Research article

Adsorptive removal of phenol from aqueous solution with zeolitic imidazolate framework-67

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A R T I C L E   I N F O

A B S T R A C T

ZIF-67(zinc-methylimidazolate framework-67), one of the zeolitic imidazolate frameworks (ZIFs), was used for the removal of phenol from aqueous solutions *via* adsorption and shows high adsorption capacity for phenol. The thermodynamic and kinetic adsorption behavior of ZIF-67 for phenol in water with concentration ranging from 50 to 300 ppm were investigated in a batch reactor and a ZIF-67 packed column, respectively. The effects of pH, contact time, zeta potential of the adsorbent and temperature on the adsorption behavior were evaluated, and the results demonstrated that the adsorption is primarily brought about by a specific favorable interaction (electrostatic interaction) between phenol and ZIF-67 surface. The suitability of the Langmuir adsorption model to the equilibrium data was investigated for each phenol-adsorbent system, which the results showed that the equilibrium data for all the phenol-sorbent systems fitted the Langmuir model. Thermodynamic parameters such as Gibbs free energy are calculated from the experimental data at different temperatures. The adsorbent could be perfectly regenerated at 120 °C with little loss in the adsorption ability.

1. Introduction

Phenols are generally considered to be one of the important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water.

The effective removal of these pollutants from waste water is a problem of great importance and interest. Great research efforts on adsorption processes and adsorbent materials for separating organic pollutants from waste streams have been developed.

The traditional methods such as adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, and reverse osmosis, *etc*. have been widely used for removal of phenols from aqueous solutions (Buscaa et al., 2008). Among them, removal of phenols by adsorption is the most powerful separation and purification method because this technique has significant advantages including high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent, and minimized the production of chemical or biological sludge (Ahalya et al., 2003). Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent. Therefore, new adsorbents, which are economical, easily available, having high loading capacity have been required. A number of adsorbents such as activated carbon (Mukherjee et al., 2007), red mud (Tor et al., 2006) and rubber seed coat (Rengaraj et al., 2002), *etc*. have been used for phenol removal. Adsorption of phenol onto activated carbons is a well-known process because activated carbon has a large surface area and high adsorption capacity. However, its high cost and the difficulties in recovering of activated carbon particles from treated water, limit its use as an adsorbent.

In recently years, Metal-Organic Frameworks (MOFs) have been widely used as adsorbents for the removal of toxic metals and organic pollutants from aqueous solutions due to their large specific surface area, chemical and mechanical stability, layered structure and high capacity (Maes et al., 2011; Hasan et al., 2012).

As a unique class of hybrid nanoporous materials, metal-

organic frameworks (MOFs) have attracted considerable interest in recent years owing to their potential in gas storage and separation, catalysis, and other emerging applications (Eddaoudi et al., 2002; Yaghi et al., 2003; Ferey, 2008; Morris and Wheatley, 2008). Zeolitic imidazolate frameworks (ZIFs), a subset of MOFs, consist of tetrahedral metal ions (*e.g.* Zn^{2+}, Co^{2+}) bridged by imidazolate ligands (Lee et al., 2009), are well-known to their permanent porosity (Phan et al., 2010), high thermal, and chemical stability (Banerjee et al., 2008), which endow them with promising application properties as catalysts (Park et al., 2006), adsorbents (Tran et al., 2011), and separation membranes (Ban et al., 2013). Nowadays, many reports about ZIFs on liquid phase adsorption have been given (Liu et al., 2011; Cousin et al., 2011; Zhang et al., 2013). Moreover, selective adsorption and separation of xylene isomers (Peralta et al., 2013), 5-hydroxymethylfurfural (HMF) Jin et al., 2015, benzotriazoles (Jiang et al., 2013), phthalic acid and diethylphthalate from water (Khan et al., 2015) over ZIFs were also reported. To the best of our knowledge, work on the adsorption of phenol over aqueous water based on ZIF-67 has not been reported.

Herein, the adsorption of phenol from aqueous system based on ZIF-67 is to be evaluated. Adsorption experiments will be performed in both batch and fixed-bed column systems. One will see that ZIF-67 perform large adsorption capacity, excellent chemical stability, and good reusability, suggesting utility as a highly potential adsorbent for separating phenol from aqueous solution.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents of analytical grade were commercially available and used as received: Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (purity 99.8%, Sigma–Aldrich), 2-methylimidazole (purity 99.8%, Sigma–Aldrich), phenol (purity 99.8%, Sigma–Aldrich), Deionized water (H_2O, home-made), were used as obtained from commercial sources and used without further purification.

The powder X-ray diffraction pattern (XRD) of the synthesized ZIF-67 were recorded on a Rigaku 2500 VBZ+/PC diffractometer using monochromatized Cu Kα radiation under 65 kV and 200 mA in the scan range of 2θ from 5° to 50° with a scan step of 0.02°. Thermogravimetric analysis (TGA) was performed on a Perkin-nElmer Pyris Diamond TG instrument at a heating rate of 5 °C/min under nitrogen atmosphere. Nitrogen physisorption isotherms were measured at 77 K, on a Quantachrome Autosorb Automated Gas Sorption instrument. Infrared spectra were acquired from a Nicolet 6700 FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance) spectrophotometer.

2.2. Synthesis of adsorbents

ZIF-67 was synthesized using 2-methylimidazole as a linker according to the previously reported protocol (Gross et al., 2012). The synthesis solution, which had a molar ratio of Co^{2+}:2-methylimidazole:H_2O = 1:8:1617, was prepared as follows: First, 3.38 kg of 2-methylimidazole was dissolved in 120 kg of DI water, and the pH of the solution was adjusted to approximately 9.5 using TEA. Second, 1.50 kg of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 30 kg of deionized (DI) water. Then, the cobalt nitrate solution was mixed with the 2-methylimidazole solution under stirring. All of the operations were performed at room temperature (20 ± 2 °C). After stirring for 20 min, the reaction solution was delivered to a filter using an air compressor. Then, the solution was filtered and washed with (DI) water several times. To accelerate the filtration rate of the

entire process, the system was pressurized using nitrogen. Finally, a purple product was obtained. The as-synthesized product contains large amounts of 2-methylimidazole and water. The activation procedure leading to a clean, empty and stable material was achieved using the following in-house procedure. Excess 2-methylimidazole and pore-occluded water were completely removed by sonication of the microcrystalline product three times in deionized water for 2 h. Then, the ZIF-67 sample was heated to 120 °C under vacuum for 3 days to remove the solvents and other guest molecules in the pores. The yield of ZIF-67 was 0.991 kg. The resulting void-cleaned sample is referred to as the "activated sample".

2.3. Adsorption experiments

2.3.1. Liquid phase batch experiments

Before adsorption, the adsorbents were dried overnight under a vacuum at 120 °C and were kept in a desiccator. An exact amount of the adsorbents (5 mg) was put into the aqueous solutions (50 mL) with phenol concentration ranging from 50 to 300 ppm. The aqueous phenol solutions (pH = 9) containing the adsorbents were mixed well with magnetic stirring and maintained for a fixed time (1 min–10 h) at 30 °C. After adsorption for a pre-determined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.45 μm), and the phenol concentration was determined with the absorbance obtained from the UV spectra. To determine the adsorption capacity at various pHs, the pH of the phenol solution was adjusted with 0.1 M HCl or 0.1 M NaOH aqueous solution. The adsorption capacity at various pHs was measured at 30 °C after mixing the phenol solution (100 ppm) and the ZIF-67 for 10 h. The amount of adsorbate adsorbed at time, q_t (mg/g) and at equilibrium condition, q_e (mg/g) was calculated according to the equations (Din et al., 2009).

$$q_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{2}$$

where C_0 and C_e are initial and equilibrium adsorbate concentrations (mg/L), respectively. C_t is adsorbate concentration at time (mg/L). V is volume of solution (L) and W is mass of adsorbent (g).

The maximum adsorption capacity was calculated with the Langmuir adsorption isotherm (Hameed and Rahman, 2008) after adsorption for 10 h under the conditions of initial concentrations = 50–300 mg L^{-1}, 30 °C and pH = 9. The adsorption isotherms in various conditions were plotted to follow the Langmuir equation (Lee et al., 2009)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{3}$$

where q_e (mg/g) is the amount of the phenol adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium phenol concentration in the solution, q_{max} (mg/g) is the Langmuir constant related to the maximum monolayer adsorption capacity, and b (L/mg) is the constant related the free energy or net enthalpy of adsorption. The linear plot of C_e/q_e versus C_e indicates that adsorption obeys the Langmuir model, and the constants q_{max} and b are obtained from the slope and intercept of the linear plot, respectively.

The essential features of the Langmuir isotherm model can be expressed in terms of 'RL' a dimensionless constant, separation factor or equilibrium parameter, which is defined by the following equation (Hall et al., 1966):