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Studies on the surface modification of diatomite with polyethyleneimine and trapping effect of the modified diatomite for phenol

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Abstract

The adsorption isotherm of polyethyleneimine (PEI) on diatomite was studied using UV spectrophotometry, the surface of diatomite was modified with polyethyleneimine by using impregnation method, and the trapping behavior of the modified diatomite for phenol was investigated by using 4-aminoantipyrine (4-AAP) spectrophotometric method. The experiment results show that negatively charged diatomite particles have very strong absorption effect for cationic macromolecule PEI, the adsorption isotherm fits in Freundlich equation. The character that there is a maximum value after intitial sharp increase of adsorption capacity on the adsorption curve indicates that there is strong affinity between diatomite particles and polyethyleneimine macromolecules, and it attributes to the strong electrostatic interaction. After modification with PEI, the electric property of diatomite particle surface changes essentially, and the isoelectric point of diatomite particles moves from pH 2.0 to 10.5. In acidic solution, phenol exists as molecular state, and the modified diatomite particles adsorb phenol through hydrogen bond interaction. However, the hydrogen bond interaction between nitrogen atoms on PEI chains and phenol is weaker because of high degree of protonation of polyethyleneimine macromolecules, so the adsorption quantity is lower. In basic solution, phenol exists as negative benzene–oxygen ion, and the modified diatomite particles adsorb phenol through electrostatic interaction. However, the electrostatic interaction between PEI and negative benzene–oxygen ion is very weak because of low degree of protonation of polyethyleneimine macromolecules, so the adsorption quantity is much lower. The modified diatomite particles produce very strong trapping effect for phenol in neutral aqueous solution via the cooperating of strong electrostatic interaction and hydrogen bond interaction, and the saturated adsorption capacity can attain to 92 mg g^{-1}.

Keywords: Polyethyleneimine; Diatomite; Phenol; Surface modification; Adsorption; Electrostatic interaction; Hydrogen bond interaction

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1. Introduction

Diatomite ($SiO_2 \cdot nH_2O$) is a pale-coloured and lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of a wide variety of shape and sized diatoms in a structure containing up to 80–90% void [1]. Diatomite's high porous structure, low density and high surface area results in a number of industrial applications such as filtration media for various inorganic and organic chemicals, absorbent, catalyst carrier, filler and so on [1–5]. In aqueous solution diatomite particles are negatively charged, and possesses strong attractability for positively charged species. Diatomite exists in large deposits around the world, and it has wide future to apply diatomite in various industrial processes.

Polyethyleneimine (PEI) is a water-soluble polymeric amine, and it behaves as a base in aqueous solution. It has property of strong affinity for protons owing to a large number of nitrogen atoms of amino groups on its macromolecular chains. It is protonated at pH lower than 10, so PEI is a cationic polyelectrolyte [6–9]. There is strong electrostatic interaction between PEI and particles charged negatively, so PEI molecules can be attracted on the latter's surface. The absorption of PEI on SiC [10] and bentonite [11] particles was investigated. However, no report has been published about the adsorption interaction between PEI and diatomite. Furthermore, it has not been investigated to use diatomite modified with functional polymer as absorbent in wastewater treatment.

The industrial wastewater containing phenol causes serious pollution of the environment, and it has very important significance for environment protection to develop new methods and materials to treat the wastewater containing phenol. Whether can the modified diatomite with functional polymer PEI be used in the treatment of wastewater containing phenol? The aim of this paper is that firstly the adsorption interaction between PEI and diatomite is examined and then the trapping effect of PEI modified diatomite for phenol is investigated. The purpose of the work is to probe into the effectiveness and probability of PEI modified diatomite for treating the wastewater containing phenol.

2. Experimental

2.1. Materials

Commercial polyethyleneimine branched polyethyleneimine (Wuhan Qianglong Chemical Engineering Company, China) was used, it contains primary, secondary and ternary amino groups in a ratio of approximately 2:1:2, respectively, and its molecular weight was $M_r = 20000–40000$; Diatomite (Shanghai Reagent Factory) was used without further purification. Other chemicals used were of analytical reagent grade. Water used in this work was deionized and then distilled.

2.2. Instruments

The UV spectra absorption of PEI was recorded using a UV-2602 spectrometer (Shanghai UNIC Company). The visible light absorption of phenol was recorded using a 721 type spectrometer (Shanghai Analytical Instrument Factory). The pH values of solutions were measured on a PHS-2 type acidometer (The Second Analytical Instrument Factory of Shanghai). An electrophoresis instrument (Najing University Institute of Applying Physics, China) was used for measuring the isoelectric point of dispersed particles.

2.3. Measuring zeta potential of diatomite

A certain amount of diatomite was added into full distilled water, the suspension was agitated for 4 h, and was statically placed for 20 h. Then the supernatant was taken out, pH value was determined, and the pH value was adjusted by adding HC1 or NaOH in range of 1–13. At different pH value, the electrophoresis speed of the colloid particles of diatomite was measured in U Type tube of electrophoresis instrument and in 15 min, and the zeta potential was calculated according to following equation:

$$\zeta = \frac{6\pi\eta\mu}{\varepsilon E} \quad (1)$$

where E is the potential grads ($E = V/L$); η is the viscosity of water; ε is the dielectric constant of water; μ is the electrophoresis speed of colloid particles; $\zeta(V)$ is the zeta potential of colloid particles.