

Adsorption Technology- Comparative Study of GAC Carbon Used as Adsorbent for Removing Heavy Metal Ions from Aqueous Solution.

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Abstract

Nickel (Ni) is present in wastewaters of a number of industries e.g. steel, electroplating, batteries manufacture, etc. Conventional heavy metal removal technologies such as ion exchange, chemical precipitation, reverse osmosis, etc. are often ineffective or expensive. Adsorption is a commonly used method for the removal of heavy metals from aqueous solutions. However, for the process to be economical, the adsorbent should be easily and cheaply available in abundance and it should require minimal pretreatment; for expensive pre-treatment procedures would add to the overall treatment cost. This work describes the use of a locally available low cost adsorbent, oil palm fibre, for the removal of Ni from aqueous solution. In this study removal of nickel(II) from aqueous solutions by adsorption on to (Granular Activated Carbon) GAC F300, & F 400 carbon was investigated as a function of agitation time, temp, and carbon dosage on the adsorption capacity has been studied. The metal adsorption yields increased with the increasing adsorbent dosage and contact time and reached to equilibrium for both adsorbents. GAC was characterized by SEM. Adsorption studies were carried out by using UV spectrophotometer to find its effectiveness.

Keywords: Adsorption; nickel(II) removal; GAC F300, & F 400.

Introduction :

High concentration of heavy metals in the environment can be detrimental to a variety of living species. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death. Increased concern by environmentalists and governments on the effects of heavy metals and an attempt to protect public health has resulted in increased research in the development of advance technologies to remove heavy metals from waters and wastewaters [2] Removal of toxic heavy metals from the environment is an important challenge. Ideally, a removal processes must be simple, effective and inexpensive. Several processes have been suggested to remove heavy metals from wastewaters. These processes include chemical precipitation, ion exchange, cementation [3], coagulation and flocculation [4], complexation, biosorption [5], and membrane processes [6]. In this study, we focus on the adsorption process because it is inexpensive, widely applicable, efficient, and creates relatively little sludge [7]. Activated carbon is an effective and inexpensive adsorbent [7]–[13] and has been widely used in various industries to purify water [11], [14]–[19]. Activated carbon removes heavy metals by complexation or by electrostatic attraction of metal ions to various surface oxygen-containing functional groups [11]. However, in commercial activated carbons, these functional groups

cover only a small portion of the carbon's surface [20]; increase in the quantity of these groups might enhance the activated carbon's capacity to adsorb metal cations. To enhance the capacity of Granular activated carbon to adsorb cations, many functional surface modification methods have been introduced. These include chemical or physical treatment [21]–[23], and surface modification [24]–[31]. Among these methods, surface modification method using surfactants (*i.e.* impregnation) can significantly enhance the capacities of activated carbons to absorb heavy metals [28]–[31].

In these work 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.

Methodology

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-400 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.

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. In present study, the carbon surface is modified by treating with concentrated nitric acid [32].

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 plot [33].

Adsorption experiments

For determining the adsorption isotherm of nickel ion on different grades of granular activated carbon like F-400, 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 & Discussion

Characterization of Adsorbent

In the present work, two grades of carbon namely Filtrasorb F-100 and F-400 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-400 are slightly larger than those of F-100 carbon sample. A gradual decrease in the porosity observed from F-400 to F-100 carbon samples. Whereas the pore volume also follow same trend, that the pore volume of F-400 is higher than that of F-100.

$$F-400 > F-100$$

Similarly, a plot between q_e and C_e plotted for different grades of oxidized carbon, namely F-400 and F-100 (Fig. 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-400 granular activated carbon. Hence a plot is plotted between $\log q_e$ and $\log C_e$ values of raw and oxidized F-400 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

$$S = N_a \cdot Q^0 \cdot A$$

where S = Surface area of the adsorbent in cm^2/g ; N_a = 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.

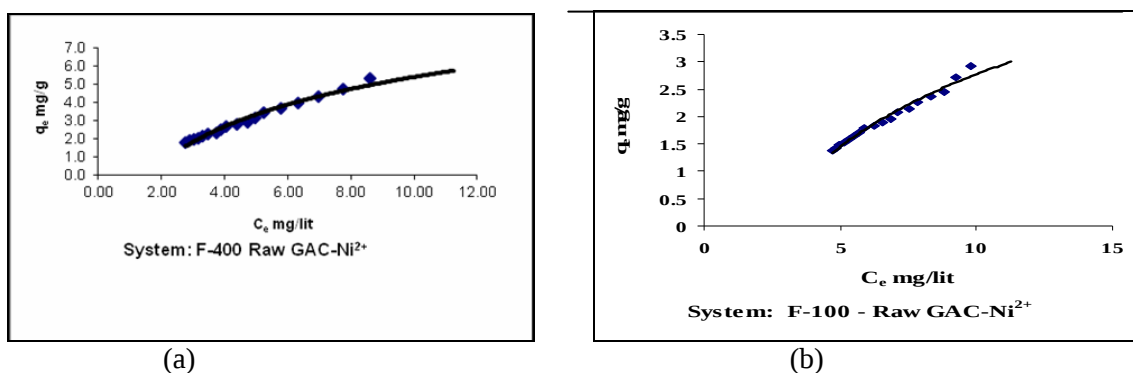


Fig. 1 (a-b) Adsorption isotherms for Ni^{2+} on different grades of raw activated carbon.

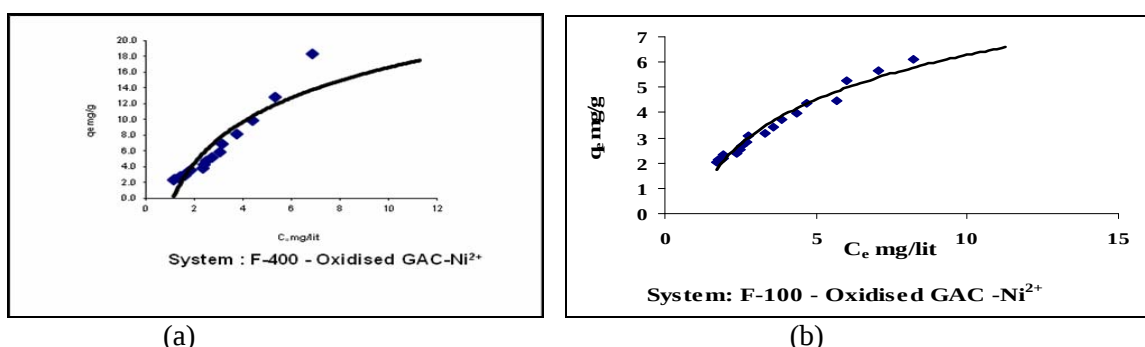


Fig. 2 (a-b) Adsorption isotherms for Ni^{2+} on different grades of oxidized activated carbon

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 (Fig.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-400 has a large number of pores as compared to the F-100.

Surface area

The surface area of Raw GAC F-100 and oxidized granular carbon F-100 is measured as 1.51×10^{10} and 3.29×10^{10} . The surface area of Raw GAC F-400 and oxidized granular carbon F-400 is measured as 2.43×10^{10} and 4.766×10^{10} . The acid treatment opens up the edges of the platelets and as a consequence, the surface area and the pore diameter increase [34] 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 water [35].

Table 1 Characteristics of granular activated carbon

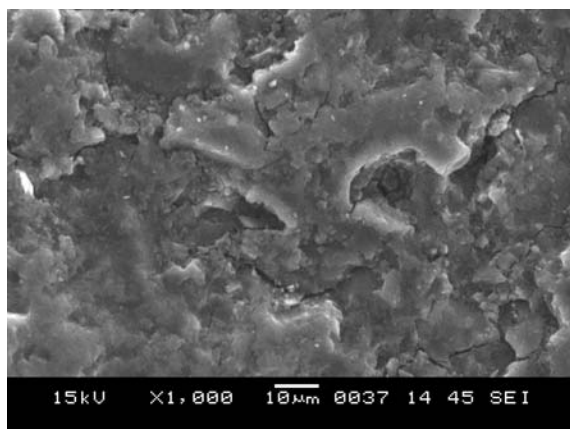
Sr. No.	Carbon Type	Origin	Surface area	Particle	Apparent	True	Pore	Porosity
			N ₂ -BET	Density	Density	density	Volume	
			m ² /g	g/cm ³	g/cm ³	g/cm ³	c/gm	
1	F-100	Bituminous coal	841	---	---	2.0790	0.549	0.26
2	F-400	Bituminous coal	998	0.795	0.4800	2.3080	0.825	0.65

Table 2 Surface area of raw GAC for F-100, F-400

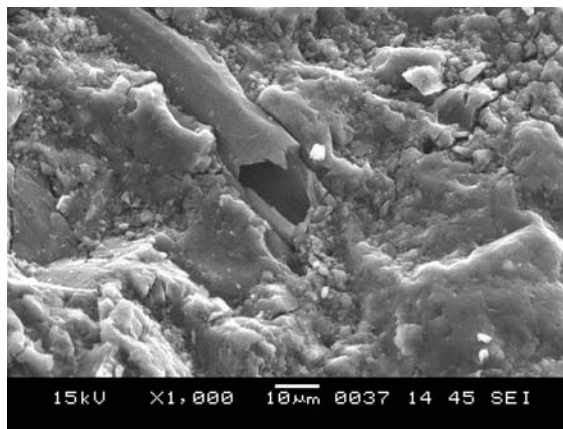
Sr. No.	Metal ion	Grades of raw GAC	Q ⁰ g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Ni ²⁺	F-100	45.4545	5.244	1.436 x 10 ¹⁰	1.51 x 10 ¹⁰
2	Ni ²⁺	F-400	83.3333	5.244	2.632 x 10 ¹⁰	2.43 x 10 ¹⁰

Table 3 Surface area of Oxidized GAC for F-100, F-400

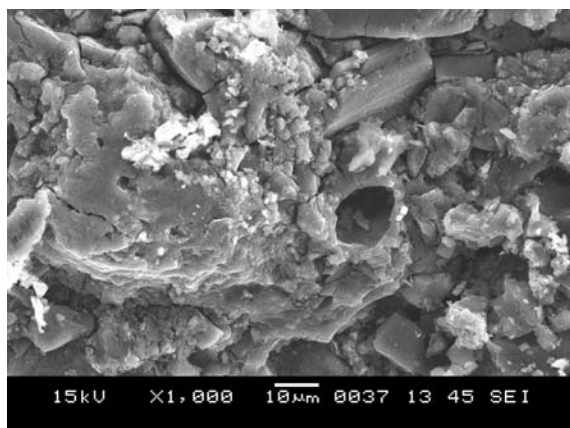
Sr. No.	Metal ion	Grades of modified GAC	Q ⁰ g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Ni ²⁺	F-100	111.111	5.244	3.509 x 10 ¹⁰	3.296 x 10 ¹⁰
2	Ni ²⁺	F-400	166.667	5.244	5.264 x 10 ¹⁰	4.766 x 10 ¹⁰



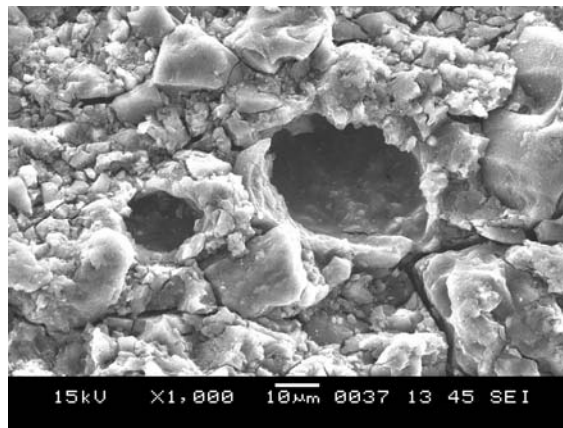
(a)



(b)



(c)



(d)

Fig. 3 Scanning Electron Micrograph (SEM) of carbon surface (a-b) F100 Raw GAC & Oxidized GAC respectively (c-d) F400 Raw GAC & Oxidized GAC

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-400 grades of carbon used are very good adsorbents for the recovery of nickel from wastewater and F-400 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.

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