of its simplicity. This equation can be written as:

\[ x = x_0 K_n C = K'C^n \]  \hspace{5mm} \text{(3)}

where \(K = x_0 K^n\) is the Freundlich adsorption constant related to adsorption energy. The logarithmic form of the Freundlich equation can be written as:

\[ \ln x = \ln K + n \ln C \]  \hspace{5mm} \text{(4)}

The linear Freundlich adsorption isotherms on log-log scale for the four activated carbons are shown in Fig. 2. The Freundlich equation constants \(K\) and \(n\) calculated from the linear plots are recorded in Table 1. It is seen that the value of \(n\), which is a measure of surface heterogeneity, is always less than unity indicating that none of the activated carbons has a completely homogeneous surface. This may be attributed to the fact that all the four carbons are associated with carbon-oxygen surface groups present at certain sites. These surface oxygen groups render the carbon surface heterogenous in character. Similar linear Freundlich adsorption isotherms were plotted for carbon samples after oxidation and after degassing. It was found that the value of \(n\) decreased on oxidation due to the formation of carbon-oxygen surface groups on certain sites and increased on degassing due to the elimination of these groups. The value of \(n\) was minimum for the carbon samples oxidized with nitric acid, which incidentally results in the fixation of maximum amount of surface oxygen on the carbon surface. The value of \(n\) was the highest and close to unity for the 950°C degassed carbon samples indicating that these samples had almost a homogenous surface.

The adsorption isotherms in Fig. 1 show that the adsorption of Ni(II) ions is larger on granulated carbons GAC-E and GAC-S than that on the fibrous activated carbons ACF-307 and ACF-310. This cannot be explained on the basis of surface area alone because ACF-310, which has about the same BET surface area as GAC-E (Table 2), adsorbs smaller amounts of Ni(II) ions, than GAC-E. This can also not be explained on the basis of the total amount of oxygen associated with these carbons because fibrous activated carbons, which show lower adsorption capacity, have larger amounts of oxygen associated with them (Table 2).

It is well known that the associated oxygen on carbon surfaces is present in the form of two types of functional groups: one which are evolved as CO₂ on evacuation in the temperature range 350-750°C. These surface groups are acidic in character and are postulated as carboxyls and lactones. These acidic groups make the carbon surface negatively charged when placed in aqueous solutions. The other oxygen groups, which are evolved as CO on evacuation in the temperature range 500-950°C, have been postulated as quinones. Furthermore, the amounts of these two types of surface groups are enhanced by oxidation of the carbon surface.

Table 2—Surface areas and gases evolved on degassing different as-received activated carbons at 950°C

<table>
<thead>
<tr>
<th>Sample identification</th>
<th>BET(N₂) surface area ((m²/g))</th>
<th>CO₂ ((g/100g))</th>
<th>CO ((g/100g))</th>
<th>H₂O ((g/100g))</th>
<th>Total ((g/100g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-307</td>
<td>910</td>
<td>1.00</td>
<td>5.30</td>
<td>1.30</td>
<td>7.60</td>
</tr>
<tr>
<td>ACF-310</td>
<td>1184</td>
<td>1.90</td>
<td>4.20</td>
<td>1.40</td>
<td>7.50</td>
</tr>
<tr>
<td>GAC-S</td>
<td>1256</td>
<td>2.10</td>
<td>1.05</td>
<td>1.24</td>
<td>4.39</td>
</tr>
<tr>
<td>GAC-E</td>
<td>1190</td>
<td>2.13</td>
<td>1.66</td>
<td>1.33</td>
<td>5.12</td>
</tr>
</tbody>
</table>
The dispositions of associated oxygen into these two types of surface oxygen groups on evacuating the as-received activated carbons at gradually increasing temperatures up to 950°C are given in Table 2. It is seen that the disposition of the associated oxygen as CO₂ and CO is different in the two groups of carbons. Granulated activated carbons have larger amounts of oxygen evolved as CO₂ while the fibrous activated carbons are associated with larger amounts of oxygen evolved as CO. Thus it appears that it is not the total...
oxygen but its disposition into CO₂ and CO which may be a factor in determining the adsorption of Ni(II) ions by carbons.

In order to examine the influence of carbon-oxygen surface groups on the adsorption of Ni(II) ions more clearly, two samples of carbons viz. ACF-307 and GAC-E were oxidized with nitric acid in solution and with oxygen gas at 350°C. The adsorption isotherms of Ni(II) ions on the oxidized samples are shown in Figs 3 & 4. The adsorption isotherms on the as-received samples are reproduced in these figures for the sake of easy comparison. It is interesting to note that for both the carbons, the adsorption increases significantly on oxidation, the magnitude of increase being different for the different oxidative treatments. The adsorption increases from 2.7% to 4.4 and 3.1% in the case of GAC-E and from 0.9% to 2.9 and 1.65% in the case of ACF-307 respectively on oxidation with nitric acid and oxygen gas. Thus the uptake of Ni(II) ions is considerably larger when the oxidation is carried out with nitric acid. Incidentally this treatment is a stronger oxidative treatment and results in the fixation of considerably larger amounts of carbon-oxygen surface groups in both the carbons (Table 3). The amount of associated oxygen increased from 5-7% to between 22-22% on oxidation of the two carbons with nitric acid and only to between 10-12% on oxidation with oxygen gas. Furthermore, it is also seen that the oxidation with nitric acid enhances the amount of surface acidic groups by several orders of magnitude while the increase on oxidation with oxygen is only small.

Thus it appears that the increase in adsorption of Ni(II) ions which is much larger in the case of carbon samples oxidized with nitric acid is due to the presence of larger amounts of the surface acidic groups.
This view receives support from the adsorption isotherm of Ni(II) ions on the oxidized carbon samples degassed at gradually increasing temperatures of 400°C, 650°C and 950°C (Figs 5-8). This treatment eliminates varying amounts of the carbon-oxygen surface groups. It is seen that the uptake of Ni(II) ions decreases gradually as the temperature of degassing is enhanced. The decrease in adsorption is only slight between 0.2-0.3% for both ACF-307 and GAC-E when degassed at 400°C. This is due to the fact that degassing at 400°C eliminates only a small part (15%) of the acidic carbon oxygen surface groups (Table 4 & 5). However, when the carbon samples are degassed at 650°C—a temperature at which a major portion (85%) of the acidic groups is removed as CO (Tables 4 & 5) the adsorption of Ni(II) ions decreases considerably although these samples still retain a larger proportion of the non-acidic surface groups evolved as CO (Tables 4 & 5). In case of the samples degassed at 950°C, the adsorption of Ni(II) ions is even smaller. This can be attributed to the fact that 950°C-degassed samples are almost completely free of any associated oxygen groups, which provide sites for the adsorption of Ni(II) ions.

The presence of acidic oxygen surface groups and their ionization in water also changes the pH of the carbon suspension. The pH of as-received ACF-307 was around 7 while that of GAC-E was around 10. However, the pH of these carbons was reduced to between 3 and 4 on oxidation with nitric acid and to between 4 and 5 on oxidation with oxygen gas. This decrease in pH of the carbon surface results in an increase in the adsorption of Ni(II) ions. In order to verify this point, the adsorption of Ni(II) ions was determined from solutions of different pH values. The effect of pH of the solution on the adsorption of Ni(II) ions in the case of ACF-307 and GAC-E shows that the maximum adsorption occurs in the pH range 3-5 (Fig. 9).

A relationship between the maximum amount adsorbed and the surface acidity as determined by titration with NaOH solution, of different as-received, oxidized and degassed carbons is shown in Fig 10. It is seen that the points for the two carbons cannot be collected along a single straight line. However, the plots for a given carbon show almost a linear variation of adsorption with surface acidity thus giving rise to two linear plots, one for each carbon. The difference in behaviour of the two carbons in giving two different linear plots may be attributed to the difference in the microporous structure of the two carbons.

*Mechanism of Ni(III) adsorption*—The carbon surface has unsaturated C-C bonds which on oxidation with oxidizing agents can add oxygen giving rise to acidic carbon-oxygen surface chemical structures. These chemical structures on hydrolysis in aqueous solution produce H⁺ ions which are directed towards the liquid phase producing an acidic effect in the solution. The carbon surface of oxidized carbons, therefore, behaves as negatively charged. Thus the electrostatic attractive interactions between the negatively charged carbon surface and the positively charged Ni(II) ions increase on oxidation thereby increasing the adsorption. On degassing, the oxygen groups are eliminated from the carbon surface and this results in a decrease of the negatively charged sites, which in turn decreases the uptake of Ni(II) ions.
ions. When the oxygen is removed almost completely by degassing at 950°C, the carbon surface attains more or less a positive character. This decreases the attractive interactions between the carbon surface and the Ni(II) ions thereby decreasing the adsorption.

Thus it is apparent from the results presented in this paper that the adsorption of Ni(II) ions from aqueous solutions is influenced by the acidic carbon-oxygen surface chemical groups. These acidic surface groups enhance ion exchange properties of the carbon surface.

Acknowledgment

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References

3 Vishwakarma P S, Pertanika, 12 (1989), 357.