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Development of response surface methodology for optimization of phenol and *p*-chlorophenol adsorption on magnetic recoverable carbon

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ABSTRACT

The powdered activated carbon impregnated with Fe_3O_4 magnetic nanoparticles (MNPs) was synthesized by a facile in situ chemical co-precipitation method. The response surface methodology (RSM) with central composite design (CCD) was used to investigate the adsorption properties of phenol and *p*-chlorophenol (PCP) onto as-synthesized composite. The RSM was also applied to study the main and interactive effects of the parameters (pH, adsorbent dosage, contact time, and initial pollutant concentration) investigated, as well as to obtain the optimum operating conditions for this novel adsorbent. Magnetic powdered activated carbon (MPAC) showed an excellent magnetic response to the magnetic field and was easily separated from the solution. Moreover, the RSM model obtained ($R^2 > 0.98$) revealed a satisfactory correlation between the experimental results and predicted values of phenol and PCP adsorption. The adsorbent dose was indicated as having the strongest positive influence on adsorption. The identified optimum conditions of adsorption was 6, 118 min, 1.6 g/L and 200 mg/L for pH, contact time, adsorbent dose, and initial phenol and PCP concentration, respectively. The adsorption kinetics fitted well with pseudo-second-order model and the adsorption capacity of phenol and PCP on MPAC inferred from the Langmuir model was 123.45 and 120.48 mg/g, respectively, at 20 °C. In addition, the adsorption activity of MPAC was preserved effectively even after five successive cycles of use owing to its good stability. The thermodynamic parameters indicated that the adsorption of phenol and PCP onto modified PAC was an exothermic and spontaneous process.

1. Introduction

Phenols and chlorinated phenols are characterized as being highly toxic and persistent in the environment. These compounds have been widely used both in industrial and agricultural activities. Due to their persistence, chlorophenols have been classified as priority pollutants that affect human health and the environment [1,2]. Furthermore, chlorophenol substances are recognized for their extreme toxicity to living cells and also their stable intrinsic nature. They can be simultaneously found in industrial effluents from pulp and paper manufacturing, pharmaceuticals, petroleum refining activities, the manufacture of plastics, resins and textiles, the iron, steel and textile industries, as well as being components of many pesticides and biocides [3]. Monochlorophenols are formed as an intermediate in the biodegradation of highly chlorinated phenols. The formation of monochlorophenols has also been reported during the chlorination of wastewater. Thus, these compounds are frequently found in various water sources (e.g. urban wastewaters, treated effluents and surface waters). It has been

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reported that, of all the monochlorophenols, acclimation and degradation of anaerobic sludge with *p*-chlorophenol (PCP) was the most difficult to achieve [4].

The future of decontamination is aiming to remove hazardous substances from water resources economically and robustly. Activated carbon (AC), due to its ability to remove toxic and adverse materials, is frequently exploited in drinking water treatment and wastewater purification [5]. During the past few years, many authors focused their attentions on use of AC for removal of phenolic compounds, especially phenol and PCP in the adsorption studies [6–10]. Some issues such as causing turbidity in the treated water or effluent and consequently need to filtration/centrifugation, however, have limited the application of AC and many nano-sized adsorbents [11]. Hence, considerate efforts have been devoted to modifying AC in order to overcome its limitations and extend its adsorption capabilities. The magnetization of adsorbents and use magnetic separation is an appropriate approach to overcome these problems [12]. Among all the studied nanoparticles, magnetic nanoparticles that were synthesized under a strong magnetic field, have extensively been applied for nanomaterial-based catalysts and environmental clean-up perspectives, due, in essence, to their noteworthy physical and chemical features. Because of their easy separation employing an external magnetic field, low cost, very large surface to volume ratio, low toxicity and lack of internal diffusion resistance, magnetic nanoparticles exhibit great ability for environmental clean-up objectives since they represent supreme biocompatibility which concerning the environmental effect of these materials is a superiority in comparison with the other metallic nanoparticles. In addition, the sorbent can be easily recovered and reused [13,14].

Until now, ferrite nanoparticles have been the most probed magnetic nanoparticles [15]. The presence of MNPs, mainly magnetite, in an adsorbent owing to basic properties of activated carbon, notably extremely small size and the high surface area-to-volume ratio may indeed provide better kinetics for the adsorption of pollutants and chemical stability [15]. Moreover, MNPs possess some advantages such as ease of fabrication and separation, biocompatibility, high stability, and in-situ application [16]. Over the past few years, researchers have strived to use magnetized adsorbents to remove different contaminants from aqueous solutions. In this regard, magnetized activated carbon has been used in adsorption studies for removal of toxic dyes [17–20], aniline [21], trinitrophenol [22], p-nitrophenol [23], cyanide [24], dibenzothiophene [25] and heavy metals [26–29].

Based on the above-mentioned studies, we hypothesize that the carbon sensitized and magnetite nanoparticles (MNPs) doped powdered activated carbon (MPAC) combining the synergistic effects of MNPs and powdered activated carbon (PAC) may have a superbly enhanced adsorption activity as well as easy separation. To the best of our knowledge, few studies on this novel modified PAC have been reported for phenol and PCP removal so far [3,7,10,30]. However, these studies can be criticized from two aspects: firstly, most of them provide a relatively low adsorption capacity for phenol and PCP under the optimum operation conditions. Second, all of them suffer from some serious operational problems such as filtration, centrifugation, and causing turbidity in effluent. Hence, the modification of PAC which not only showed a rapid and simple separation, but also did not cause secondary pollution should be considered. The present study was therefore focused on magnetization of PAC to synthesize MPAC using chemical co-precipitation method, which is the first study on adsorption of phenol and PCP from aqueous solution. Herein, MPAC could not only provide a good adsorption capacity for contaminants due to high surface area, but also could be easily and rapidly separated from solution.

The response surface methodology (RSM) has been corroborated to be a powerful means to get optimum conditions for adsorption and evaluating the interactions of mutually influencing parameters with a limited number of experiments [31]. In this study, the influence of affecting parameters on the adsorptive removal of phenol and PCP was assessed in details using RSM, and based on the central composite design (CCD), in order to identify the optimized conditions. The synergistic effects of MNPs doping on surface area and adsorption behavior of PAC were also evaluated. Isotherm, kinetic and thermodynamic studies were thence carried out in detail. The stability and reusability of the adsorbent were indeed evaluated for five consecutive cycles.

2. Materials and methods

2.1. Preparation of MNPs and MPAC

In this work, all chemicals were of analytical-laboratory grade, purchased from Merck Company (Darmstadt, Germany), and used without further purification. MNPs were prepared by the in situ chemical co-precipitation of Fe^{2+} and Fe^{3+} in an alkaline solution. Initially, deionized water (DI-water) was purged with nitrogen gas for 30 min. The aqueous solutions of ferrous chloride (4×10^{-2} mol/L) and ferric chloride (6×10^{-2} mol/L) were prepared; and the whole mixture was thence stirred for 45 min at 70 ± 1 °C. Afterwards, 30 mL of 28% (w/w) ammonia solution (NH_4OH) was added dropwise into the Fe^{2+}/Fe^{3+} mixed solution for 30 min to raise the suspension pH to about 10–11. The suspension was then mixed on a magnetic stirrer and heated to 80 °C for 1 h. After being cooled, the generated black solid (MNPs) was collected by magnetic separation, repeatedly washed with DI-water followed by ethanol until the pH became neutral. Finally, the black solid was dried overnight at 105 °C in a hot air oven for 2 h and stored in an air tight container for subsequent experiments. The formation of MNPs can be well described by the possible reaction as below [32]:

$$Fe^{2+} + 2Fe^{3+} + 8NH_3 - H_2O \rightarrow Fe_3O_4 + 8NH_4^+ + 4H_2O \quad (1)$$

The impregnation of the magnetite onto the surface of PAC was carried out using a co-precipitation technique. MPAC composite was synthesized by a similar method as described above, except that a known amount of PAC was added in to the Fe^{2+}/Fe^{3+} mixed solutions before the addition of ammonia. Briefly, 10 g PAC was added into the Fe^{2+}/Fe^{3+} solution after 45 min mixing on a magnetic stirrer, and 28% ammonia solution was subsequently added drop by drop to the mixture in a way that the pH of the final solution adjusted to be in the range of 10–10.5. After being rapidly stirred under 80 °C for 1 h the solution was cooled down to the room temperature. The black precipitate (MPAC and MNPs) was separated from the suspension by placing an external magnet on the edge of the flask. It is notable that the all nonmagnetic PAC particles were excluded from the sample during the washing cycle. The obtained MPAC composite was then washed several times with DI-water followed by ethanol until the pH reached to neutral and dried in an oven at 70 °C for 12 h.

2.2. Characterization of MPAC

X-ray diffraction (XRD) spectra of PAC, magnetite and MPAC were obtained using a Quantachrome, NOVA 2000X-ray Diffractometer with graphite monochromatic copper radiation (Cu Kα, λ = 1.54 Å). Samples were placed in a zero background metal holder and scanned in a 2θ range of 10° to 80° with a scanning speed of 2° 2θ min^{-1}. The physicochemical properties of PAC, magnetite and MPAC were analyzed using the Brunauer, Emmett and Teller (BET,