SCAVENGING OF COPPER(II) FROM AQUEOUS SOLUTION USING GRANULAR ACTIVATED CARBON.

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Abstract:

The present work deals with the removal of Cu(II) ion using Granular activated carbon(F100) as a low-cost adsorbent .The influence of concentration, adsorbent dosage, particle size, and temperature (room temp.) on removal of Cu(II) ion have been studied by the batch adsorption technique. The removal of Cu(II) ion increases with the increases in the adsorbent dosage. The experimental data were analyzed by the Langmuir and Freundlich isotherms and the corresponding sorption constants were evaluated. The present study showed that Granular activated carbon (F100) was capable of removing copper ions from aqueous solution.

Keywords: Removal; Copper; Granular activated carbon (F100); Aqueous Solution; Isotherm.

Introduction

Chemical substances such as heavy metals, organic and synthetic compounds generated from industrial activities have resulted in deterioration of the ecosystem due to improper discharge. Unlike other pollutants, heavy metal contamination in the environment poses serious health problems due to their accumulation in living tissues throughout the food chain as non biodegradable pollutants [1]. Today contamination of water by toxic heavy metals resulting from the discharge of industrial wastewater is a worldwide environmental problem. Many industries, particularly in metal processing operations and refineries, represent significant sources of heavy metal emissions. Unlike organic compounds, soluble heavy metals, such as copper, cadmium, lead, and chromium, are non-biodegradable and toxic even at trace levels. Heavy metals can accumulate in living organism and cause various diseases [2–5]Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. The continued intake of copper by humans leads to necrotic changes in the liver and kidney, mucosal irritation; wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer.[6] According to the Safe Drinking Water Act, the permissible limit of copper in drinking water is 1.3 mg/L.[7] Excessive copper concentrations can lead to weakness,lethargy and anorexia, as well as damage to the gastrointestinal tract.[8] Therefore, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. The metal needs to be removed from industrial effluents before discharge into the environment to mitigate any impact on plant, animal and human receptors[9-13].The commonly used traditional methods for the treatment of metal containing effluents are chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange and evaporation. Several disadvantages are associated with these methods, such as high cost, incomplete metal removal, low selectivity, high energy requirements and generation of toxic slurries that are difficult to eliminate [14].Among all the methods adsorption is highly effective and economical.Though the use of commercial activated carbon is a well known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low-cost adsorbents from agriculture wastes such as coconut coirpith [15], sawdust [16] rice husk [17], banana pith [18], cottonseed hulls [19], apple wastes [20], sugarcane bagasse pith [21], peanut hull carbon [22], activated carbons obtained from agricultural by-products [23].and Mn-oxide coated granular activated carbon [24].for the removal of copper and cadmium from water and wastewater. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of copper and cadmium from aqueous solutions.The goal of this research was to demonstrate the efficacy of using Granular Activated Carbon for removal of copper from aqueous solutions.

Material & Methods

Apparatus

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

Adsorption Material

The various grades of Granular Activated carbon were used in this work because f its easy availability,varied pore structure & pore volume & surface area. It wase obtained from M/S Calgon Corporation, Pittsburgh, USA. In this study raw & activated granular activated carbon ie Filtrasorb- 100 (F-100) was used.

Reagents and Chemicals

All the reagents and chemicals used are of A.R. Grade. hydrated cupric chloride (E. Merck India Ltd.) was used for the preparation of standard nickel solution and it was diluted proportionately to prepare the experimental solution., HCl , dilute ammonia solution, Mureoxide indicator, buffer solution (citric acid + liquid ammonia) of the pH = 8.5 , sodium diethyldithiocarbamate solution, chloroform, anhydrous sodium sulphate 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:

$$S = N_a.Q^o.A$$

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

$$A = 4 \times 0.866 \, [M / (4\sqrt{2}. Na .d)]^{2/3}$$

Where, M = Atomic weight of nickel, Na = The Avagadro number, d = the density of Copper 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 °C ±2 °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 surface (Liu 2007).

Preparation of the solution of the Copper ion and its estimation.

A standard copper solution was prepared by dissolving 0.8524 gm of hydrated cupric chloride (E. Merck India Ltd.) in 500ml of distilled water. . The copper solution used for the preparation of standard Beer's law was estimated with UV Visible spectrophotometer and was found that 1 ml = 0.614mg/ml. 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 copper. Working standard solutions were prepared by appropriate dilution of stock solution. The dilute copper stock solution of the concentration range of 10^{-4} M was used for standard Beer's law plot. The amount of copper in solution was determined colorimetrically using the standard Beer's law plot [25]. Vogel AI Quantitative Inorganic Analysis, 4th Ed. Longmann Green & Co., London, **747 (1982).**

Adsorption experiments

All the experiments were carried out under ambient conditions.For determining the adsorption isotherm of Copper ion on F-100 grade raw granular activated carbon & oxidized granular activated carbon was taken with 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 ± 28°C. Aliquots of 5 ml of copper ion solution were then withdrawn from the flask and analyzed calorimetrically for copper ion concentration. The initial and final concentration of copper 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 copper adsorbed on the GAC was determined by following expression.

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

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, four grades of carbon namely Filtrasorb F-100 grade raw granular activated carbon & oxidized granular activated carbon were used for isotherm and kinetic studies. The characteristic properties of all the grades of carbon are given in Table 1. It is observed that the surface areas oxidized GAC F-100 are slightly larger than those of F-100 raw granular activated carbon sample.

A layered, loosely packed structure with lots of cavities, cracks, irregular protrusions with widely dispersed pores in all grades of carbon are observed by scanning electron microscope. This is due to the fact that all these grades of carbon are bituminous coal based samples.

Adsorption Isotherm of copper on F-100 Grade of GAC

A set of twenty points of equilibrium concentration of copper was adsorbed on GAC in different experimental setups. The concentration of copper ion on GAC in mg/g of carbon was calculated by using following expression

$$qe = (C_0 - Ce) \times V/W$$

where, qe = Concentration of Nickel ion on GAC in mg/g of carbon; C_0 = Initial concentration of Nickel ion in solution in mg dm^{-3}; Ce = 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.

Result & Discussion

Characterization of Adsorbent

In the present work, carbon namely Filtrasorb F-100 was used for isotherm study. A plot of qe versus Ce represented an adsorption isotherm with F-100 Raw carbon & F100 Oxidized carbon are given in Fig 1(a-b). A remarkable increase in adsorption capacity is observed in Fig. 1(a-b) case of raw & oxidized F-100 granular activated carbon.

A layered, loosely packed structure with lots of cavities, cracks, irregular protrusions with widely dispersed pores in F100 Oxidized GAC grade of carbon than F100 Raw GAC are observed by Scanning Electron Micrograph Fig.2(a-b).

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. The Nitric acid modified activated carbon showed a significant improvement in the adsorption of copper ions compared to that of raw granular activated carbon. This was due to the formation of more no. of surface functional groups. The time of oxidation also plays an important role in surface modification. These modified carbons thus can be useful in treating wastewater in effectively.

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Table. 1

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	Cu^{2+}	F-100	30.303	5.559	1.015 x10^{10}	1.623 x10^{10}

Table. 2

Sr. No.	Metal ion	Grades of modified /oxidized GAC	Q^o g/mg	A $10^{-16} cm^2$	S cm^2/gm	S' cm^2/gm
1	Cu^{2+}	F-100	71.429	5.559	2.256 x 10^{10}	2.737 x 10^{10}

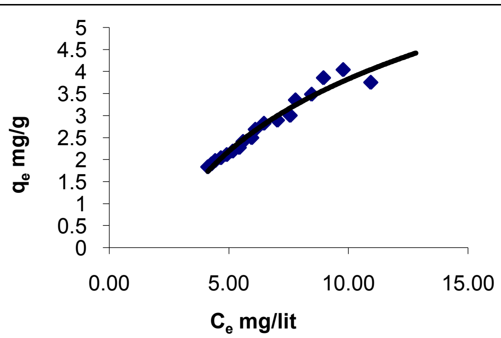

Fig 1 (a). : Adsorption Isotherm System: F-100 - Raw GAC-Cu^{2+}

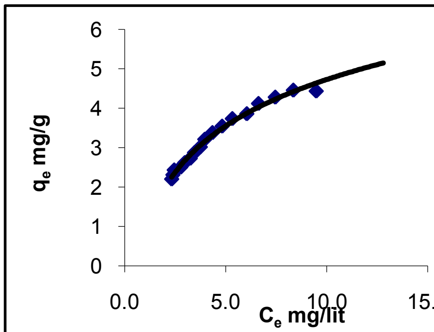

Fig 1 (b).: Adsorption Isotherm System : F-100 - Oxidised GAC-Cu^{2+}

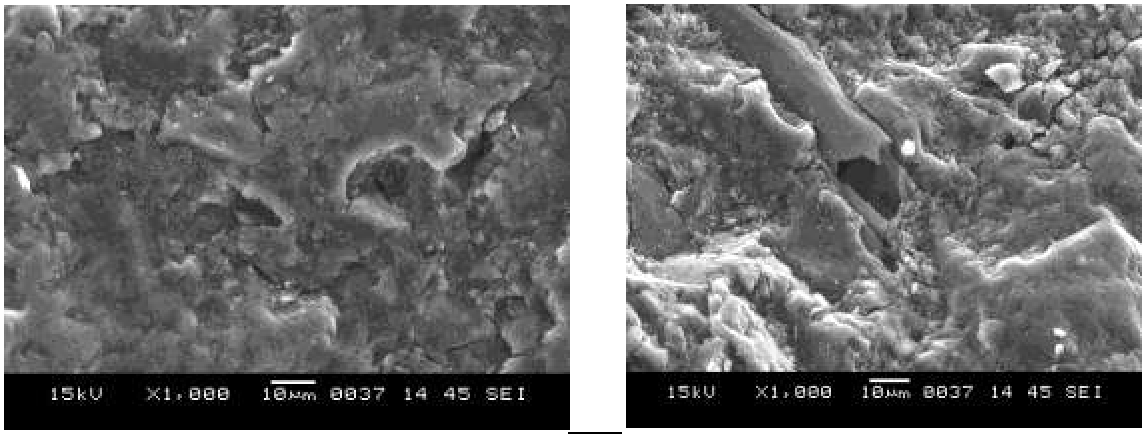

Fig. 2 Scanning Electron Micrograph (SEM) of carbon surface (a-b) F100 Raw GAC & F 100 Oxidized GAC.

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