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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 5, No.4, pp. 814-819, October 2008

Surface Modification of Activated Carbon for Enhancement of Nickel(II) Adsorption

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Received 9 February 2008; Accepted 5 April 2008

Abstract: A carbon prepared from coconut shells by simple carbonization was oxidized with different oxidizing agents, namely, hydrogen peroxide, ammonium persulphate and nitric acid. The surfaces of the unoxidized and oxidized carbons were characterized by Boehm and potentiometric titrations and IR spectra. The carbon materials prepared were tested for their ability to remove Ni(II) ions from aqueous solutions by batch mode adsorption experiments. Oxidations increased the surface acidic groups on the carbon which resulted in increased affinity of the carbon towards Ni(II).

Keywords: Activated carbons, Surface chemistry, Ni(II) adsorption, Isotherm

Introduction

Nickel is commonly used in refining, electroplating and welding industries and human exposure to nickel is highly probable in such environments. Nickel can cause a variety of pathologic effects like skin allergy, lung fibrosis and cancer¹⁻⁵. The most important health problems due to exposure to nickel and nickel compounds are allergic dermatitis (nickel itch) and increased incidence of cancers. Nickel is genotoxic and mutagenic as well⁵. Though there are very many harmful effects of nickel on human health, production of its compounds is essential and one has to look at the ways of reducing its input into the environment from the waste streams.

Various physico-chemical treatments have been developed and successfully used for the removal of heavy metals like nickel from contaminated wastewater. A particular focus has been given to chemical precipitation, coagulation-flocculation, flotation, ion exchange and membrane filtration⁶ although biosorption⁷⁻⁸ and adsorption onto low-cost materials like activated carbons⁹ are finding increased importance nowadays.

Activated carbon adsorption has been a promising technique for the removal of heavy metal ions from water. Though the removal efficiency of a carbon is primarily decided by the pore structure and total surface area of the carbon the chemistry of the surface (the nature

and density of surface functional groups) is of paramount importance in the removal of ionic or polar species.

The present work aims at modifying the surface of an activated carbon prepared from coconut shells by oxidation with such reagents as concentrated nitric acid, hydrogen peroxide and ammonium persulphate for the enhancement of copper adsorption.

Experimental

Adsorbents

An activated carbon prepared from locally available coconuts shells (CSC) was selected for this study. The carbon was prepared by carbonizing the shells in a muffle furnace at a temperature of 400°C for 1 hour. It was ground, sieved to get particles of size 150-250 µm; washed with double distilled water and finally dried in air oven at 120°C overnight for further use. CSC was oxidized with concentrated nitric acid, hydrogen peroxide and ammonium persulphate¹⁰. Briefly, the preparations involve mixing of 5 g of CSC with 50 mL of each oxidizing agent for a period of 10 hours. After the reaction time, the carbon masses were separated and excess reagents were removed by washing in a Soxhlet apparatus for a couple of days. Nitric acid, hydrogen peroxide and ammonium persulphate treated CSCs were given the name, respectively, CSCN, CSCH and CSCA.

Chemical characterizations of the carbon surfaces

The carbons prepared were assessed by the Boehm titration method for the determination of acidic and basic functional groups. Acidic sites were determined by titrating with NaOH and basic sites with HCl and the details can be found elsewhere^{11,12}. Potentiometric titrations were performed to find out the surface acidity constants and the pH of zero point charge, pH_{ZPC}, following the methodology of Devranche *et al*¹³. Cation-exchange capacity (CEC) of the carbons were determined by the ability of them to exchange cobalthexamminetrichloride complex from aqueous solutions¹³.

FT-IR spectra

IR spectra of the carbon samples were recorded in a Nicolet Impact 410 IR spectrophotometer using KBr for pellet making.

Analysis of nickel(II)

Nickel(II) was estimated colorimetrically¹⁵ by monitoring the absorption of the DMG complex at 470 nm in a Spectronic 20D⁺ spectrophotometer.

Batch adsorption experiments

For equilibrium adsorption studies, 50 mL of synthetic wastewater containing Ni(II) was mixed with the desired amount of adsorbent; the slurry is shaken in a mechanical shaker for 2 hours and filtered using Whatmann No. 41 filter paper. The filtered samples were then analyzed for the unadsorbed Ni(II) concentration. pH adjustments were done with dil. HCl or dil HNO₃. A systronics pH meter with combined glass and calomel electrodes was used. The adsorption capacity, q_e , is given in milligrams of metal ion loaded per gram of adsorbents (equation 1).

$$q_e = (C_o - C_f) / m_s \quad (1)$$

where C_o and C_f are the initial and final metal ion concentrations (mg/L), and m_s is the mass of activated carbon (g/L).

Results and Discussion

Chemical characterization results

The reagents selected for modification of the carbon surface are all oxidizing agents and the purpose is to increase the density of surface functional groups. That this task is achieved successfully is evident from the chemical characterization results of the modified carbons. It is seen from Figure 1 that the acidity of the carbons in moving from CSC, the unmodified to CSCH, CSCA and finally CSCN, increase in the same order (as is reflected in the crossings of the x-axis). The increased acidity is due to the presence of such acidic groups as carboxyl, phenolic, *etc.*

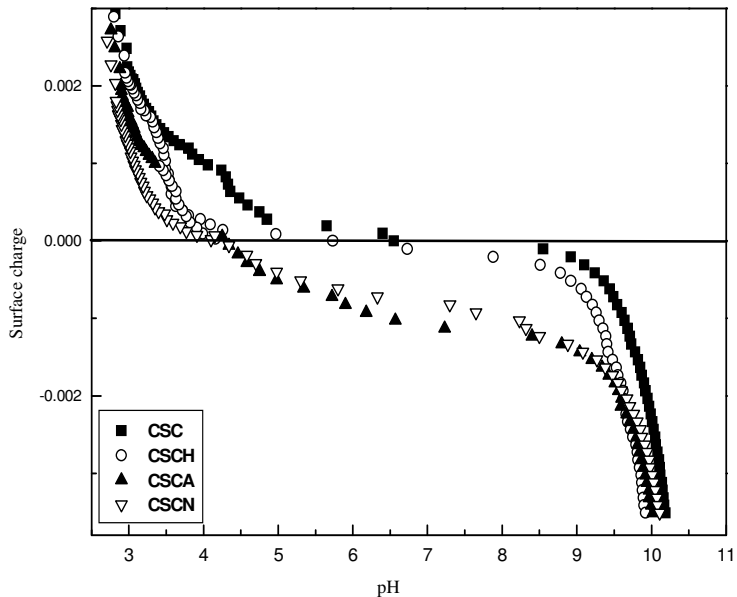


Figure 1. Effect of oxidation on the surface charges CSC.

Surface acidity constants evaluated for the carbons are presented in Table 1 along with their pH_{ZPC} and cation-exchange capacity values. Mention has to be made regarding the increased ion-exchange capacity values of the oxidized carbons.

Table 1. Surface acidity constants and CEC of activated carbons

| Carbon | pK_{a1}^S | pK_{a2}^S | pH_{ZPC} | CEC, mol/g |
|--------|-------------|-------------|------------|------------|
| CSC | 9.91 | 4.98 | 7.45 | 7.6 |
| CSCH | 9.47 | 3.97 | 6.72 | 9.6 |
| CSCA | 9.45 | 4.07 | 6.76 | 11.2 |
| CSCN | 9.24 | 3.57 | 6.40 | 11.3 |

The results of Boehm titrations (Table 2) also confirm the view. Table 2 suggests that the numbers of all acidic sites, namely, lactonic, phenolic and carboxyl increase when CSC is reacted with the oxidizing chemicals. The numbers of basic sites, on the other hand, are generally reduced with these modifications, the effect being most pronounced for concentrated nitric acid. This could be due to the fact that nitric acid can neutralize and even destroy basic sites.

FTIR spectra

The FTIR spectral results (Figure 2) are consistent with the chemical characterization results. After oxidation, it is observed that, the intensities of all the peaks that are

characteristic of C-O functional groups increase. This is true for peaks at about 3500 cm^{-1} which are characteristic of (O-H) stretching of carboxyl groups; peaks centered around 1600 cm^{-1} which are finger prints of carbonyl groups as their stretching frequencies fall in this range. The C-O stretching vibrations of carboxylic and phenolic groups in the region $1100\text{-}1200\text{ cm}^{-1}$ also increase in their intensity with the extent of oxidation.

Table 2. Boehm titration results for CSC and modified CSCs

| Carbon | Surface groups, mequiv/g | | | | | Total |
|--------|--------------------------|----------|------------|--------|-------|-------|
| | Lactonic | Phenolic | Carboxylic | Acidic | Basic | |
| CSC | 0.023 | 1.021 | 0.280 | 1.324 | 0.562 | 1.886 |
| CSCH | 0.023 | 0.882 | 0.558 | 1.463 | 0.235 | 1.698 |
| CSCA | 0.095 | 1.021 | 0.764 | 1.880 | 0.400 | 2.280 |
| CSCN | 0.162 | 1.160 | 0.697 | 2.019 | 0.235 | 2.254 |

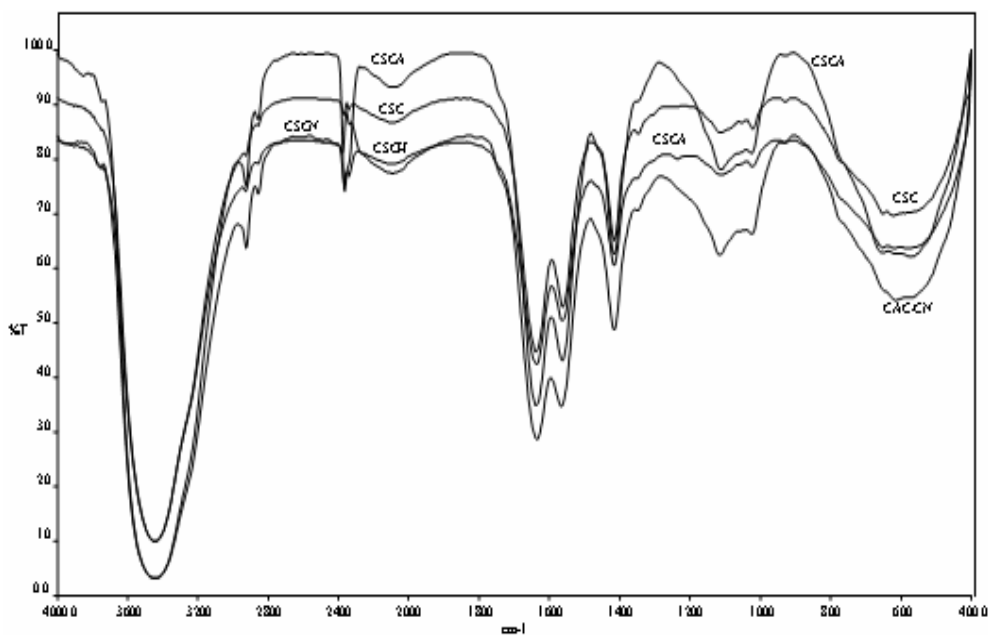


Figure 2. FTIR spectra of activated carbons

Adsorption of nickel(II)

Equilibrium adsorption experiments were conducted with CSC and the modified carbons for assessing their ability to remove divalent nickel from aqueous media using synthetic Ni(II) wastewaters. The experiments were conducted by equilibrating with 0.1 g adsorbents with 50 mL Ni(II) solutions of concentration ranging from 10 mg/L to 250 mg/L and the results are shown in Figure 3.

Equilibrium adsorption data obtained are also fitted to the well-known Langmuir isotherm equation in the following form

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

Where q_m is the Langmuir monolayer capacity (mg/g), b is the Langmuir constant and C_e is the equilibrium concentration of metal ion (mg/L). The isotherm constants associated with each adsorption system is given in Table 3.

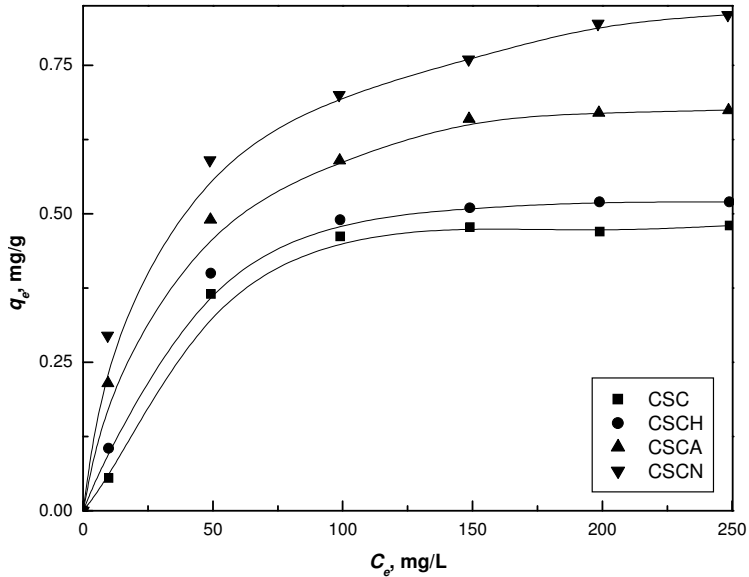


Figure 3. Adsorption isotherms of Ni(II) on activated carbons

Table 3. Langmuir isotherm constants for the adsorption of Ni(II)

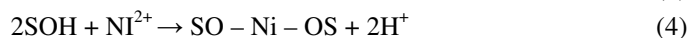
| Carbon | q_m mg/g | b | r^2 |
|--------|------------|--------|--------|
| CSC | 0.5813 | 0.0272 | 0.9696 |
| CSCH | 0.6099 | 0.0325 | 0.9863 |
| CSCA | 0.7507 | 0.0401 | 0.9983 |
| CSCN | 0.8881 | 0.0451 | 0.9927 |

Langmuir monolayer capacities, the q_e values for the carbons increase in the following order:
 CSC > CSCH > CSCA > CSCN

The increased capacities of the oxidized carbons are due to the presences of large amounts of acidic groups which can exchange their protons with the cationic Ni(II) present in aqueous solution.

The role of surface groups in the removal of Ni(II) is further confirmed by pH variation studies. Adsorptions are strongly influenced by pH as shown in Figure 4. Studies were performed only up to the pH value of 7, for Ni(II) precipitates above this pH.

The higher adsorptions at high pH are due to the fact that the surface functional groups of the oxidized carbons ionize leading to greater retentive power towards the positively charged Ni^{2+} ions. The interaction of nickel ions with the surface can, therefore, be represented by the following equations (where S represents the carbon surface):



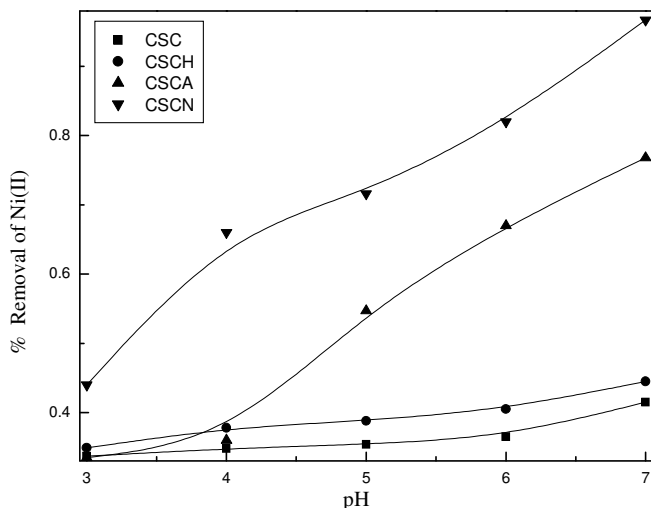


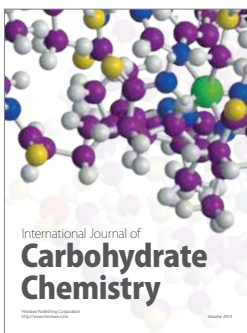
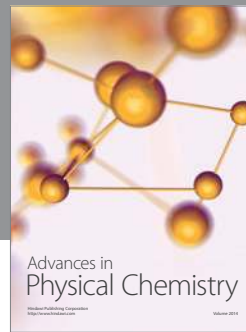
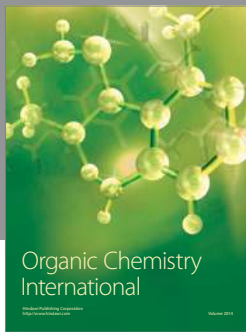
Figure 4. Effect of pH on the adsorption of Ni(II)

Conclusions

Modification of coconut shell carbon with hydrogen peroxide, ammonium persulphate and nitric acid significantly improved Ni(II) retentivity. The maximum adsorption capacity of the carbon increased from 0.5813 mg/g to 0.8881 mg/g by nitric acid modification. The increase in adsorption extents of Ni(II) on the oxidized coconut shell carbons is due to the surface acidic groups which were produced during oxidation.

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