



Adsorption of trichlorophenol on zeolite and adsorbent regeneration with ozone



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HIGHLIGHTS

- FAU zeolite can efficiently adsorb trichlorophenol.
- The adsorption follows Freundlich model and Pseudo-second-order kinetics.
- Ozonation can significantly increase the specific surface of FAU zeolite.
- Regeneration of loaded zeolite with ozonation is highly feasible.

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ABSTRACT

A FAU-type zeolite was studied as an adsorbent to remove 2,4,6-trichlorophenol (TCP), a frequently detected recalcitrant pollutant in water bodies. Both adsorption isotherm and kinetics were studied with TCP concentrations from 10 to 100 mg/L. It was observed that TCP was effectively adsorbed onto the zeolite with a high adsorption capacity and a high kinetic rate. Freundlich model and pseudo-second-order kinetics were successfully applied to describe the experimental data. The influence of solution pH was also studied. Furthermore, ozone was applied to regenerate the loaded zeolite. It was found that an effective adsorption of TCP was kept for at least 8 cycles of adsorption and regeneration. The ozonation also increased the BET specific surface of zeolite by over 60% and consequently enhanced the adsorption capacity.

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1. Introduction

Chlorophenols (CPs) are widely used in the production of various industrial products, such as wood preservatives, pesticides, disinfectants, etc. As a result, CPs have been widely detected in water bodies. For example, 2,4,6-trichlorophenol (TCP) was found at a maximal concentration of 28.65 µg/L in Yellow River, China [1]. When the contaminated water bodies are used for the production of drinking water, it is highly possible that CP would pass through the treatment facilities and finally appear in drinking water [2]. Many studies have demonstrated the ecological toxicity and potential impact of CPs on human health. Researchers also found the potential genotoxicity of CPs, e.g., with point mutations of *p53* gene in the liver genome of zebrafish which was exposed to 5 µg/L

TCP for 10 d [3]. Consequently, CPs are listed as priority pollutants in many regions [4].

Various removal technologies (e.g. chemical oxidation, biodegradation, membrane separation, etc.) have been so far developed and applied to remove CPs from water [5]. Adsorption, in which pollutants (adsorbates) are adhered onto a solid material (adsorbent), has some advantages compared with other technologies, such as low investment, high flexibility of design, ease of operation and high tolerance to toxicity. It is widely applied for the removal of a broad range of organic and inorganic pollutants from water [6]. Many adsorbents have been used to adsorb CPs from water, including activated carbons, agricultural and industrial wastes, natural materials, and synthetic resins [7–9].

However, adsorption is a separation process where pollutants are only transferred to adsorbents but not degraded to harmless substances. Furthermore, an adsorbent has a limited adsorption capacity and will be saturated after a certain time of operation. Therefore, the used adsorbent will be either regenerated or disposed and replaced with new one. The popular regeneration

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methods include thermal calcination, decreasing pressure, wave irradiation, and chemical elution (e.g., with a different pH or an organic solvent) [10,11]. Recently, some researchers start to make efforts to apply a chemical oxidation method to regenerate the adsorbents via oxidizing the organic adsorbates. This method can in situ restore the adsorption capacity of used adsorbents and furthermore can also degrade or mineralize organic pollutants. Nevertheless, the method is not suitable for all adsorbents. For instance, it was found that ozone can transfer basic sites of activated carbon into acid sites and also can decrease the specific surface area, which resulted in a declined adsorption of methylene blue [12]. Therefore, it is of great interest to study a material which can adsorb recalcitrant pollutants like TCP and whose adsorption capacity cannot be compromised during the regeneration process.

Zeolite is a group of porous materials based on aluminosilicate and could be a promising candidate for the purpose. The hydrophobicity of zeolite can be easily adjusted during the manufacturing process to adsorb different pollutants, e.g. by changing the ratio of Si/Al, the pore size and structure [13]. However, the adsorption of CPs on zeolite has not been fully studied and only several studies were reported [14–16]. Their adsorption kinetics on zeolite is rarely available in literature.

On the other hand, the regeneration of loaded zeolite with chemical oxidation is only reported in limited studies, most of which used the Fenton reaction. Koryabkina et al. coated Fe^{2+} on zeolite by a reaction with sodium borohydride and achieved a stable adsorption of disinfection byproducts in 4 cycles of adsorption and regeneration with the Fenton reaction [17]. Wang et al. used the homogeneous Fenton oxidation to regenerate MCM-22 zeolite loaded with methylene blue but only 60% of its adsorption capacity was recovered [18]. However, the Fenton reaction normally requires a strong acidic condition and leaching of immobilized Fe^{2+} would lead to a decreased oxidation rate [19].

Ozone can be an alternative oxidant to regenerate zeolites, which was rarely reported in literature. To our knowledge, only one study was reported in scientific journal by Reungoat et al., who obtained a complete recovery of the adsorption capacity for nitrobenzene [20]. Therefore, the objective of this study was firstly to investigate the adsorption of TCP onto a commercial zeolite, including both adsorption isotherm and kinetics, and secondly to apply ozone to regenerate the used zeolite.

2. Experimental

2.1. Materials

The adsorbent used in this study was a high-silica FAU zeolite (pore size 9 Å, diameter 1.6–2.5 mm), supplied by CWK Chemiewerk Bad Köstritz GmbH. The chemical composition of zeolite is $(\text{H,Na})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ($x \geq 30$), as described by the supplier. 2,4,6-Trichlorophenol (98% purity) and methanol of HPLC grade were purchased from Sigma–Aldrich, Germany.

2.2. Adsorption tests

All adsorption kinetics and isotherm tests were conducted with a batch equilibrium procedure. In the isotherm test, 1 g of zeolite was added to 50 mL of TCP solution with deionised water at different concentrations (10, 25, 50, 75, and 100 mg/L). The adsorption was carried out at room temperature in a 100-mL Erlenmeyer flask which was shaken at a speed of ~110 rpm. No buffer was applied in order to avoid the interference of ions. However, pH values in all test stayed around 6.2–6.5. Samples (1.5 mL) were taken out of the solution after 24 h when the equilibrium was assumed. The samples were filtrated through a syringe filter with a 0.45 μm polycarbonate

membrane and analyzed with HPLC to determine the concentration of TCP. The kinetic tests followed a similar procedure except that samples were taken in a given time interval during 6 h.

The effect of initial pH was studied between pH 3 and pH 10, which was adjusted by adding 10 mM HCl or 10 mM NaOH at the beginning. The test solution had a volume of 50 mL and contained 1 g of zeolite and 100 mg/L of TCP. Other conditions were the same as above. A sample was taken after 24 h.

All tests were conducted in triple and an average value was used. The TCP adsorption on the zeolite at given time was calculated according to:

$$q_t = V \frac{C_0 - C_t}{W}$$

where q_t is the adsorbed TCP at time t (mg/g); C_0 initial TCP in water (mg/L); C_t TCP in water at time t (mg/L); V the solution volume (L); W the adsorbent weight (g). The equilibrium data (q_e , C_e) in the isotherm tests were calculated with the same method.

2.3. Regeneration with ozone

A glass bottle was used to contain 10 g of the zeolite and 400 mL of 50 mg/L TCP solution. The zeolite was suspended by a magnetic stirrer. After 2-h adsorption, a sample was taken and then the ozone-containing gas (45–50 ppm) was bubbled into the solution for 30 min to regenerate the zeolite. The ozone in the water phase (7 mg/L) was measured with the Indigo colorimetric method [21]. Ozone was produced from pure oxygen with an ozone generator (SORBIOS GSF 010.2). After the ozonation, air was used to strip out the ozone residue in the solution. After air stripping, ozone in water phase was below 0.07 mg/L, which was almost the detection limit. A new adsorption test was started by replacing half of the old solution with a new TCP solution (100 mg/L) and the final TCP concentration was 50 mg/L again.

A lot of intermediates may be formed during the above test, which could influence the adsorption of TCP. Therefore, FAU was washed and dried after 10 adsorption cycles, 1 g of which was added into 40 mL TCP solution (50 mg/L) for a clean adsorption test. A sample was taken after 2 h to compare the adsorption with the previous adsorption/regeneration cycles.

The specific surface areas of FAU before and after 10 cycles of ozonation were determined with the BET method (Autosorb-1, Quantachrome) with nitrogen gas.

2.4. HPLC conditions

TCP in all water samples was determined with a HPLC system (Agilent 1200) equipped with a Phenomex Gemini-NX 5 μm column. 50 μL of sample was injected into the system and the elution was conducted with a mixture of methanol and Milipore water (85:15) at a flow rate of 1 mL/min. The column oven was set at 30 °C. The eluted TCP was monitored with a UV detector at a wavelength of 290 nm. The quantification limit of TCP was 0.2 mg/L.

3. Results and discussion

3.1. Effects of initial pH

The solution pH can influence the adsorption process via altering the ionic states of both adsorbent and adsorbate. In addition, the excessive H^+ or OH^- ions can also compete with an adsorbate for the active sites of adsorbent. In this study, the adsorption of TCP on FAU zeolite was tested in pH 3–10. As shown in Fig. 1, a clear declination of the adsorption capacity can be found with the increase of initial pH. The adsorption capacity dropped down from 4.3 mg/g at pH 3.5–2.6 mg/g at pH 10. The similar effect was also found in

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