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Original Research Paper

The Influence of the Coexisting Anions on the Adsorption of Perchlorate from Water by the Modified Orange Peels

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ABSTRACT

Activated carbons obtained from agricultural by-products have the some advantage like efficiency and low cost, if they are compared with non-renewable coal-based granular activated carbons. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbon production. The modified orange peels were prepared from orange peels by the chemical activation. The effect of pH value and coexisting anions (NO_3^-, SO_4^{2-} and PO_4^{3-}) were discussed in detail. Furthermore, adsorption isotherm for adsorption of ClO_4^- ions on the modified orange peels was studied. The experimental results showed that the values of pH and coexisting anions have an important influence on the adsorption of ClO_4^- ions by the modified orange peels. The Freundlich adsorption isotherm model was suitable for the ClO_4^- ions in solution. The adsorption process of ClO_4^- ions in solution by the modified orange peels is not uniform.

INTRODUCTION

Perchlorate (ClO_4^-) contamination is highly soluble, non-volatile and kinetically inert in the surface and ground water bodies. It is widely used in manufacture of rocket propellants, missiles, road flares, automobile airbags and fireworks, which would finally enter the water resources. According to previous toxicological studies, perchlorate has a direct effect on thyroid gland iodine up-taking (Song et al. 2015). Furthermore, mega dose of perchlorate may cause fatal bone marrow disorders. It was reported that the drinking water of at least 15 million people in the United States was affected by perchlorate contamination (Luo et al. 2015). Therefore, perchlorate was added in the drinking water candidate contaminant list in 1998. It was important to treat the wastewater containing of perchlorate (Oliveira et al. 2013.).

Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation are used in the removal of dyes from wastewater (Köseoglu & Akmil-Basar 2015). However, adsorption is one of the most effective processes of advanced wastewater treatment. Therefore, many industries use adsorption techniques (mainly in the tertiary stage of biological treatment) for reducing hazardous inorganic/organic pollutants present in effluents. Numerous works have been recently published with primary goal in the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials (Yagub et al. 2014). There are various adsorbent materials used for the removal of perchlorate from aqueous solutions: peanut hull, olive pomace, spent tea leaves, mango bark, rice husk, coffee husks, peanut husk and eggshells; agricultural peels present great interest (Bharathi & Ramesh 2013).

Activated carbon obtained from agricultural by-products has some advantages like efficiency and low cost, if they are compared with non-renewable coal-based granular activated carbons (Fernandez et al. 2014, Fernandez et al. 2015). The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbon production (Anastopoulos & Kyzas 2014). In recent years, this has promoted a growing research interest in the use of alternative waste materials from industry and agriculture for activated carbon production. One of the main challenges in the commercial manufacture of activated carbons is to identify new precursors that are cheap, therefore, a lot of research has been reported on activated carbons from agricultural wastes, including corn cob, coconut shell, palm shell, apple pulp, chickpea husks, grain sorghum, pistachio nut shell, jute fibre, olive stones and walnut shell, cherry stones, coir pith, wild rose seeds, rice bran, gopher plant, jackfruit shell waste, oil palm shell, rubber tree seed coat, cotton stalk, flamboyant, beach casuarina, lantana weed, tea waste, sugarcane bagasse and empty oil palm fruit bunches. Palmyra tree leaves, inflorescence and fruit nutshell waste have been found to be suitable precursors owing to their high carbon and low ash contents (Hashemian et al. 2014).

The cultivation of orange and its transformation is a major industry in many countries in the world. About 70% of the oranges produced are transformed into juice, marmalade and other foods, leading to the production of an amount of citrus peel waste that represents about 50% of the processed fruit. Therefore, it can be assessed that orange transformation industry produces about 30 Mt of orange peel waste per year (Schiewer & Iqbal 2010). The orange peel waste contains water, mono and disaccharides and polysaccharides (Sayed et al. 2012). So, they have been proposed to produce the fertilizers, pectin, ethanol, cattle feed, absorbent material, and so on (Khatod 2013, Khalfaoui et al. 2014).

The main goal of this work is to provide the recent progress regarding the use of orange peels as perchlorate adsorbents. The effect of pH value and coexisting anions (NO_3^-, SO_4^{2-} and PO_4^{3-}) were discussed in detail. Furthermore, adsorption isotherm for adsorption of ClO_4^- ions on the modified orange peels was studied.

MATERIALS AND METHODS

Materials

The orange peels were obtained from Guangdong province. They were washed with the distilled water, dried, ground into powder and then sieved into 40 meshes for experiments.

Experimental Methods

Preparation of the modified orange peels: The 40 mL of propylene oxide and 80 mL of dimethylformamide were put into 250 mL Erlenmeyer flasks containing 6 g of 40 meshes orange peels. They were shook for 1 h in the contact temperature shaker at a speed of 120 rpm. Then, they were activated for 1 h at 373 K. The 15 mL of pyridine was added to the flask, and they were activated for 1 h at 373 K again. They were cooled at a room temperature, and washed respectively by the 0.1 mol/L NaOH, 0.1 mol/L HCl and 50% C_2H_5OH and 0.1 mol/L NaCl. Then, they were dried for 12 h at a temperature of 333 K. The modified orange peels were obtained, and stored for experiments.

Adsorption of perchlorate in aqueous solution by the modified orange peels: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.2 g the modified orange peels and 100 mg/L ClO_4^-. The solutions containing 100 mg/L NO_3^-, SO_4^{2-} and PO_4^{3-} were added respectively. The value of pH in aqueous solution was adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH. The flasks were placed for 24 h in a shaker at a constant temperature (308 K) and 200 rpm. The sample was determined by the ion chromatography.

Analytical methods: The ClO_4^-, NO_3^-, SO_4^{2-} and PO_4^{3-} were determined by the ion chromatography. The amount of adsorbed perchlorate ion q_t (mg/g) at different time was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad ...(1)$$

Where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of perchlorate ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at α=0.05 unless otherwise specified.

RESULTS AND DISCUSSION

Effect of pH with the coexisting anions in aqueous solution: In order to investigate the influence of pH in solution, the adsorption experiments were carried out. The value of pH was ranged from 2.0 to 12.0. The experimental results are shown in Fig. 1.

As shown in Fig. 1, the value of pH in solution has an important influence on the adsorption. When the value of pH in solution was below 4.0, pH in solution was not benefit for the adsorption of ClO_4^- ions. Adsorption rate of ClO_4^- ions by the modified orange peels was increasing, while the value of pH in solution was increasing. In acid solution,

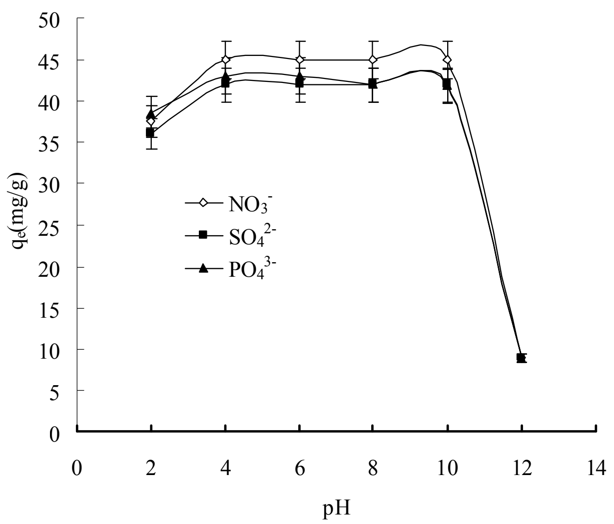

Fig. 1: Effect of pH with the coexisting anions in aqueous solution.

Table 1: The adsorption parameters for ClO_4^- ions adsorption on the modified orange peels by Langmuir adsorption isotherm and Freundlich isotherm.

Langmuir parameters			Freundlich parameters.		
q_{max} mg(g)	K_L (L/mg)	R^2	n	K_F	R^2
217.6	0.052	0.965	0.415	27.69	0.992

ClO_4^- ions may be changed into $HClO_4$, and it caused to decrease the adsorption capacity. However, the addition of Cl^- ions in solution may be harmful for the adsorption of ClO_4^- ions, when the value of pH in solution was adjusted with HCl. When the value of pH in solution ranged from 4.0 to 10.0, the value of pH in solution had little influence of adsorption. When the value of pH in solution was above 10.0, the adsorption rate of ClO_4^- ions was decreased. It may be the reason that OH^- in solution had an important role in the adsorption process. The OH^- ions inhibited the adsorption of ClO_4^- ions onto the modified orange peel, and the adsorption rate of ClO_4^- ions was decreased.

Effect of coexisting anions: Effect of coexisting anions (NO_3^-, SO_4^{2-} and PO_4^{3-}) on the adsorption of ClO_4^- ions by the modified orange peels is shown in Fig. 1. When pH was below 3.0, the order of competitive influence was SO_4^{2-} >NO_3^- >PO_4^{3-}. The electric charge of coexisting anions has an important influence on adsorption of ClO_4^- ions. The more the electric charge was, the more the competitive influence was. However, the form of PO_4^{3-} ions is H_3PO_4 and $H_2PO_4^-$ ions, and the competitive influence is decreased. When the value of pH in solution ranged from 3.0 to 10.0, the effect of coexisting anions is steady. The order of competitive influence was SO_4^{2-} >PO_4^{3-} >NO_3^-. When the value of pH in solution was above 10.0, the effect of coexisting anions began to decrease. It may be the reason that the number of OH^- ions had important role for the adsorption of ClO_4^- ions by the modified orange peels. While the value of pH in solution was increasing, the adsorption capacity of ClO_4^- ions was decreasing. The competitive influence of coexisting anions was concealed by the OH^- ions in solution.

Adsorption isotherm for adsorption of ClO_4^- on the modified orange peels: The Langmuir adsorption model and the Freundlich adsorption isotherm model are applied in this research (Freundlich 1906, Langmuir 1916).

The Langmuir adsorption model is given as:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad ...(2)$$

Where q_e is the solid phase equilibrium concentration (ng/g); C_e is the liquid equilibrium concentration of ClO_4^- ions in solution (mg/L); K_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg); Q_m is the maximum amount of ClO_4^- ions per unit weight of adsorbent for complete monolayer (mg/g).

The Freundlich adsorption isotherm model, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \quad ...(3)$$

Where q_e and C_e are defined as above, K_F is the Freundlich constant representing the adsorption capacity (mg/g), and n is the heterogeneity factor depicting the adsorption intensity.

According to the experimental data, the adsorption parameters were obtained from the Langmuir adsorption isotherm and Freundlich adsorption isotherm. They are listed in Table 1.

It was shown that the Freundlich adsorption isotherm model was more suitable for the ClO_4^- ions in solution than the Langmuir adsorption isotherm model. The adsorption process of ClO_4^- ions in solution by the modified orange peels does not show uniformity.

CONCLUSIONS

In this work, the modified orange peels were obtained from the chemical activation. The effect of pH value and coexisting anions (NO_3^-, SO_4^{2-} and PO_4^{3-}) were discussed in detail. When pH was below 3.0, the order of competitive influence was SO_4^{2-} >NO_3^- >PO_4^{3-}. The order of competitive influence was SO_4^{2-} >PO_4^{3-} >NO_3^- at the value of pH in solution ranged from 3.0 to 10.0. The Freundlich adsorption isotherm model was more suitable for the ClO_4^- ions in solution than the Langmuir adsorption isotherm model. The adsorption process of ClO_4^- ions in solution by the modified orange peels is not uniform.

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