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Adsorption of fluoride in aqueous solutions using KMnO₄-modified activated carbon derived from steam pyrolysis of rice straw

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Abstract

Fluoride in drinking water above permissible levels is responsible for human and skeletal fluorosis. In this study, activated carbons (AC) prepared by one-step steam pyrolysis of rice straw at 550, 650, 750 °C, respectively, were modified by liquid-phase oxidation using HNO_3, H_2O_2 and $KMnO_4$. Characterization of these 12 carbons was made by their surface area, porosity, acidity, basicity, pH_{pzc}, pH and ability to remove fluoride anion. Based on the data of the latter factor, the $RS_2/KMnO_4$ carbon was selected. Along with batch adsorption studies, which involve effect of pH, adsorbate concentration, adsorbent dosage, contact time, temperature, and Co-ions (SO_4^{2-}, Cl^-, Br^-). The effects of natural organic matter (NOM) were also made to remove the fluoride from natural water. On the basis of kinetic studies, specific rate constants involved in the adsorption process using $RS_2/KMnO_4$ carbon was calculated and second-order adsorption kinetics was observed. Equation isotherms such as Langmuir (L), Freundlich (F), Langmuir–Freundlich (LF) and Dubinin–Radushkevich (DR) were successfully used to model the experimental data. From the DR isotherm parameters, it was considered that the uptake of F^- by $RS_2/KMnO_4$ carbon proceeds by an ion-exchange mechanism ($E = 10.46$ kJ mol^{-1}). The thermodynamic parameters of fluoride sorption were calculated and the sorption process was chemical in nature. The ability of $RS_2/KMnO_4$ to remove F^- from Egyptian crude phosphoric acid ($P_2O_5 = 48.42\%$) was tested and the adsorption capacity of F^- in H_3PO_4 was greater than that in distilled water. This is may be due to fluoride adsorption enhanced at lower pH of crude acid.
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1. Introduction

Of all chemical elements in the Periodic Table, fluorine is the most electronegative and the most reactive element [1]. Because of its great reactivity, fluorine cannot be found in nature in its elemental state. It exists as fluorides.

Fluoride pollution in the environment occurs through two different channels, which are natural and anthropogenic sources. Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by the slow natural degradation of fluorine contained in rocks. Fluorine and its compounds are extensively used in industry; elemental fluorine is necessary in the preparation of many fluoride compounds, which play an important role in semiconductors, fertilizers (e.g. phosphate fertilizers), production of high purity graphite, electrolysis of alumina and in nuclear applications.

Toxic wastes containing fluorine/fluoride are generated in all industries using fluorine or its compounds as a raw material [2].

The other perspective is that fluoride is recognized as essential in the human diet. Maintaining fluoride concentrations of 1 mg/l in the dietary intake can prevent particularly skeletal and dental problems. However, when the fluoride concentration is above this level, it affects the metabolism of elements such as Ca, P in human body and leads to bone diseases (fluorosis), mottling of teeth and lesions of the endocrine glands, thyroid, liver and other organs [3]. According to the World Health Organisation, the maximum acceptable concentration of fluorides is 1.5 mg/l [4]. It had been reported that the concentration of fluoride ions in groundwater of many places exceeds the permissible values [3]. So, it is imperative and significant for removing excessive fluorides from water.

There are different materials have been used for defluoridation including activated carbon (AC), tricalcium phosphate, synthetic ion exchangers, lime activated alumina, and alum. However, in recent years, considerable attention of scientists has been devoted to the study of different types of low-cost

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materials such as: spent bleaching earth, wollastonite and chine clay, bentonite and activated bentonite, kaolinitic clay, agricultural by products, fly ash, carbon slurry, biogas residual slurry, zeolite, bone char and flax shive [5].

Many methods have been developed to remove excessive fluoride from water, namely adsorption, ion exchange, precipitation, electrolysis, donnan dialysis, and electrodialysis [3]. Among these methods, adsorption is still one of the most extensively used methods for defluoridation of water.

Activated carbon has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media. AC modification are gaining prominence due to the need to enable ACs to develop affinity for certain contaminants to cater for their removal from varying types of wastewater in the industries. It is an established fact that the AC surface can display acidic, basic and/or neutral characteristics depending on the presence of surface functional groups. As such, modification of chemical characteristics in this paper is taken to mean treatment to modify the inherent surface functional groups of AC. It has been widely recognized that chemical species removal by AC adsorption is due predominantly to the surface complex formation between the species and the surface functional groups. This is especially significant in the case of removing inorganics and metals from aqueous solutions.

The objective of the present work is to asses the ability of modified activated carbon derived from steam pyrolysis of rice straw for the removal of fluoride from water at different concentrations, contact times, temperatures, and pH, as these parameters are some of the main factors influencing the uptake of solute at the solid–solution interface.

2. Materials and methods

All solutions were prepared using sodium fluoride in double distilled water and all reagents were of A.R. grade.

2.1. Preparation of activated carbons

0.5 kg of rice straw was dried and fed into fluidized bed reactor, described elsewhere [6] at heating rate of 50 °C/10 min in presence of N_2 flow (300 ml/min). The steam was introduced with flow rate of 5 ml/min when the furnace reached 350 °C. The heating continues up to final temperature of 550, 650 and 750 °C, respectively. The hold time was 1 h. Then, furnace is switched off. The carbons were left to cool down and the products are taken the abbreviations RS_1, RS_2 and RS_3, respectively.

2.2. Liquid-phase oxidation of carbons

Activated carbons (RS_1, RS_2, RS_3) were oxidized using HNO_3, H_2O_2 and $KMnO_4$ to produce modified carbons according to the procedures described earlier [7] (cf. Table 1).

2.3. Characterization of the carbons

The surface area and pore characteristics of the prepared carbons were determined by nitrogen adsorption at 77 K using (Quantachrome Instruments, Model Nova1000e series, USA). The samples were outgased at 250 °C under N_2 flow for 16 h. The pH of a particular adsorbent is measured with pH meter (Acton, MA) as mentioned elsewhere [8]. The simple mass titration method was used to estimate the pH_{pzc} of carbons as reported [9]. The Boehm titration method [10] was used to estimate the acidic and basic properties of carbons.

2.4. Carbon selection

Fifty millilitre aliquots of F^- of initial concentration $C_o = 50$ ppm were mixed with 0.1 g of each carbon and shaken for 24 h. The filtrate was analyzed for residual F^- anion concentration using ion chromatography (IC).

2.5. Adsorption experiments

Series of experiments were carried out using 20 ml solution of F^- of initial concentration of 20 ppm using $RS_2/KMnO_4$ carbon to define the factors influencing the sorption process. In this concern, the following conditions were tested: the carbon dosages (5–100 mg), pH (2–11), temperature (25–55 °C); contact time (1–24 h). The pH of the solutions were adjusted

Table 1
Characterization of activated carbons

Notation	S_{BET} (m^2/g)	V_p (cm^3/g)	Basicity (meq/g)	Acidity (meq/g)	F^- removal, R (%)	pH_{pzc}	pH	Ash content (%)
RS_1/550	71.35	0.055	6.22	5.6	5.6	9.5	9.2	49.0
RS_2/650	76.2	0.063	8.13	2.0	5.6	9.3	9.3	44.0
RS_3/750	63.0	0.052	3.06	1.79	5.56	9.4	9.07	41.0
RS_1/HNO$_3$	87.2	0.118	2.79	8.93	46.56	3.0	3.23	64.1
RS_2/HNO$_3$	68.8	0.083	5.91	7.35	50	3.3	3.26	64.1
RS_3/HNO$_3$	66.3	0.081	3.14	9.26	100	2.95	3.42	66.8
RS_1/H$_2$O$_2$	110.9	0.078	5.21	3.75	5.6	8.0	8.08	59.1
RS_2/H$_2$O$_2$	96.8	0.06	3.01	2.6	5.5	7.6	7.04	57.2
RS_3/H$_2$O$_2$	85.1	0.053	6.12	5.21	10.99	5.6	6.0	52.0
RS_1/KMnO$_4$	87.75	0.095	5.29	4.39	100	8.6	8.25	57.9
RS_2/KMNO$_4$	122.9	0.1	5.77	5	100	7.8	7.8	55.8
RS_3/KMNO$_4$	91.5	0.092	6.44	4.81	100	7.8	7.7	51.2