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Improved removal of 2-chlorophenol by a synthesized Cu-nano zeolite

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ABSTRACT

This study was conducted to investigate advanced removal characteristics of toxic 2-chlorophenol in water by copper supported nano zeolite (Cu-nano zeolite). The surface area and surface positive charged of the nano zeolite were increased after doping with copper ions, leading to enhance in 2-chlorophenol adsorption capacity. Advanced adsorption characteristics of 2-chlorophenol by Cu-nano zeolite were evaluated studying the effect of pH, reaction time, adsorbent dose, initial solution concentration, regeneration of adsorbent and even adsorption cost and the process was applied to the direct treatment of wastewater. The maximum adsorption capacity for 2-chlorophenol by Cu-nano zeolite was 204.68 mg/g at optimum pH 6.0 with 150 min of reaction time. Regeneration characteristics of 2-chlorophenol loaded adsorbent were also analyzed. Even after 9 cycles of adsorption–desorption, the percentage removal of 2-chlorophenol was maintained at more than 80% of the initial value. The adsorption cost required for removal 2-chlorophenol by Cu-nano zeolite was 0.58 US$/g, which is lower by 14% than those of activated carbon. The Cu-nano zeolite method was applied to treat industrial wastewater containing high concentration of toxic 2-chlorophenol (420 mg/L) collected from chemical plants. The result showed that 81.8% of 2-chlorophenol was removed from wastewater. Based on these findings, Cu-nano zeolite can be used for effective and economic removal of 2-chlorophenol from wastewater.

1. Introduction

Many phenolic compounds are regulated as priority pollutants for environmental control because of their high toxicity to human beings even at low concentration exposure (Janet et al., 2013; Tsai et al., 1995; Xue et al., 2013; Yagu et al., 2014). Chlorophenols have been extensively used in the production of fungicides, herbicides, insecticides, pharmaceuticals, preservatives, glue, paint, fibers, leather, and as intermediates in chemical synthesis. Due to their toxicity and adverse effects upon human and biota, the United States Environmental Protection Agency (US EPA) has classified them as toxics or hazardous pollutants (Annual Reports Hot Spots, 1997; WHO Environmental health criteria 93, 1989). However, exposure to 2-CP may cause carcinogenic and teratogenic properties in humans and the environment (Igbinosa et al., 2013; Karci, 2014). Various treatment strategies have been applied for the removal of 2-chlorophenol from wastewater (Hussain et al., 2013; Chiang et al., 2002; Lingling et al., 2011; Shah et al., 2011; Koubaissy et al., 2011). The traditional technologies based on adsorption, frequently involving the use of activated carbon for the removal of organic contaminants in water. However, it is well known that regeneration of active carbon is complicated and expensive (Mollah and Robinson, 1996; Ahmaruzzaman, 2008; Monsalvo et al., 2011; Zhang et al., 2015). Many researchers have focused on various materials that are able to remove organic pollutants from water (Hussain et al., 2013; Chiang et al., 2002; Kim et al., 2007; Buitron and

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Moreno-Andrade, 2011; Goh et al., 2009; Monsalvo et al., 2009; Khan et al., 1997; Xue et al., 2013). Zeolites are an important class of hydrated aluminosilicates: they possess cage-like structures with internal and external surface areas of up to several hundred square meters per gram. An important property of these materials is the capacity to be regenerated while keeping their initial properties. Synthetic and natural zeolites have been widely used as adsorbents for removal of phenolic compounds from wastewaters (Gómez-Hortigüela et al., 2014; Mahmoud and Lobo, 2014; Nakasaka et al., 2013; Syamsiah and Iwan, 2004; Cao et al., 2015; Kuleyin, 2007). Currently, the global market for zeolite demand was estimated at around 4 million tons in 2010. Recent research interest in zeolites has been focused on different aspects in the synthesis of nano size zeolites, which have favorable properties for adsorption. The reduction of particle size from the micrometer scale to the nanometer scale leads to substantial changes in the properties of these materials, which impact on the performance of nano zeolites in traditional application areas, particularly for adsorption processes (Lingling et al., 2011; Nakasaka et al., 2013).

However, the structure of nano zeolite with hydrated aluminosilicates includes three-dimensional lattices that are composed of SiO_4^{4-} and AlO_4^{5-}. Partial replacement of Si^{4+} by Al^{3+} in the zeolite structure results in an excess of negative charge that hinders the adsorption of chlorophenol. Therefore, modification with metal ions could change the surface area and decrease the excess negative charge of nano zeolite and thus contribute to improving the adsorption capacity of organic pollutants.

Copper is one of the most popular metals that has been used for millennia. It is essential to all living organisms, has low toxicity and is cheaper than other metals. In addition, Cu ions can be doped into the pores of the nano zeolite, thereby narrowing its pore diameter, increasing its surface area and expanding the possibilities for its utilization as an adsorbent for the removal of organic pollutants.

The main objective of the present study is to evaluate the feasibility of applying Cu-nano zeolite to the removal of toxic 2-chlorophenol from aqueous solutions. We focused on enhancing adsorption capacity and reducing adsorption cost of toxic 2-chlorophenol by loaded Cu ions on the synthesized nano zeolite surface. However, regeneration and the field application of Cu-nano zeolite to removal 2-chlorophenol containing high concentration in wastewater were also investigated.

2. Materials and methods

2.1. *Materials*

Nano zeolite was prepared by mixing of 0.35 g of NaOH with 0.147 g of sodium aluminate salt in H_2O and aging it for 5 h at 20 °C with magnetic stirring. After 6.6 g of silica sol was added dropwise, the resulting mixture was stirred at room temperature for 12 h to give a homogenous mixture that was then heated for 24 h at 180 °C under autogenously pressure. The solid product was centrifuged and washed with deionized water until its pH reached 6.0. After drying the synthesized crystalline nano zeolite, an appropriate amount was immersed in 0.5 M $Cu(NO_3)_2$ solution to obtain Cu ion-doped nano zeolite solid. The resulting solid was recovered by filtration, washed with distilled water, dried at 50 °C for 12 h and then used for characterization of the physical and chemical properties.

2.2. *Characterization of the adsorbent*

Scanning electron microscopy (SEM) analysis was conducted using a Hitachi S-4700 scanning electron microscope for the nano zeolite and Cu-nano zeolite. As preparation for SEM analysis, the samples were dried for 4 h at 100 °C. The measurements were carried out with a heating rate of 10 °C/min. The specific surface areas of the nano zeolite and Cu-nano zeolite were determined using the Brunauer–Emmett–Teller (BET) method. An X-ray diffractometer (XRD, Bruker AXS, Germany Model D8 Advance), with Cu Kα radiation, a generator voltage of 40 kV and current of 30 (mA) was used to analyze the crystallinity of nano zeolite and Cu-nano zeolite. A scan speed of 1° (2θ)/min with a scan step of 0.01° (2θ) was used to continuously run between 5° and 80° (2θ) range. The thermo gravimetric analysis (TGA) was carried out in the air at a heating rate (10 °C/min) and temperature range 50–600 °C.

2.3. *Adsorption and desorption*

Bath adsorption experiments were carried out by agitating 0.4 g of adsorbent in 100 ml of 2-chlorophenol solution at desired concentrations (50, 100, 200 and 300 mg/L) of 2-chlorophenol and solution pHs ($2.0 \le pH \le 10$) with a mechanical shaker rotating at 150 rpm. The 2-chlorophenol concentration was measured by monitoring the absorbance at 273 nm using a UV–Vis spectrophotometer (Model UV 2100). The solution pH of the reaction mixture was measured using a pH meter (Orion 5 Star). The adsorption effect of the solution pH was analyzed by adjusting the pH of the 2-chlorophenol solutions using 0.1 M HCl and 0.1 M NaOH solutions. The effect of the adsorbent dosage was investigated by agitating 100 ml of 2-chlorophenol solution (100 mg/L) with different adsorbent doses (0.05–1 g) for an equilibrium time of 150 min. Langmuir and Freundlich adsorption isotherms were used to analyze the equilibrium adsorption. The kinetic studies were performed using a similar procedure to the adsorption study described above. Each experiment was repeated at least two times and their mean values were used for kinetic analysis. The amount of 2-chlorophenol adsorbed per unit mass of adsorbent at equilibrium was obtained using the following Eq. (1):

$$q_e(\text{mg/g}) = [C_0(\text{mg/L}) - C_e(\text{mg/L})] \times V(\text{L})/W(\text{g}) \quad (1)$$

where V is the volume of the solution (L), C_0 is the initial solution concentration (mg/L), C_e is the solution concentration at equilibrium (mg/L), and W is the weight of the adsorbent (g).

After adsorption, 2-chlorophenol loaded Cu-nano zeolite was washed with distilled water before being treated with 100 ml of 10% C_2H_5OH, 20% C_2H_5OH and 50% C_2H_5OH eluents for a contact time of 150 min at room temperature 20 ± 1 °C. The amount of 2-chlorophenol desorbed was measured with a UV-Vis spectrophotometer (Model UV 2100). The percentage desorption was calculated by the following Eq. (2):

$$\%\text{Desorption} = \left[\frac{C_e - C_d}{C_e}\right] \times 100 \quad (2)$$

where C_d (mg/L) represents the final 2-chlorophenol concentration identified in the desorption medium. After desorption,