Utility of adsorbents in the purification of drinking water: A review of characterization, efficiency and safety evaluation of various adsorbents

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Abstract: Clean drinking water is one of the implicit requisites for a healthy human population. However, the growing industrialization and extensive use of chemicals for various concerns, has increased the burden of unwanted pollutants in the drinking water of developing countries like India. The entry of potentially hazardous substances into the biota has been magnifying day by day. In the absence of a possible stoppage of these, otherwise, useful chemicals, the only way to maintain safer water bodies is to develop efficient purifying technologies. One such immensely beneficial procedure that has been in use is that of purification of water using 'adsorbents'. Indigenous minerals and natural plants products have potential for removing many pollutants viz. fluoride, arsenic, nitrate, heavy metals, pesticides as well as trihalomethanes. Adsorbents which are derived from carbon, alumina, zeolite, clay minerals, iron ores, industrial by products, and natural products viz. parts of the plants, herbs and algal biomass offer promising potential of removal. In the recent years attention has been paid to develop process involving screening / pretreatment / activation / impregnation using alkalies, acids, alum, lime, manganese dioxide, ferric chloride and other chemicals which are found to enhance their adsorbing efficiency. Chemical characterization of these adsorbents recapitulates the mechanism of the process. It is imperative to observe that capacities of the adsorbents may vary depending on the characteristics, chemical modifications and concentration of the individual adsorbent. Removal kinetics is found to be based on the experimental conditions viz. pH, concentration of the adsorbate, quantity of the adsorbent and temperature. It is suggested that isotherm model is suitable tool to assess the adsorption capacities in batch and column modes. Safety evaluation and risk assessment of the process/products may be useful to provide guidelines for its sustainable disposal.

Key words: Efficiency, Characterization, Langmuir, Freundlich, BET

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Introduction

Problems in drinking water quality include presence of excess fluoride, arsenic, natural organic matters, trihalomethanes, heavy metals and variety of pathogens that are a major cause of various water-borne diseases. The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment (Gaikwad, 2004; Tseng, 2007; Yoon et al., 2008). These pollutants enter the water bodies through wastewater from metal plating industries, batteries, phosphate fertilizer, mining, pigments and stabilizers alloys (Low and Lee, 1991). Although preventive measures have been adopted to remove pollutants however, these methods are not found suitable for removing heavy metals. Much attention is being paid on the various adsorbents, which have metal binding capacities and are able to remove unwanted pollutants from contaminated water at low cost. Abundantly available materials have been studied for the adsorption of pollutants, for example, bark and other tannin – rich materials, lignin, chitosan, dead biomass, xanthate, zeolite, clay and peat moss (Orhan and Buyukgungor, 1993; Bryant et al., 1992; Rorrer et al., 1993; Hsien and Rorrer, 1995; Roy et al., 1993; Sharma and Foster, 1993). Among these adsorbents, chitosan, zeolite, lignin and seaweed (Kertman et al., 1993) showed high adsorption capacities. Since coffee residues hold several functional groups, they have high potential for pollutants adsorption. Tea leaves are also used as adsorbent (Bailey et al., 1992).

Natural zeolite gained a significant interest, due to their valuable properties such as ion exchange capability. Clay minerals are found to be an important inorganic component in the soil and their sorption capabilities are due to high surface area and exchange capacities. Industrial byproducts such as waste slurry, lignin, ferric hydroxide and red mud have been explored for their technical feasibility to remove pollutants from contaminated water (Kumar et al., 2000).

In recent years adsorption processes have been developed using a large diversity of adsorbents. Activated carbons, activated mineral surfaces (silica, bauxite, alumina), fly ash, industrial waste, agricultural wastes and coral limestone have also been used as adsorbents.

Adsorption: The search for new technologies involving the removal of toxic pollutants from wastewater has directed attention to adsorption,
based on binding capacities of various biological materials (Babel and Kurniawan, 2003). The major advantages of sorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, regeneration of sorbents, and possibility of metal recovery (Ahalya et al., 2003).

**Adsorption equilibrium:** Adsorption capacity of the adsorbent can be determined by making a contact between the adsorbate and adsorbent. If adsorption is the removal mechanism, then the residual concentration will be reached that will remain unchanged with time, which is also known equilibrium, and the process is adsorption equilibrium. Two types of adsorption processes are mentioned: a) Physical adsorption, which is a reversible phenomenon. It results from the action of van der Waals forces. It is usually dominant at low temperatures and is multilayered. b) Chemisorption is generally irreversible, because chemical interactions are involved between the adsorbate and adsorbent moiety. Factors affecting the adsorption process are pH, temperature, adsorbent quantity, and particle size including other chemical properties of the adsorbate and adsorbent.

**Adsorption isotherms:** It is the relationship between the amount of adsorbate adsorbed on the surface of adsorbent and equilibrium concentration of the adsorbate at a certain temperature and other conditions. The equilibrium data is formulated into an isotherm model. Brunauer (Brunauer et al., 1972) classified adsorption isotherm in six types. These types may be monolayer, multilayer or condensation in pores/capillaries. An isotherm model is suitable tool to assess the adsorption capacities in batch and column study. Batch study consists of contacting an adsorbate with a definite quantity of adsorbent in batch stirred system. The mixture is agitated to facilitate the adsorption process. In column study, adsorbent is packed in a column reactor and almost no flow or movement of adsorbent takes place inside the column.

Different theoretical and empirical models have been proposed to describe the different types of isotherms in batch study. Most commonly used models are discussed here which are generally used for the interpretation of adsorption isotherms.

**Langmuir isotherm:** According to this isotherm surface is homogeneous. It assumes that all the adsorption sites have equal affinity for the adsorbate molecules and adsorption at one site does not affect adsorption at an adjacent site (Langmuir, 1918; Weber 1972). The Langmuir equation may be written as:

\[ q_e = \frac{Q^e b C_e}{1 + b C_e} \quad \text{(non-linear form)} \]  

\[ C_e = \frac{1}{Q^e} + \frac{1}{Q^e} C_e \quad \text{(linear form)} \]  

where \( q_e \) is the amount of solute adsorbed per unit weight of adsorbent (mg g\(^{-1}\)), \( C_e \) = Equilibrium concentration of solute in bulk solution (mg l\(^{-1}\)), \( Q^e \) = Monolayer adsorption capacity (mg g\(^{-1}\)) and \( b \) = constant related to the free energy of adsorption/desorption (kcal mol\(^{-1}\)). Sorbents with highest possible \( Q^e \) and high \( b \) value are desirable for a process.

**Freundlich isotherm:** Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm. It describes the equilibrium on heterogeneous surfaces. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

\[ q_e = K_F C_e^{1/n} \quad \text{(non-linear form)} \]  

where \( q_e \) is the adsorption density (mg of adsorbate per g of adsorbent), \( C_e \) is the concentration of adsorbate in solution (mg l\(^{-1}\)), \( K_F \) and \( n \) are the empirical constants dependent on several environmental factors and \( n \) is greater than one.

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{(4)} \]

A plot of \( \ln C_e \) against \( \ln q_e \) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept. \( 1/n \) is the intensity of the adsorption process, \( K_F \) is the relative adsorption capacity of the adsorbent (mg g\(^{-1}\)) (Freundlich, 1906).

**BET isotherm:** This isotherm assumes the multilayer adsorption of adsorbate on adsorbent surfaces (Brunauer et al., 1972; Weber 1972).

\[ q_e = \frac{BCQ^o}{(Cs - C) + [1 + (B - 1)/(C/Cs)]} \quad \text{(non-linear form)} \]

\[ q_e = \frac{C}{(Cs - C)q_e} = \frac{B - 1}{BQ^o} + \frac{1}{C/Cs} \quad \text{(linear form)} \]

where \( q_e \) is the amount of solute adsorbed per unit weight of adsorbent (mg g\(^{-1}\)), \( B \) = A constant related to the energy of interaction with the surface, \( C \) = The equilibrium concentration of adsorbate in solution (mg l\(^{-1}\)), \( Q^o \) = The number of moles of adsorbate per unit weight of adsorbent to form a complete monolayer, and \( Cs \) = The saturation concentration of the adsorbate.

**Efficiency of the adsorbents:** Natural products as adsorbents for the removal of heavy metals, nitrates, arsenic, fluoroarsenides, natural organic materials, trihalomethanes have gained important credibility during recent years because of their good performance and low cost. The adsorbent developed offers a viable alternative to traditional metal removal technologies. There are several adsorbents commonly used for the removal of arsenic (Katsoyiannis and Zouboulis, 2002; Elson et al., 1980), fluoroarsenides (Srimurali et al.,...
Scanning electron microscopy (SEM): Fig. 1: Uncoated sand, Fig. 2: FeCl₃ coated sand, Fig. 3: Activated alumina, Fig. 4: Iron oxide coated activated alumina, Fig. 5: Activated carbon powder, Fig. 6: Carbonized ground nut husk
Factors that effect the capacity of an adsorbent include its surface area, pore size, and polarity. Activation is the process that enhances the porous structure essential for effective adsorption. The two types of activation process widely used are chemical and physical activation. Carbonization of the material of the vegetable origin with the addition of the activating agents is generally known as chemical activation. Physical activation or gas activation is a process in which inactive carbonized product is allowed to react with suitable substance, usually gaseous (carbon dioxide or steam). The sorption capacities for the sorbents are usually very low before activation and the maximum sorption capacity rarely exceeds 0.1-0.2 mmol g⁻¹. In the case of chitosan, arsenic sorption capacity is significantly lower than the levels reached with other metal ions (Guibal et al., 1995; Guibal et al., 2000; Jansson Charrier et al., 1996).

Several processes have been developed to increase the efficiency of sorbents for metal ion uptake especially by ligand grafting. The chemical modification of silica surface by using chemical ligating groups provides scopes for trapping metal ions specially and selectively even at ultra trace level (Jal et al., 2004).

NOx adsorption on KOH impregnated activated carbon also give positive support to this concept that chemical impregnation increase the removal efficiency of the adsorbent (Lee et al., 2002). Activated carbon was produced from almond shells through chemical activation, by several activating agents (H₃PO₄, ZnCl₂, K₂CO₃, and Na₂CO₃). ZnCl₂ activated material was noticed to be the best product with high adsorption capacity (Bèvla et al., 1984a; Bèvla et al., 1984b).

Activated carbons were prepared from untreated and phosphoric acid treated coconut shells, and increased adsorption capacity was found (Laine et al., 1989). Ammonium chloride impregnated and untreated almond shell and hazelnut shell samples were tested for their surface area at different temperatures. Chemical activation carried out at 350°C gave products with surface area values above 500 m² g⁻¹. However, the surface area values observed for the products obtained from untreated raw materials were reported about half of this value. It was also observed that, the surface area of products obtained from NH₄Cl impregnated samples reached values of over 700 m² g⁻¹ when the carbonization temperature was increased 700°C (Balci et al., 1994). The granular activated carbon samples activated, either chemically, with H₃PO₄ or physically, with CO₂, under a variety of conditions. The product obtained by chemical activation had higher BET surface areas and greater product yields than the CO₂-activated carbons. The products were also compared with the commercial activated carbon, which have higher adsorption ability (Toles et al., 1997). Phosphoric acid impregnated apricot stones were carbonized at 300, 400 and 500°C respectively, were found to increase the BET surface area increased from 700 m² g⁻¹ up to 1400 m² g⁻¹ with rise in temperature. The highest BET surface area was obtained from the sample that was impregnated with 30% (vol) phosphoric acid and carbonized at 500°C (Girgis and Daifullah, 1998). Activated carbons were produced from canes from Arundo donax, a rapid-growing plant, by phosphoric acid activation under four different activation atmosphere, to develop carbons with substantial capability to adsorb Cd(II) and Ni(II) ions from dilute aqueous solutions. Surface areas and total pore volumes of the activated carbons used were of around 1100 m² g⁻¹. It is established that, the content of carbons' polar or acidic surface oxygen functional groups, with their development depending on the atmosphere used, influenced predominantly metal adsorption. Carbons derived under flowing air, possessing the largest total content of these groups, showed the best adsorption effectiveness (>90%) for both ions, even superior to that determined for a commercial sample used as a reference (Basso et al., 2002). Denizi et al. (1997) incorporated dye ligand onto synthetic polymers to enhance their metal ion sorption properties. Similar modifications have been performed on activated carbon; the impregnation with metal ions significantly enhances arsenic sorption on activated carbon (Huang and Vane, 1989; Rajakovic, 1998).

Characterization of the adsorbents: Chemical characterization of the products and spent adsorbent may be explored to understand the mechanism of the process involved. Amorphous and crystalline nature of the adsorbent can be determined by the use of X-ray Diffraction XRD and identification of various constituents in adsorbents can be determined with the help of IR spectra. The specific surface area of the adsorbent can be calculated from the N₂-BET equation (Mohan et al., 2005). Porosity can be investigated using surface area analyzer and mercury porosimeter. Scanning electron Microscopy (SEM), Extended X-ray adsorption fine structure, nuclear magnetic resonance (NMR) and high performance liquid chromatography (HPLC) may give the details regarding the texture (Huggins et al., 2002; Singh et al., 2003) and delineate the mechanism of process of the water purification. The trace element contents of the coals have been determined by a combination of instrumental neutron activation analysis (INAA), inductively coupled plasma mass spectrometry (ICP – MS) and ICP atomic adsorption spectroscopy (ICP-AES) (Shhtepenko et al., 2005). X-ray photoelectron spectroscopy (XPS) analysis was used for the study of sorbent and the metal speciation on the sorbent. Desorption studies were also carried out to elucidate the interactions between the metal and the sorbents. A sorbent for metal removal has been
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produced from anhydrous calcium silicate/ aluminate by means of an accelerated carbonation process. Iron treatment increases the adsorption capacity by 10–fold. XPS studies supported that iron is into the protein matrix. Shifts in XPS spectra suggest that dichromate binding occur with the iron at active adsorption sites (Fathima et al., 2005).

Surface–reaction phenomenon of adsorbent caused by the KOH impregnation and NOx adsorption were investigated by using SEM, time of flight secondary ion mass spectrometry (ToF – SIMS) and SIMS depth profile. In the results of ToF – SIMS and SIMS depth profile, NO2 and NO3 increased at the surface distribution by forming oxide crystals of KNO3, and KNO2 due to bond formation with potassium ions (Lee et al., 2002).

Safety evaluation of the adsorbents: It is prerequisite to assure the water quality as recommended by regulatory and health agencies, which are desired in the daily intake of the drinking water (Gopal et al., 2004). The physico-chemical and bacteriological characteristics of the produced water may be compared with the test water as per the standard methods (APHA, 2005). In the process of adsorption of the minerals/plant products it is apparent that synthesis of large amount of the product is required, in which large amount of sludge is also generated. Once this sludge is added to the soil, the leachates eventually find its way to the surface water. The soil and water contains living organism, which are responsible for the biotransformation and biodegradation of the material and also the translocation of the energy into food chain. Therefore the standard protocols are to be developed for the safety evaluation of the products and spent wash/solid waste.

Multispecies testing e.g. fish bioassay chimorous, daphnia, earthworm and algal bioassays are recommended protocols that may be carried out for ecotoxicological assessment (OECD, 2002). Identification of suitable disposal sites are prerequisite in case of community water supply.

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References


