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Adsorption behaviour of functional grafting particles based on polyethyleneimine for chromate anions

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ABSTRACT

Polyethyleneimine (PEI) was first grafted on the surfaces of micro-sized silica gel particles in the manner of the coupling graft, forming the grafting particles PEI/SiO_2. Afterward, for the grafted PEI, two polymer reactions, tertiary amination reaction and quaterisation, were allowed to be carried out in turn, and a kind of functional composite particles, QPEI/SiO_2, was obtained. QPEI/SiO_2 particles were used as solid adsorbent in the removal of chromate anions from aqueous solution. The static adsorption experiments (batch method) were performed, the effects of various factors on the adsorption capacity of QPEI/SiO_2 were examined, and the dynamic desorption experiments were also carried out. The experimental results show that QPEI/SiO_2 particles have strong adsorption ability for CrO_4^{2-} ions by right of electrostatic interaction, and the saturated adsorption amount actually reach up to 0.14 g/g. The isothermal adsorption behaviour is fitted to Langmuir model. The adsorption ability of QPEI/SiO_2 particles for CrO_4^{2-} ions is affected greatly by the quaterisation degree of the grafted PEI macromolecules. The QPEI/SiO_2 particles with higher quaterisation degrees have greater adsorption capacities. The adsorption ability of QPEI/SiO_2 particles for CrO_4^{2-} ions is nearly independent of pH values of the medium. QPEI/SiO_2 particles have excellent eluting and regenerating property as a mixed solution of NaOH and NaCl is used as eluent.

1. Introduction

The contamination caused by heavy metals is a serious environmental problem because of their toxicity to many life forms. Among various heavy metals, chromium poses severe threats to public health. Chromate as a species of hexavalent chromium is known to be high toxic and have powerful carcinogenic effect [1–5], and the maximum permissible level of chromate salt in drinking and industrial wastewater were set by the Environmental Protection Agency (EPA) to be 50 and 200 μg/L, respectively [6]. The chromium pollution mainly results from the wastewater and wastes discharged by leather tanning, electroplating, metallurgy, chemical engineering, mining industries, and so on. Chromate anion is readily transported in ground water and causes the contamination of drinking water because it is highly water-soluble and mobile. In the face of the seriousness of chromium contaminations, efforts have been devoted to treating chromate-contaminated water with several methods, such as adsorption, chemical reduction, ion exchange, membrane-based separation and biological treatment [7–13]. Among these methods, the adsorption technique is better effective and simply, and have widely been studied in the past decades. Except to anion exchange resins [14,12], clay minerals (for example bentonite) and zeolite often are used as solid adsorbent for the removal of chromate from wastewater because of their high specific area and low cost. However, the surface of these materials is usually charged negatively, so the adsorption and elimination effect for the chromate anions is poorer. Therefore, the researchers modify these clay minerals with cationic surfactants, and utilize the cationic characteristics of these surface-modified materials to enhance the removal efficiency for chromate anions [15–19].

Are there more effective solid adsorbents for the removal of chromate? It can be expected that the solid adsorbents with high performance can be prepared by grafting functional polymers onto the surfaces of inorganic micro-particles. The resulted composite materials can combine well the functionality of the functional polymers and the many excellent properties of inorganic microparticles, such as high specific area, strong mechanical property, fine chemical and thermal stability and low cost.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there is a mass of nitrogen atoms of amine groups on its macromolecular chains. The commercial PEI always is a branched macromolecule which chemical structure is given in Scheme 1, and the ratio of primary, secondary and ternary amine groups on PEI macromolecule chains is equal to 1:2:1 approximately [20]. In this work, polyethyleneimine was grafted onto the surfaces of micron-sized silica gel particles in the manner of "grafting onto" [21], and grafting particles PEI/SiO_2 were obtained. Afterward, the grafted PEI on SiO_2 particles was quaternized via two polymer reac-

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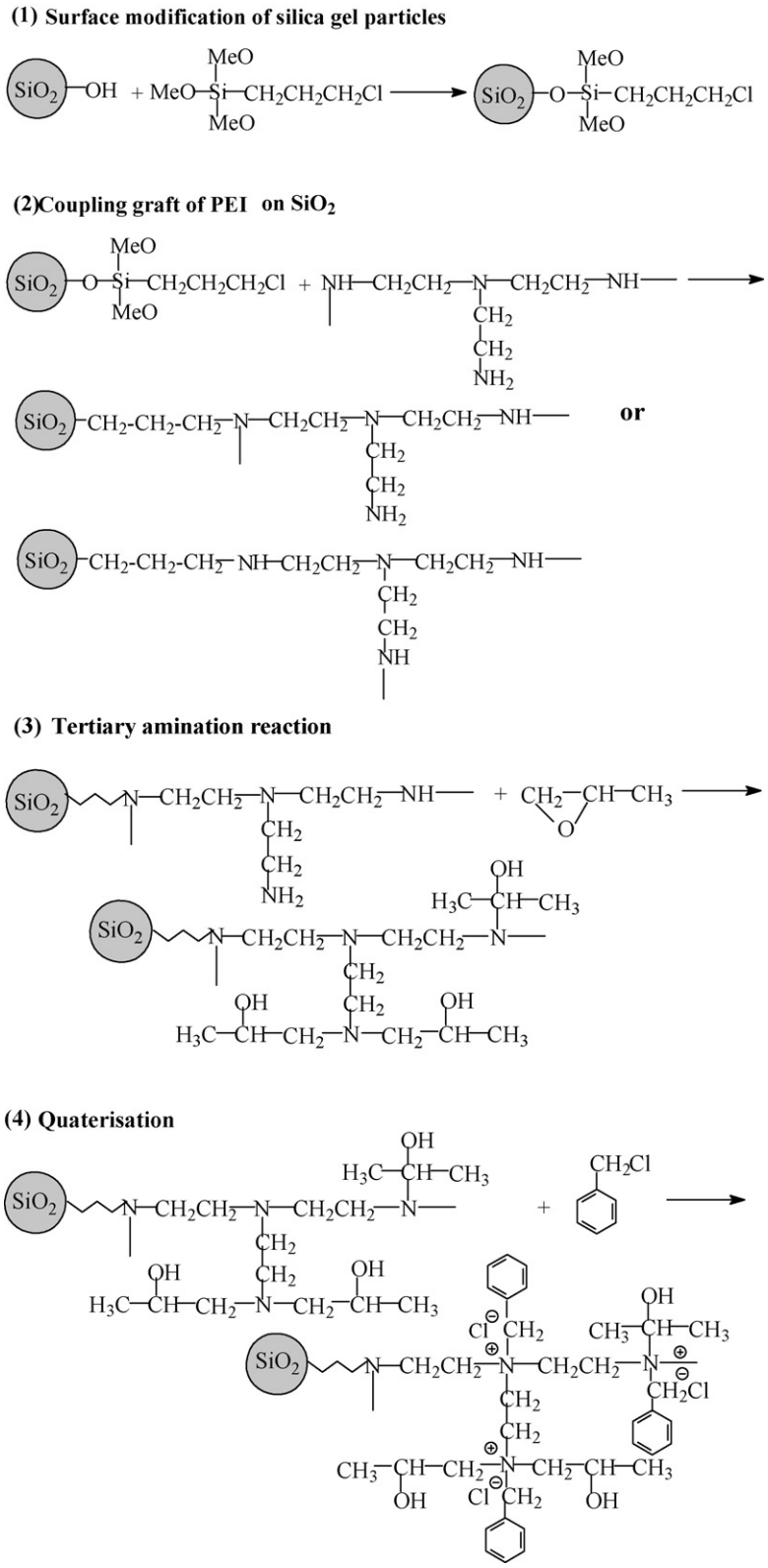

Scheme 1. Schematic representation of preparing process for QPEI/SiO_2.

tions, tertiary amination reaction and quaternisation. Finally, the functional composite particles, QPEI/SiO_2, on which a great deal of quaternary ammonium groups were supported, were prepared. The functional particles QPEI/SiO_2 were used in the adsorption and removal of chromate anions from aqueous solutions for the first time, and the adsorption mechanism was also researched. As compared with those clay minerals surface-modified with cationic surfactants [16,18], the particles QPEI/SiO_2 have much stronger adsorption ability for chromate anions owing to the high density of the cationic groups on their surfaces. In addition, the particles QPEI/SiO_2 combine well the sorption function of QPEI towards chromate anions and the excellent physicochemical properties of silica