



Functionalized granular activated carbon and surface complexation with chromates and bi-chromates in wastewater

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HIGHLIGHTS

- ▶ Physico-chemical adsorption using functionalized activated carbon (FACs) is applied.
- ▶ FACs have hydrophilic, acidic external surface with functional surface sites.
- ▶ FACs make surface complexes easily with CrO_4^{2-} and HCrO_4^- .
- ▶ Surface complex formation is maximized in the order $\text{FAC-HNO}_3 > \text{FAC-HF} > \text{FAC-HCl}$.
- ▶ Pseudo kinetic, intra-particle pore and film diffusion models are applied.

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ABSTRACT

Cr(VI) is present in the aqueous medium as chromate (CrO_4^{2-}) and bi-chromate (HCrO_4^-). Functionalized granular activated carbons (FACs) are used as adsorbents in the treatment of wastewaters containing hexavalent chromium. The FACs are prepared by chemical modifications of granular activated carbons (GACs) using functionalizing agents like HNO_3 , HCl and HF . The Brunauer, Emmett and Teller surface areas of FAC-HCl (693.5 m^2/g), FAC- HNO_3 (648.8 m^2/g) and FAC-HF (726.2 m^2/g) are comparable to the GAC (777.7 m^2/g). But, the adsorption capacity of each of the FAC- HNO_3 , FAC-HCl and FAC-HF is found to be higher than the GAC. The functional groups play an important role in the adsorption process and pH has practically no role in this specific case. The FACs have hydrophilic protonated external surfaces in particular, along with the functional surface sites capable to make complexes with the CrO_4^{2-} and HCrO_4^- present. Surface complex formation is maximized in the order $\text{FAC-HNO}_3 > \text{FAC-HF} > \text{FAC-HCl}$, in proportion to the total surface acidity. This is also confirmed by the well-known pseudo second-order kinetic model. Physio-sorption equilibrium isotherms are parameterized by using standard Freundlich and Langmuir models. Langmuir fits better. The formation of surface complexes with the functional groups and hexavalent chromium is also revealed in the images of field emission scanning electron micrograph; energy dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy analysis after adsorption. The intra-particle diffusion is not the only rate-controlling factor. The Boyd's film diffusion model fits very well with R^2 as high as 98.1% for FAC- HNO_3 . This result demonstrates that the functionalization of the GAC by acid treatments would increase the diffusion rate, predominantly with a boundary layer diffusion effect.

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1. Introduction

As an effective adsorbent for the adsorption of metal ions, activated carbon has the largest market share. Metal ion adsorption by activated carbon from aqueous solution is sometimes complex. Along with the physical force of attraction it may also involve ion exchange, electrostatic effects and surface complexation with functional groups on activated carbon surfaces. The adsorption of metal ions on activated carbon is

affected by several factors, such as specific surface area, pore-size distribution, pore volume, surface charge and presence of surface functional groups (Song et al., 2010). Surface functional groups and the corresponding changes of physiochemical properties can be introduced on the surface of activated carbon by oxidation with suitable oxidizing agents, either in gas phase or in solution (Afkhami et al., 2007; Moreno-Castilla et al., 1995; Malik et al., 2002).

Functionalized activated carbon (FAC) is produced due to the introduction of functional groups on carbon surfaces by several oxidation treatments. These oxidation processes can increase a large amount of oxygen containing groups on the surfaces of FACs, like $-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$ which are called functional groups. These oxygen-containing functional groups are mostly hydrophilic in nature and these can easily

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adsorb the polar species from the solution (Xiao and Thomas, 2005). With oxidation, not only acidic groups, but basic and neutral surface groups can also be introduced (Bansal et al., 1988; Mattson and Mark, 1971). The acidic and the basic oxygen functional groups can show the properties of ion exchange and coordination with polar species (Jia and Thomas, 2000). Jia et al., 2002 show that chemical modification can enhance the adsorption power of activated carbon and modify its selectivity to various ion species in solution. Therefore, specific modification of activated carbon is necessary in order to enable activated carbons to develop affinity for respective metal ions in aqueous solution and remove them effectively. For the oxidation, various reagents including concentrated nitric acid (HNO_3), sulfuric acid (H_2SO_4), sodium hypochlorite (NaOCl), permanganate, hydrogen peroxide (H_2O_2) and ozone-based gas mixtures are used as oxidizers (Donnet et al., 1974; Lisovskii et al., 1997). These treatments might modify the surface area and porosity of the sample independently.

Apart from oxidizing acids, non-oxidant acids like hydrochloric acid (HCl), hydrofluoric acid (HF), etc. are frequently used for the demineralization for the activated carbon (Lopez-Ramon et al., 1993; Rivera-Utrilla et al., 1987). During this reduction process the surface area and pore texture of the activated carbon can be changed depending on the amount and nature of the mineral matter as well as its distribution in the carbon matrix (Moreno-Castilla et al., 1998). It can be explained by the fact that the surface of the FAC is opened and fractures can take place at the location where some defects exist after oxidation with non-oxidant acids. Thus the sorption capacity of FAC can also attribute to their surface defects, which can easily provide numerous chemical sorption sites.

On the other hand, the treatment of activated carbon with oxidant acids, such as HNO_3 , introduces oxygenated functional groups easily, which can also change the surface chemistry, surface area and porosity of the original sample (Barton et al., 1984; Puri, 1970). The changes of surface chemistry due to the formation of acidic oxygen groups will affect the adsorption behavior when these are used as adsorbents. Many researchers (Foger, 1984; Leon y Leon and Radovic, 1994; Rivera-Utrilla et al., 1987) have shown that the surface chemistry is, in general, more important than the surface area and the pore texture of the adsorbents for the adsorption of inorganic compounds from aqueous solution. It is commonly believed that the chemical interaction between the ions and the surface functional groups of FAC is the major sorption mechanism (Lisovskii et al., 1997; Pittman et al., 1997). This reveals that adsorption of metal ions by the FAC is mostly a chemisorption process, and not only physical.

Among the various heavy metals, hexavalent chromium [Cr(VI)] is one of the most important pollutants as it is abundant in the wastewater of leather, textile, metal plating, and battery and pigment industries. So the effluents from these industries, if disposed into the inland surface water body, can contaminate the aqueous media easily by Cr(VI) . Therefore, it is essential to remove Cr(VI) from waste water before disposal. Cr(VI) is present mainly in the chromate (CrO_4^{2-}) and bi-chromate (HCrO_4^-) forms. There are various methods for the removal of Cr(VI) from the aqueous solution. Among them, the adsorption in activated carbon is a very effective process of removal due to the high specific surface area and pore volume (Duranoğlu et al., 2012) of the activated carbons. According to Mahmudov and Huang, 2010, inorganic anion adsorption on activated carbon may be of two types; one is specific, where the chemical interaction is involved with the formation of surface complexes and the other is nonspecific, where adsorption takes place in the diffuse part of the electrical double layer by electrostatic force. In the case of the nonspecific adsorption (Steenberg, 1944) protons adsorb specifically on oxygen-containing functional groups, creating a positive surface, which then promotes nonspecific electrostatic adsorption of anions in the diffuse layer. Other studies also suggested that the important mechanism of anion adsorption by activated carbon is surface complexation rather than ion exchange (Aoki and Munemori, 1982; Namasivayam and Sangeetha, 2005).

The objective of this study is to investigate the changes of surface properties of the GAC after functionalizing it with specific acids. Three kinds of samples are prepared by oxidizing the commercially available granular activated carbon (GAC) with HNO_3 , HCl and HF and these are named as FAC- HNO_3 , FAC- HCl and FAC- HF respectively in this paper. The changes of physiochemical properties of FAC with respect to the GAC are investigated by N_2 adsorption, field emission scanning electron micrograph (FE-SEM), energy dispersive X-ray spectroscopy (EDAX), Fourier transform infrared spectroscopy (FTIR), etc. before and after adsorption. Points of zero charge are also estimated against a range of pH values and their effects are investigated. Surface acidic groups (lactonic, phenolic and carboxylic) are determined by Boehm titration and correlated to the oxygen content, estimated by elemental analysis. The adsorption efficiency of these newly developed FACs is examined by equilibrium adsorption of Cr(VI) by experiments and isotherms, kinetics and diffusion studies including intra-particle and film diffusion. A probable surface complexation scheme is developed to justify the adsorption of Cr(VI) using FACs.

2. Materials and methods

2.1. Functionalization of the precursor GAC with acid treatments

All the precursor activated carbon used in this study is in granular form. The GAC is of LR grade (IMDG Code: 4.2/III; UN: 1362 IATA: 4.2) from SDFCL (SD Fine Chemicals Limited, India). The GAC is first sieved through a BS 8 mesh screen and the larger fraction is retained. Then these are washed with distilled water (in order to remove the fine powder and contaminants adhered to it), left to dry in an oven at 110°C for 4 h before use, to remove the moisture and any volatile material present on the surface and within the pores of the grains. After cooling down to room temperature, this purified GAC is used for the experimental study.

The cleaned GAC is oxidized with three acids; HCl , HF and HNO_3 to modify the surface of the carbon and to introduce oxide and some other groups onto the surface. 1 g of GAC is mixed with 10 mL of concentrated HCl (11.3 N), and the solution is heated at 333 K until the solvent is totally evaporated leaving behind the dried carbon. For treatment with HF , the purified GAC is mixed with concentrated HF (22.6 N) in the ratio 1 g/10 mL. This mixture is then stirred for 1 h at 333 K in a magnetic stirrer. Finally, for the HNO_3 treatment, 1 g GAC is added to 10 mL of concentrated HNO_3 (15.45 N) and heated at its boiling temperature for 2 h. After these acid treatments all the acid modified GACs are washed thoroughly with deionized water until the pH of the effluent water becomes approximately 7 or close to the pH value of the deionized water. All these FACs are then dried at 110°C for 4 h in an oven and are kept ready for the next stage of batch equilibrium analysis. All the chemicals used in this study are either of analytical reagent (AR) or laboratory reagent (LR) grades.

2.2. Surface textural and chemical characterization of GAC/FACs

2.2.1. Characterization of porous structure

The determination of Brunauer–Emmett–Teller (BET) surface area and pore volume of the samples is carried out by nitrogen adsorption isotherms by using a Beckmann Coulter SA3100 surface area analyzer at 77 K. Prior to the measurement, the samples are degassed at 393 K for 12 h, the maximum pressure used being 1 bar. The BET equation is applied to the N_2 adsorption–desorption isotherms to know the S_{BET} of GAC/FACs. The pore size distribution curves of micropores and mesopores for all the samples are initially obtained by the H–K method (Horvath and Kawazoe, 1983). Then the non-local density functional theory (NLDFT) is used to analyze the pore size distribution of the modified and unmodified GACs.

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