



Removal of Nickel (II) from Aqueous Solutions by Adsorption with Granular Activated Carbon (GAC)

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Abstract

Metal ion contamination of drinking water and waste water, especially with heavy metal ion such as nickel, is a serious and on-going problem. In this work, granular activated carbon was used for the removal of Ni²⁺ from aqueous solution. The impacts of the Ni²⁺ adsorption capacities of the acid-modified carbon oxidized with HNO₃ were also investigated. Metal sorption characteristics of raw and modified granular activated carbon were measured in batch experiments. An increase in adsorption capacity of the modified carbon than raw granular activated carbon towards nickel ion adsorption is observed

Keywords: Granular activated carbon (GAC), nickel, nitric acid-surface treatment, isotherms, scanning electron micrograph (SEM).

Introduction

Water is the most common and widespread chemical compound in nature which is a major constituent of all living creatures¹. Heavy metal pollution of the environment has become a growing ecological crisis and concern and therefore the subject of many research². These heavy metals are continuously released into the aquatic environment from natural process like volcanic activity and weathering of rocks. Industrial processes like electro plating, metal finishing, metallurgical, chemical manufacturing and mining industries have greatly enhanced the concentration of heavy metals in the water. Ions of heavy metals like copper, nickel, zinc, cadmium, lead, chromium and mercury have a significant impact on the environment³. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms⁴. Out of these ions, Nickel (Ni²⁺) is the most abundant element in the Earth's crust, comprising about 3% of the composition of the earth. It is the 5th most abundant element by weight after iron, oxygen, magnesium and silicon. It is released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material. Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources⁵⁻⁸. Nickel and nickel compounds have many industrial and commercial uses. Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel metal and its alloys are used widely in the metallurgical, chemical and food processing industries, especially as catalysts and pigments. The nickel salts of greatest commercial importance are nickel chloride, sulphate, nitrate, and carbonate, hydroxide, acetate and oxide^{6,7}. The exposure to nickel is known to cause asthma and is related to hard metal related respiratory diseases. Excess risk of lungs and

nasal cancers are associated with sulphide and oxide forms of nickel. Due to this, World Health Organization (W.H.O) has prescribed standards for desirable nickel concentration in drinking water as 0.1 mg/L and industrial effluents as 3.0 mg/L. Therefore, it is necessary to bring the nickel concentration below the prescribed limits⁹.

Removal of toxic metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, adsorption etc.¹⁰⁻¹². Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness¹³⁻¹⁶. Adsorption is commonly used technique for the removal of metal ions from various industrial effluents¹⁷. Some widely used adsorbents for adsorption of metal ions include activated carbon^{18,19}, clay minerals²⁰, biomaterials^{21,22}, industrial solid wastes^{23,22} and zeolites^{13,15}. In these context varieties of activated granular carbon was tried for the removal of nickel (II) ions from aqueous solution. The main objective of this paper was to correlate the adsorption performance of acid modified activated carbon with the unmodified activated carbon.

Material and Methods

Apparatus: All absorbance measurements are taken by Digital Spectrophotometer (Type-166, Systronics India Ltd.) with matched cells of 1 cm optical path length.

Reagents and Chemicals: Varieties of carbons of Calgon Corporation Filtrasorb used namely F-100, F-200 Pittsburg(USA). All the reagents and chemicals used are of A.R. Grade. Nickel sulphate hepta hydrate (E. Merck India Ltd.) was used for the preparation of standard nickel solution and it

was diluted proportionately to prepare the experimental solution. Bromine water, ammonia solution and DMG (dimethyl glyoxime) used in the experiment were of analytical grade HNO_3 from E. Merck India Ltd. was also used for oxidizing the carbon surface.

Surface area: Estimation of the specific surface area of granular activated carbon are based upon measurement of the capacity of the adsorbent expressed in mol/gm of GAC and related to the surface area using Langmuir equation for monomolecular adsorption. The relation relates the surface area to the monolayer capacity factor by the relation:

$$S = N_a \cdot Q^o \cdot A$$

Where, S = Surface area of the adsorbent in m^2/g ; N_a = Avagadro's number; Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in mg/g ; A = cross sectional area of the adsorbate molecule in m^2 .

Since the values of Q^o can be obtained from Langmuir plots of $1/q_e$ versus $1/C_e$, the value of S for any particular GAC sample can be calculated. Here, q_e is the concentration of metal ion on GAC in mg/g of carbon and C_e is equilibrium concentration of adsorbate in solution in mg/L . The occupied surface area of adsorbent by nickel ion due is calculated from the following expression $A = 4 \times 0.866 [M / (4\sqrt{2} \cdot N_a \cdot d)]^{2/3}$

Where, M = atomic weight of nickel, N_a = The Avagadro number, d = the density of nickel using $M = 58.70$, $N_a = 6.023 \times 10^{23}$ and $d = 9.0$

Modification of Granular Activated Carbon: In the present work an effort has been made to modify the carbon surface by using oxidizing agents called as chemical modification of the surface. The raw carbon was washed with boiled distilled water followed by cold distilled water. The process was repeated till all fine powdered activated carbon were removed and the supernatant liquid become almost clear. It was then in an air oven for almost for about 24 hours at temp of $110 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. In present study, the carbon surface is modified by treating with concentrated nitric acid. The dried granular activated carbon was taken in round bottom flask, concentrated HNO_3 is added. The content is stirred for 30 minutes it was then cooled and dried. It was called as oxidized activated carbon. This acid treatment oxidizes the porous carbon surface, enhanced the acidic property, removes the mineral elements and improved the hydrophilic of surface²⁴.

Preparation of Nickel solution: A standard Nickel stock solution was prepared by dissolving 1.401 gm of nickel sulphate (E. Merck India Ltd.) in 500 ml of distilled water. The nickel solution used for the preparation of standard Beer's law was estimated with UV visible spectrophotometer and was found that 1 ml = 0.586 mg. A standard calibration curve was plotted using standard procedure. 10 ml of each stock solution was titrated against standard 0.01M EDTA solution following the

standard procedure for the estimation of nickel. Working standard solutions were prepared by appropriate dilution of stock solution. The dilute nickel stock solution of the concentration range of 10^{-4} M was used for standard Beer's law plot. The amount of nickel in solution was determined colorimetrically using the standard Beer's law plot²⁵.

Adsorption experiments: For determining the adsorption isotherm of nickel ion on different grades of granular activated carbon like F-200, F-100, varying weight of GAC was taken into a 1 liter round bottom flask and placed carefully in thermostat for each set of experiment. A fixed concentration of 200 ml of nickel ion in solution was then introduced. The stirrer was placed in position and the contents were stirred for six hours at $\pm 28^\circ\text{C}$. Aliquots of 5 ml of nickel ion solution were then withdrawn from the flask and analyzed calorimetrically for nickel ion concentration. The initial and final concentration of nickel ion in mg/lit was then determined spectrophotometrically. Usually equilibrium was reached with the period of shaking for six hours. Using both values C_o and C_e , the value of q_e , the amount of nickel adsorbed on the GAC was determined by following expression.

$$q_e = (C_o - C_e) \times V/W$$

Where, q_e = concentration of nickel ion on GAC in mg/g of carbon; C_o = initial concentration of nickel ions in solution in mg/l ; C_e = equilibrium concentration of nickel ions in solution in mg/L ; V = volume of solution taken in liters; W = weight of carbon taken in g.

Result and Discussion

Characterization of Adsorbent: In the present work, two grades of carbon namely filtrisorb F-100 and F-200 were used for isotherm and kinetic studies. The characteristic properties of these grades of carbon are given in table 1. It is observed that the surface areas of F-200 are slightly larger than those of F-100 carbon sample. A gradual decrease in the porosity observed from F-200 to F-100 carbon samples. Whereas the pore volume also follow same trend, that the pore volume of F-200 is higher than that of F-100.

A layered, loosely packed structure with lots of cavities, cracks, irregular protrusions with widely dispersed pores in both grades of carbon are observed by scanning electron micrograph (figure 3). This is due to the fact that all these grades of carbon are bituminous coal based samples. It is also observed that the F-200 has a large number of pores as compared to the F-100.

Adsorption Isotherm of Nickel on Different Grades of GAC: A set of twenty points of equilibrium concentration of Nickel was adsorbed on GAC in different experimental setups. The concentration of Nickel ion on GAC in mg/g of carbon was calculated by using following expression $q_e = (C_o - C_e) \times V/W$

where, q_e = concentration of nickel ion on GAC in mg/g of carbon; C_o = initial concentration of nickel ion in solution in mg

dm^{-3} ; C_e = equilibrium concentration of Nickel ion in solution in mg dm^{-3} ; V = volume of solution taken in liters; W = weight of the carbon taken in g.

A plot of q_e versus C_e represented an adsorption isotherm with different grades of carbon, namely F-200 and F-100 and is given in figure 1(a-b). The comparative adsorption capacities (saturation values of q_e) of nickel on different grades of raw GAC used in the present work can be assessed from figure 1(a-b). The trend in the q_e values at the saturation level are in the order

F-200 > F-100

This may be probably due to the fact that F-200 and F-100 have almost the same surface area which is comparatively more than that of F-200 and F-100.

Similarly, a plot between q_e and C_e plotted for different grades of oxidized carbon, namely F-200 and F-100 (figure 2 a-b). In oxidized carbon, similar trend in the q_e values at the saturation level observed as in case of raw activated carbon. A remarkable increase in adsorption capacity is observed in case of oxidized F-200 granular activated carbon. Hence a plot is plotted between $\log q_e$ and $\log C_e$ values of raw and oxidized F-200 granular activated carbon and linear relation is obtained. The plot of $1/q_e$ versus $1/C_e$ is also linear. It can be concluded from these plots that the Freundlich equations as well as the Langmuir equations are applicable in almost the entire range of concentrations used in this work.

The Langmuir equation is helpful in determining the surface area of the adsorbent under the present experimental conditions. Estimations of the specific surface areas of GAC are based upon measurement of the capacity of the adsorbent for a selected solute having a well accepted molecular cross sectional area. This is done by using the isothermal equilibrium data by determining the monolayer capacity of the adsorbent expressed in mole/g of GAC and related to the monolayer capacity factor by the relation

$$S = \frac{Na}{Q^0} \cdot A$$

where S = surface area of the adsorbent in cm^2/g ; Na = Avogadro number; A = cross sectional area of the adsorbate molecule in m^2 ; Since the value of Q^0 can be obtained from Langmuir plots of data the value of S for any particular GAC sample can easily be calculated and is given in the following table 2 and 3. The data revealed that the pore size of oxidized activated carbon increases and Ni^{2+} gets adsorbed inside the pores of oxidized granular activated carbon.

Surface area: The surface area of raw GAC F-100 and oxidized granular carbon F-200 is measured as 1.436×10^{10} and 3.509×10^{10} . The surface area of raw GAC F-200 and oxidized granular carbon F-200 is measured as 1.755×10^{10} and 3.948×10^{10} . Ravichandran and Sivasankar reported a specific surface area for montmorillonite ($19\text{m}^2/\text{g}$) which on treatment with HCl (0.1 to 0.7 M) increased up to $188.3 \text{m}^2/\text{g}$ ²⁶. The acid treatment

opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase²⁴. which is in conformity with the results obtained in this work. Kara et al. reported that increase in the surface area of sepiolite upon acid activation followed by calcinations is attributed to the removal of water molecules both formed during acid activation and those inherently present as crystal water²⁸.

Conclusion

Adsorption by granular activated carbon is a very effective technique for the removal of heavy metals from wastewater as seen from literature in recent years. Both F-100, F-200 grades of carbon used are very good adsorbents for the recovery of nickel from wastewater and F-200 grade was found to be the most suitable. Uptake of nickel ions by the granular activated carbon was enhanced after oxidation with nitric acid. This may be due to the formation of more no. of surface functional groups. These modified carbons thus can be useful in treating wastewater in effectively. The present investigation thus throws light in providing a cost effectiveness of the process for the removal of metal ions through use of modified activated carbons.

Acknowledgement

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Table-1
Characteristics of granular activated carbon

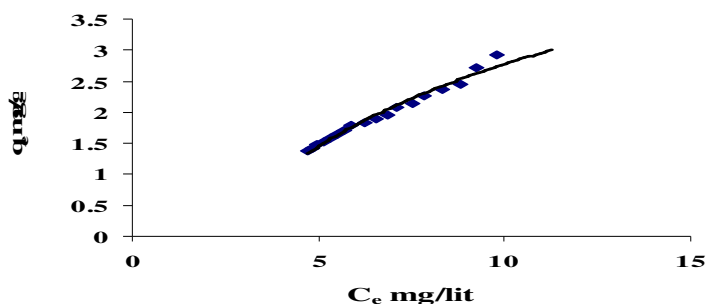
Sr. No.	Carbon Type	Origin	Surface area	Particle	Apparent	True	Pore	Porosity
			N ₂ -BET	Density	Density	density	Volume	
			m ² /g	g/cm ³	g/cm ³	g/cm ³	c/gm	
1	F-100	Bituminous coal	841	---	---	2.0790	0.549	0.26
2	F-200	Bituminous coal	825	0.8580	0.5300	2.2670	0.724	0.53

Table-2
Surface area of raw GAC for F-100, F-200

Sr. No.	Metal ion	Grades of raw GAC	Q ^o g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Ni ²⁺	F-100	45.4545	5.244	1.436 x10 ¹⁰	1.51 x10 ¹⁰
2	Ni ²⁺	F-200	55.5555	5.244	1.755 x10 ¹⁰	1.67 x 10 ¹⁰

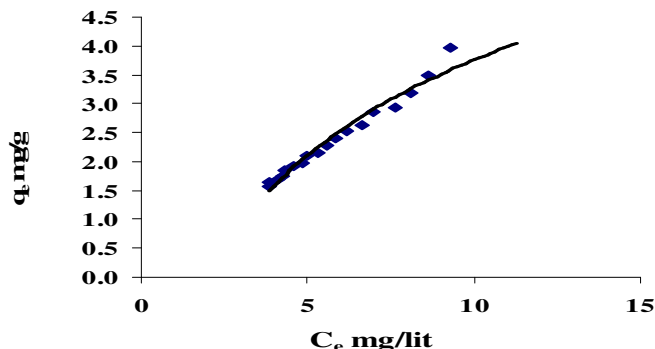
Table-3
Surface area of Oxidized GAC for F-100, F-200

Sr. No.	Metal ion	Grades of modified GAC	Q ^o g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Ni ²⁺	F-100	111.111	5.244	3.509 x10 ¹⁰	3.296 x10 ¹⁰
2	Ni ²⁺	F-200	125.000	5.244	3.948 x 10 ¹⁰	3.404 x 10 ¹⁰



System: F-100 - Raw GAC-Ni²⁺

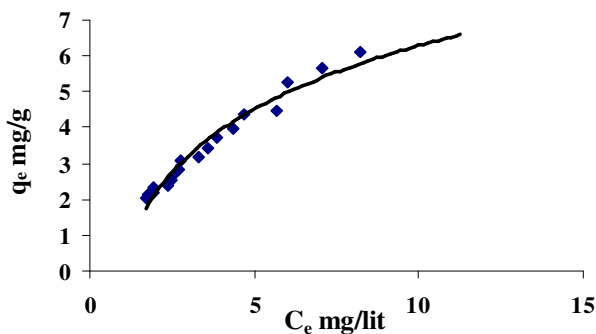
(a)



System : F-200 - GAC Raw-Ni²⁺

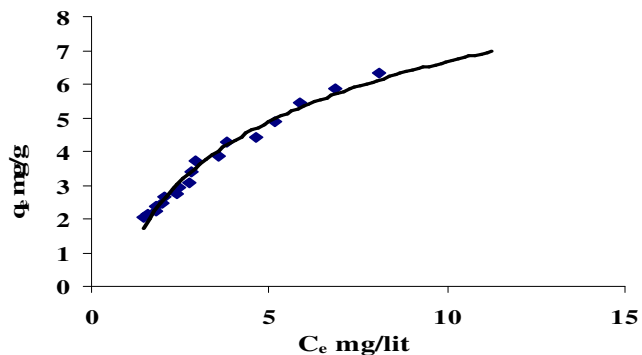
(b)

Figure-1
 (a-b) Adsorption isotherms for Ni²⁺ on different grades of raw activated carbon



System: F-100 - Oxidised GAC -Ni²⁺

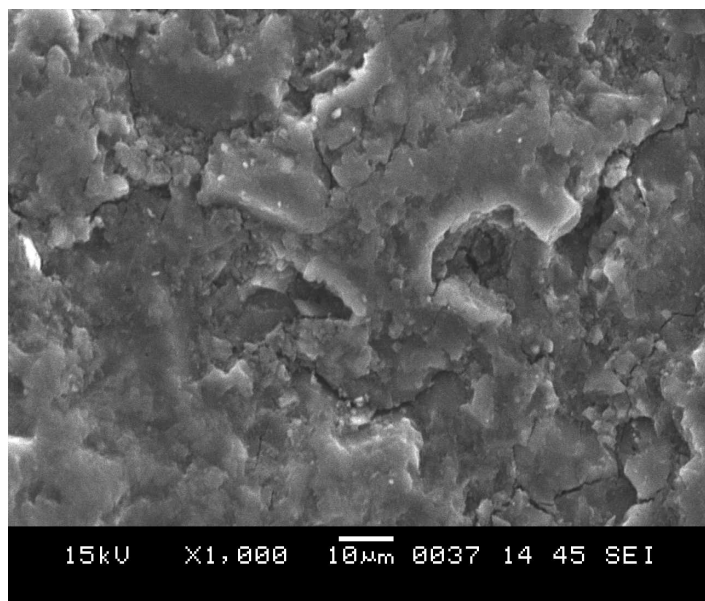
(a)



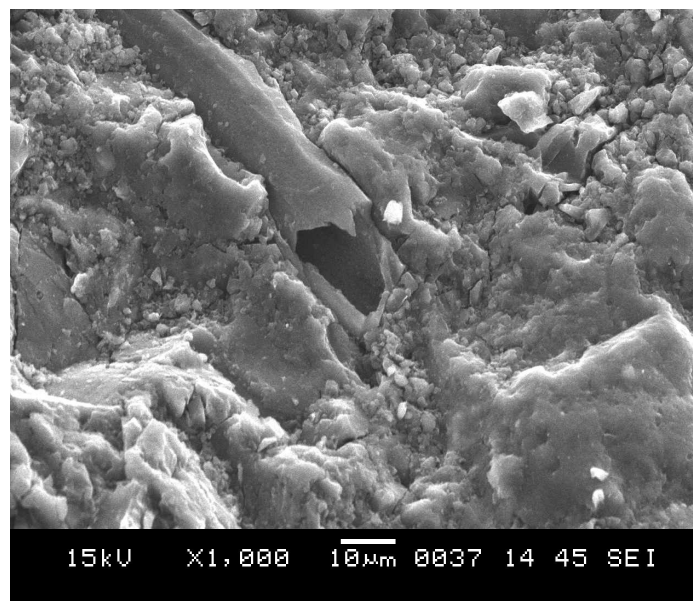
System: F-200 - Oxidised GAC-Ni²⁺

(b)

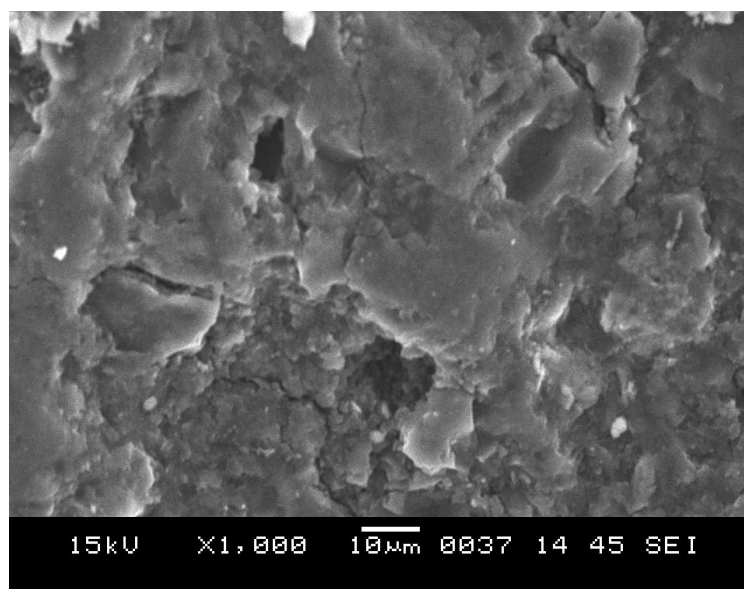
Figure- 2
 (a-b) Adsorption isotherms for Ni²⁺ on different grades of oxidized activated carbon



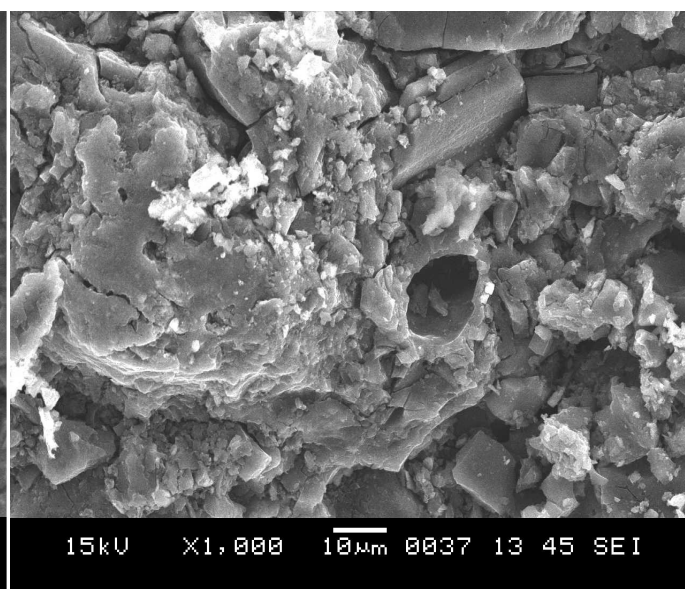
(a)



(b)



(a)



(b)

Figure-3
Scanning Electron Micrograph (SEM) of carbon surface (a-b) F100 Raw GAC and Oxidized GAC respectively (c-d) F200 Raw GAC and Oxidized GAC