

Adsorption of Mercuric Ion from Aqueous Solutions Using Activated Carbon

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Received: 26 May, 2004

Accepted: 10 August, 2004

Abstract

Activated carbon (AC) was prepared from hazelnut shells using two steps of carbonization followed by steam activation. Methylene blue dye was used as a probe for evaluation of the prepared activated carbon. In order to have a better comparison, a commercial grade of activated carbon (powdered) obtained from the Merck Company has also been used in this research as standard. In this paper we have also investigated adsorption of mercuric ion by impregnated activated carbon with different chemicals. It was found that sorption of mercuric ion from aqueous solution by activated carbon can be improved by impregnating AC with suitable chemicals such as sulfur-containing compounds.

Keywords: activated carbon, adsorption, impregnation, methylene blue, mercuric ion

Introduction

Activated carbon is a microcrystalline, non-graphitic form of carbon with a porous structure that has been processed to develop its internal porosity [1]. This material can be characterized by a large specific surface area of 500-2500 m²/g, the most important physical property of activated carbon which allows the physical adsorption of gases or vapors and dissolved or dispersed substances from liquids. Activated carbons (AC) are an effective adsorbent for many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment [1-10]. Its first use came into prominence through its use as an adsorbent for certain poisonous gases in gas masks during World War I.

The major use of activated carbon is in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils. In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of activated carbon for control of air and water pollution. Activated carbon is a broad-spectrum agent

that effectively removes toxic and biorefractive substances such as insecticides, herbicides, chlorinated hydrocarbons, and phenols, typically present in many water supplies. The use of activated carbons is perhaps the best broad-spectrum control technology available at present. Commercial grades of activated carbon are assigned as either gas-phase or liquid phase adsorbents. Liquid-phase carbons, generally in the form of powdered or granular, are characterized as having larger pores (3 nm in diameter and larger) because of the need for rapid diffusion in the liquid decolorizing activated carbon are usually employed as powdered. Powdered activated carbon has an extremely high ratio of area to volume, and since adsorption is a surface phenomenon, this increases its effectiveness but also makes it slow to settle and difficult to remove once added.

Any carbonaceous material (natural or synthetic) with high carbon content can be used as raw material for preparation of AC. The most common raw materials are agricultural byproducts such as wood, sawdust, rice husk, nut shells, fruit pits, and charcoal, brown and bituminous coals, lignite, peat, bone, paper mill waste (lignin), and synthetic polymers like PVC, are used for manufacturing of activated carbon. In fact, any carbonaceous low-cost materials (of animal, plant, or mineral

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origin) with high carbon and low ash content can simply be changed into activated carbon under the proper thermal decomposition process.

Activated carbons are commonly prepared using two basic processes [1-3]:

- (i) Physical or gas activation method, and
- (ii) Chemical activation.

In gas activation, the raw material with less than 25% moisture is carbonized first at 400-500°C under inert atmosphere to eliminate the bulk of the volatile matter and then the carbon is subjected to oxidizing gases, usually carbon dioxide or steam at 800-1000°C. The carbonization process results in fine and closed pores filled with high MW hydrocarbons and tarry materials. The activation process sweeps the tarry materials, opens the pores, develops porosity, and increases surface area significantly. In the chemical method, both carbonization and activation processes are carried out simultaneously. The raw material generally used is sawdust or peat, which is first mixed with chemical agents such as zinc chloride or phosphoric acid in proper ratio. The resultant paste is dried and then carbonized at high temperatures (450-700 °C) under vacuum. After carbonization, the residual chemical activating agent is removed by washing with water.

Approximately 60% of the activated carbon manufactured for liquid phase applications are prepared by chemical activation and are used in powdered form. High-density starting materials such as coconut shells are used for preparation of AC for gas phase applications in granulated form. Activated carbon can also be used for removal of poisonous heavy metal ions from aqueous solutions [5-10]. Heavy metals such as mercury, lead and cadmium in drinking waters are very dangerous even in trace amounts, and the adsorption method for removing these ions can be essential for water and wastewater contaminated by heavy poisonous metal ions. These ions cannot be removed from water with classic physical or chemical treatments completely.

Adsorption is due to the surface complex formation between the metal ions and the acidic surface function group of activated carbon. Removal efficiency is influenced by various factors such as solution concentration, solution pH, ionic strength, nature of adsorbate, adsorbent modification procedure, physical properties (surface area, porosity), and chemical nature of the activated carbon. Removing of heavy metal ions adsorption using activated carbon can be increased by impregnation of activated carbon with suitable chemicals which is based on simple chemical reactions that are common in chemistry such as acid-base or neutralization, complex formation, redox, precipitation, hydrolysis and catalytic reactions. For example, if activated carbon is impregnated by molecules, ions and chelating agents that can combine with transition metal ions to form precipitation, complex or chelates, they can improve adsorption of metal cations significantly.

Impregnations of activated carbon with different mineral and organic compounds have also been described by some previous investigators [4-10]. Activated charcoal impregnated with organic compounds with active groups

like -SH, -NH can provide more effective adsorption and elimination of heavy metals from the effluents. The rate of adsorption and completeness of removal being dependent upon pH of solution, temperature, initial concentration, molecular size and molecular weight, complexity of molecular structure of the adsorbents, the type and physical form of the activated carbon applied. Other important factors that determine the adsorption properties of an activated carbon are the pore size distribution and surface functional groups. Activated carbons possess not only carbon, but also small amounts of chemically bonded O and H atoms in the form of various functional groups that usually give acidic character to solid carbon, plus mineral matters which are usually indicated as ash or residue after ignition.

Experimental

Reagents

The chemicals used for this investigation and analysis were all analytical grade purity and the solutions were prepared in distilled water. Powdered activated carbon was obtained from the Merck Company (charcoal activated 2186) as a standard commercial type. Activated carbon was also prepared from hazelnut shells in our lab as powdered form by gas (steam) activation method.

Instrumentation

A homemade rotating electric kiln was designed and used for both carbonizing and activation processes in order to prepare AC from hazelnut shells. A single beam Spectrophotometer was employed for measuring the concentration of unabsorbed methylene blue and mercuric ion.

Procedure of Preparation AC

In this study, hazelnut shells were used in the preparation of AC by the physical method. Water steam was used as an oxidizing gas. Heat treatments, carbonization, and activation were carried out in two stages, in a rotating electric kiln designed by the author. The carbonizing step was carried out at 500°C for one hour and then the activation process (steam activation) was completed at a final temperature of 800°C for a period of 2.5 hours. Activated carbon was then cooled slowly (absence of air) and powdered in a mortar as a finely divided form, and sieved before the experiment.

Adsorption Experiments

0.10 grams of activated carbon (powdered form) were weighed accurately and treated by selected chemical solutions at room temperature for 30 min. The solutions were

Table 1. Adsorption of methylene blue with prepared and commercial activated carbon.

Adsorbent	Charcoal	AC (Merck)	AC(Hns)*
% Adsorption	7-8	70	>99

* Hns stands for activated carbon prepared from hazelnut shell in the lab. 0.10 g of AC was treated with 50 mL of 200 mg/L solution of methylene blue in water. The exposure time was 30 min. The data reported are the average of three measurements for each test. Uncertainty in adsorption is less than 1%.

Table 2. Adsorption of Hg²⁺ from aqueous solution using different activated carbons*.

Type of AC*	AC ¹	AC ²	AC ³	AC ⁴	AC ⁵	AC ⁶	AC ⁷	AC ⁸
C _o (ppm)	20	20	30	40	50	50	50	60
C (ppm)	9.7	17.1	23.1	38	43.5	45	49.5	50
x / m	4.8	8.5	11.6	19	22	22.5	24.8	25

*All experiments were carried out in aqueous solution and batch system at room temperature using 0.10 g of AC and 50 mL mercuric contaminated solution. Shaking time was 30 minutes. Impregnated AC with KMnO₄ and K₂Cr₂O₇ were prepared by treating 1.0 g commercial AC with 100 mL of 0.1 M KMnO₄ and K₂Cr₂O₇ (10 mmole) solutions in H₂SO₄ 0.1M separately. The treated activated carbons were filtered and dried before Hg²⁺ sorption. AC samples impregnated with methylene blue(mb), dithizone (DZ), EDTA and Na₂S were prepared by treating 1.0 g AC with 300 mL of 200 ppm of mb., 100 mL 500 ppm of DZ in ammonia solution(3M), 50 mL 0.01 M EDTA at pH 2 and 100 mL 0.01 M Na₂S for duration of 1 hour, respectively. C, C_o and x/m, stand for initial concentration of Hg²⁺, concentration of Hg after treatment by AC and mg of mercuric ion adsorbed per gram of AC, respectively. C³-C⁸ are impregnated commercial AC. The data reported in Table 2 are the average of at least three measurements. Maximum uncertainty in concentration analysis is 0.1 ppm.

*AC¹ stands for commercial AC treated with Hg²⁺ solution at pH=2. AC² stands for AC prepared from hazelnut shells treated with Hg²⁺ solution at pH 2. AC³, AC impregnated with EDTA, treated with Hg²⁺ solution. AC⁴, AC impregnated with Na₂S was treated with Hg²⁺ solution. AC⁵, AC impregnated with K₂Cr₂O₇, treated Hg²⁺ solution at pH=2. AC⁶, AC impregnated with dithizon was treated with Hg²⁺ solution. AC⁷, AC impregnated with mb was treated with Hg²⁺ solution at pH=2. AC⁸, AC impregnated with KMnO₄ was treated with Hg²⁺ solution at pH=2.

stirred using a magnetic stirrer. The carbons were then filtered, washed with distilled water, and then the filtrate analyzed for unabsorbed selected test materials. Mercuric ion was measured spectrophotometrically after extraction with diphenyl thiocarbazon (dithizon, DZ) in chloroform as solvent $\lambda_{\max} = 485\text{nm}$. Methylene blue (mb) was also measured spectrophotometrically ($\lambda_{\max} = 655\text{nm}$).

Results and Discussion

As our results indicate (Table1), AC prepared from hazelnut shells in our lab had superior decolorizing properties to AC obtained from commercial grade (Merck) and much more efficient than normal charcoal prepared from wood. Activated carbon prepared from hazelnut shells had 99 percent decolorizing of methylene blue test solution. The AC that we obtained from Merck Company used as a standard activated carbon only decolorized 70% of the methylene blue solution. Quantitative analysis showed that the adsorbing limit of methylene blue for each gram of AC obtained from Merck Co. was 0.34 mmole (100mg) and for AC prepared in our lab was 0.47mmole (150mg).

The synthesized AC in powdered form shows a higher ability for adsorbing the relatively large molecules such as dyes, which was proved by our results. Poor absorbability of charcoal can be due to its limited surface area due to filling its pores largely with resins and products

of incomplete combustion which are formed during the preparation of charcoal. We also prepared AC from some other low-cost raw materials such as walnut shells, pistachio shells, and rice husks, all of which were inferior to the AC prepared from hazelnut shells when methylene blue dye was used as the probe.

Adsorption of Hg²⁺ Ion by AC and Modified Activated Carbons

The results obtained from the investigation of the adsorption of mercuric ion using both AC and impregnated AC under the specified experimental conditions has been summarized in Table 2. As our results show (Table 2), AC prepared in our lab from hazelnut shells has higher absorbability for adsorption of mercuric ion. Pretreatment or impregnation of AC with chemicals such as permanganate, dichromate, EDTA and dithizone (chelating agents), methylene blue (a sulfur containing dye), and Na₂S increases efficiency adsorption of mercuric ion from aqueous liquids. AC impregnated with methylene blue and dithizone that have sulfur atom in their structures leads to a considerable improvement in adsorption of mercuric ions. The strong tendency of mercuric ion to sulfur atom can be the reason of this result. EDTA is a popular ligand that can form very stable complexes with many metals. So, it is predicted that it may be possible to increase ad-

sorption of poisonous heavy metals such as mercury, if we use activated carbon impregnated with EDTA. We found that adsorption of mercuric ion with AC impregnated with EDTA was lower than AC impregnated with mb and DZ. This can be due to the high solubility and stability of Hg-EDTA²⁻ complex in water. Increasing adsorbability of AC after treatment by chemical oxidants such as KMnO₄ and K₂Cr₂O₇ can be partly due to surface oxidation and the changing surface chemistry of AC. Pretreatment of AC with Na₂S improve sorption efficiency of mercuric ion via precipitating reaction (HgS is extremely insoluble). Among the chemicals investigated in this research, Na₂S and EDTA have only showed poor adsorption by AC. This can be due to their high solubility in water.

Though AC is a hydrophobic or non polar adsorbent material and it is especially known for its effective adsorbing organic compounds, it can also adsorb inorganic polar substances from aqueous solutions. The effectiveness of adsorption of substances by AC is inversely related to compound solubility in water. Heavy metal ions are not usually good adsorbates by AC in their free states, because of their good solubility in aqueous solutions. Therefore, the better solubility (higher polarity) may lead to a poor adsorbability of the adsorbate. However, it is possible to increase the rate of adsorption with impregnation of AC with suitable chelating agents or surface chemical modification of the adsorbents. The amount of adsorption of heavy metal ions depends on the nature (charge, size) of the ion, physical properties of AC and pH of solution. In general, it may conclude that the higher solubility of materials in water leads to a lower adsorbability by a hydrophobic adsorbent such as activated carbon. Impregnation of AC in order to increase the sorption efficiency, although it decreases the available adsorption sites of AC, instead it increases the selectivity and the capacity of adsorption, since sorption nature by impregnated AC is mostly chemisorption. Chemisorption is both stronger and more irreversible than physical adsorption, which normally happened by pure AC. Adsorption of heavy metal ions using activated carbon can also be partly due to the surface complex formation between metal ions and the acidic surface functional groups.

Final Conclusions

Hazelnut shells were found to be an effective raw material for preparation of activated carbons used for water and wastewater treatments. AC prepared from hazelnut shells using steam activation showed superior adsorption properties toward both methylene blue and mercuric ion than the commercial grade AC under the

same experimental conditions. Commercial production of AC from hazelnut shells for depollution and decolorizing of industrial wastewaters (e.g. textile industries) is both economical and efficient because of its low cost and high capacity of adsorption. Pretreatment or impregnating AC with sulfur-containing compounds increases sorption capacity of AC for removal of poisonous heavy metal ions such as mercuric ion from industrial wastewaters. However, in considering the removal of heavy metal ions from aqueous solutions using AC, the importance of some other parameters such as nature, the physical and physiochemical properties of AC (surface chemistry), pH of the solution, contact time and solution temperature should not be ignored.

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