Adsorption of phenol and p-chlorophenol from aqueous solutions by magnetic nanopowder

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ABSTRACT

A new magnetic iron oxide nanopowder (MNM) was prepared, characterized and tested as adsorbent for the removal of phenol and p-chlorophenol (PCP) from aqueous solution. The iron oxide was obtained by a new combustion method which allows the direct obtaining of magnetic nanopowder covered with some organic residues resulting from fuel combustion. The magnetic powder was characterized in terms of phase composition, structure, texture, magnetic properties and carbon content. The adsorption kinetics was examined by the pseudo-first-order and pseudo-second-order models and the equilibrium data were fitted with Langmuir and Freundlich isotherms. The results confirmed the good adsorption capacity of the new magnetic nanopowder for the removal of phenol and PCP from aqueous solutions and its great potential for practical applications.

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 (Ahmaruzzaman 2008). Phenol and its derivatives are common organic pollutants in effluents from paint, pesticides, pharmaceuticals, plastics, leather, petroleum and petrochemical industries. Considering their adverse effects on human health and their toxicity even at low concentrations, the U.S. Environmental Protection Agency and the European Union have designated phenols as priority pollutants (Ahmaruzzaman 2008; Wenjue et al. 2015).

Various treatment methods have been applied to remove phenolic compounds from aqueous solutions, such as biological treatment using anaerobic granular sludge, catalytic wet oxidation, photochemical treatment, solvent extraction, incineration, reverse osmosis and adsorption (Al’a et al. 2011). Compared to alternative technologies, adsorption is still the most attractive and widely used for its relative simplicity of design/operation, high capacity and favorable rate, insensitivity to toxic substances and low cost (Soto et al. 2011). Many sorbents, such as activated carbon, bentonite, synthetic polymeric adsorbents and others (Subramanyam & Das 2009; Michelle et al. 2009; Hasan et al. 2009; Yahia 2009), have been extensively studied. However, the disadvantage of high cost production, high regeneration cost, low mechanical properties and difficulty of phase separation limits the use of common adsorbents for large scale wastewater treatment.

Recently, great attention was paid to magnetic iron oxides which are considered as promising adsorbents for the removal of different pollutants from wastewater at industrial scale. These adsorbents possess many valuable properties including low cost, chemical stability, extended lifecycles and easy separation by applying an external magnetic field (Xu et al. 2012). Also, the adsorption capacity of these adsorbents can be greatly improved by their surface modification with suitable functional groups (Zhang et al. 2010; Dias et al. 2011).

Many reports in the literature have demonstrated the efficiency of magnetic iron oxide nanosorbents for the removal of heavy metals and dyes from aqueous solution. White et al. (2009) used maghemite ($\gamma$-Fe$_2$O$_3$) nanoparticles coated with poly-L-cysteine for the removal of As(III), Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II). Ge et al. (2012) reported effective removal of Cd$^{2+}$, Zn$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ from aqueous solution by polymer-modified magnetic nanoparticles. Methylene blue, methyl orange and congo red dyes were also successfully removed by adsorption onto magnetic iron oxide nanopowders (Ai et al. 2011; Chang et al. 2011; Zhu et al. 2011).
In this work we reported a new magnetic oxide nanoadsorbent. The adsorption capacity of the new magnetic nanomaterial (MNM) was tested by using the phenol and p-chlorophenol (PCP) as model pollutants, considering the very few reports regarding the magnetic removal of these pollutants. The novelty of this study lies in the synthesis method which is economic, simple and environmentally friendly technique.

The performance of a new magnetic nanopowder covered with some organic residues which are responsible for the adsorption capacity.

The kinetics of phenol and PCP adsorption onto MNM was investigated by the pseudo-first-order and pseudo-second-order models and the equilibrium data were analyzed by the Langmuir and Freundlich isotherms using the non-linear regression analysis.

**METHODS**

**Synthesis of magnetic nanopowder**

The magnetic nanopowder (MNM) was obtained by the new combustion synthesis method reported by Ianos et al. (2012). Iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, Roth) was used as oxidizing agent and glucose (d-(-)-C$_6$H$_12$O$_6$, Riedel-de-Haën) was used as fuel. The molar ratio fuel/metal nitrate was 2/1. The reaction was conducted in the absence of air, in a round bottom flask. In these conditions, the combustion reaction was smouldering and accompanied by a large amount of gases which were bubbled in a large beaker filled with distilled water. The reaction product was hand ground, washed with distilled water and dried.

**Characterization**

The powder was characterized in terms of phase composition, structure, texture, magnetic properties and carbon content. The X-ray diffraction was carried out using a Panalytical XPERT-PRO diffractometer with CuK$_\alpha$ radiation. The Fourier transform infrared spectroscopy (FTIR) spectrum was recorded using a Shimadzu Prestige-21 spectrometer in the range 4,000–400 cm$^{-1}$, using KBr pellets and a resolution of 4 cm$^{-1}$. N$_2$ adsorption-desorption isotherms were performed on a Micromeritics ASAP 2020 instrument, at 77 K after the sample was degassed at 100 °C under high vacuum for 24 h.

The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation while the pore diameter and pore volume were determined by the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was computed using the BJH method from the adsorption curve. Magnetic properties were measured at room temperature by vibrating sample magnetometry, using a VSM 880 ADE/DMS magnetometer. The carbon content of the powder was performed by ‘Dynamic Flash Combustion’ using an Elemental Analyzer EA 1108, according to the ASTM D 5373-08 standard test procedure.

**Adsorption experiments**

The adsorption experiments were performed at a temperature of 25 °C, constant pH 6.5, adsorbent dose 2 g L$^{-1}$ and different initial phenol and PCP concentrations of 25–150 mg L$^{-1}$. All experiments were performed in a thermostated shaker with a shaking speed of 200 rpm for 24 h to ensure the equilibrium was reached. The adsorbent was separated from the aqueous solution with the aid of a magnet. The concentration of phenol and PCP was monitored spectrophotometrically, using a UV–Vis spectrophotometer model UVmini-1240 SHIMADZU. The absorbance values were measured at the wavelength of 270 nm for phenol and at 280 nm for PCP.

The adsorbed amount, $q_t$ (mg g$^{-1}$) was calculated according to Equation (1):

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

where $C_0$ and $C_t$ are the initial concentration and the concentrations at time $t$ (mg L$^{-1}$), respectively; $V$ is the volume of solution (L); and $W$ is the mass of adsorbent (g).

The adsorption kinetic of PCP onto MNM was investigated by fitting the experimental data with two kinetic models, namely pseudo-first-order and pseudo-second-order.

The linearized form of the pseudo-first-order equation is (Ru-Ling et al. 2010):

$$ \ln (q_e - q_t) = \ln q_e - k_1 t $$

where $q_e$ and $q_t$ are the amount of solute adsorbed at equilibrium and at time $t$, respectively (mg g$^{-1}$), $k_1$ is the adsorption rate constant (min$^{-1}$). The values of $k_1$ and $q_e$ result from the slope and intercept of the plot ln($q_e - q_t$) versus $t$.

The linearized form of the pseudo-second-order equation is (Jianhan 2009):

$$ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} $$

where $k_2$ is the adsorption rate constant (g mg$^{-1}$ min$^{-1}$).
The equilibrium adsorption capacity, \( q_e \) and the pseudo-second-order rate constant, \( k_2 \) result from the slope and intercept of the plot \( t/q \) versus \( t \).

The experimental data were fitted with Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes an entirely homogeneous surface of the sorbent, the monolayer coverage of the adsorption surface, no interactions between the adsorbed molecules and the heat of adsorption is not dependent on surface coverage (Zhang et al. 2009).

The Langmuir isotherm is represented by the equation (Kaili et al. 2009):

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]

where \( q_e \) is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg g\(^{-1}\)), \( q_m \) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of the solute in the bulk solution (mg L\(^{-1}\)) and \( K_L \) is the Langmuir sorption constant (L mg\(^{-1}\)).

The Freundlich isotherm is an empirical model, appropriate for adsorption on heterogeneous surfaces, with interaction between adsorbed molecules expressed as follows (Hasan et al. 2009):

\[
q_e = K_F C_e^{1/n}
\]

where \( K_F \) is the Freundlich constant (mg\(^{1-1/n}\) L\(^{1/n}\) g\(^{-1}\)), indicating the adsorption capacity of the adsorbent and \( n \) (dimensionless) is a constant related to the intensity of adsorption.

The optimum isotherm was determined by non-linear regression analysis, using ORIGIN 8 software.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Some properties of the adsorbent are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD phase composition</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Volume of pores (cm(^3) g(^{-1}))</th>
<th>Average pore diameter (nm)</th>
<th>Saturation magnetization (emu/g)</th>
<th>Carbon content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNM</td>
<td>Fe(_3)O(_4)</td>
<td>73</td>
<td>0.089</td>
<td>9.0</td>
<td>24</td>
<td>33</td>
</tr>
</tbody>
</table>

The pore size distribution is shown in Figure 1. According to the pore size distribution (Figure 1), MNM is basically a mesoporous material that also has some micropores.

Figure 2 shows the FTIR spectrum of MNM (prepared with the molar ratio fuel/metal nitrate-2/1) in comparison with the FTIR spectrum of MNM 1/1 (prepared with stoichiometric molar ratio fuel/metal nitrate).

Both spectra show a broadband between 560 and 640 cm\(^{-1}\), assigned to the Fe-O vibration in Fe\(_3\)O\(_4\) (Gong et al. 2012) confirming the presence of magnetite. Unlike MNM 1/1, the spectrum of MNM shows additionally bands at 1591.27 cm\(^{-1}\) and 1678.07 cm\(^{-1}\) assigned to C=O stretching vibration and the band at 1429.25 cm\(^{-1}\) associated to C-H bending vibration (Nakanishi & Solomon 1977). These bands which are evidenced only on the spectrum of MNM, prepared with an excess of fuel, clearly confirm the presence of some residual organic groups on the particle surface. These residues resulted directly from the combustion reaction, in good agreement with the results obtained from the elemental analysis (carbon content–33%).

Adsorption studies

Effect of initial concentration on adsorption

The amount adsorbed at equilibrium increases with increase in the initial concentration from 25 to 150 mg L\(^{-1}\), both for phenol and PCP. Also, the amount of PCP adsorbed at equilibrium is much larger compared with phenol, for all the initial concentration investigated, which means that MNM shows better adsorption capacity for PCP than for phenol.

Effect of contact time

The amount of phenol and PCP adsorbed on MNM versus the contact time, for different initial concentrations, is shown in Figures 3 and 4 respectively.

It can be seen that both the phenol and PCP adsorption onto MNM is fast in the first 10 hours, especially for high initial concentration, and then it becomes slower near the equilibrium. This can be explained by the large number of
available vacant sites on the MNM surfaces which are gradually occupied in time as a result of the sorption process.

The adsorption equilibrium was reached after 22 hours both for phenol and PCP, independently of the initial concentration used.

Adsorption kinetics

The experimental data were fitted with the linearized form of the pseudo-first-order (Equation (2)) and of the pseudo-second-order (Equation (3)) (figures not shown). The values of the correlation coefficient (Table 2), much higher for the pseudo-first-order as compared with the pseudo-second-order, indicate that the adsorption kinetics of phenol and PCP onto MNM is described by the pseudo-first-order model.

The calculated values of \( k_1 \) and \( q_e \) for the adsorption of phenol and \( p \)-chlorophenol onto MNM adsorbent according to the pseudo-first-order model are listed in Table 2. The calculated values of \( q_e \), very close to the experimental ones also confirm that the adsorption kinetics of PCP was described by the pseudo-first-order model.

Adsorption isotherms

The experimental equilibrium data for the adsorption of phenol and PCP onto MNM were fitted to the Langmuir and Freundlich isotherms by plotting \( q_e \) versus \( C_e \) (Figure 5).
The isotherm parameters and the correlation coefficients for the adsorption of phenol and PCP onto MNM adsorbent are listed in Table 3. Comparing the correlation coefficient of the two isotherms show that the Langmuir model fitted better the equilibrium data compared with the Freundlich model, both for phenol and PCP due to $R^2 > 0.99$, indicating the homogeneous nature of the adsorbent surface and the monolayer adsorptive process.

The adsorption capacity of a system is dependent on many factors such as the physical nature of the adsorbent (porosity, surface area, particle size, functional groups), the nature of adsorbate (solubility, $pK_a$, functional groups, polarity, molecular weight and size) solution conditions (pH, ionic strength, solute concentration), interactions at the solid–liquid interface and experimental conditions (Dabrowski et al. 2005; Busca et al. 2008; Soto et al. 2011).

The maximum adsorption capacity calculated from the Langmuir isotherm both for phenol and for PCP, may be related to the predominately mesoporous structure of the adsorbent, with relatively small surface area (73 m² g⁻¹) and small total volume of pores (0.089 cm³ g⁻¹).

The interactions at the solid–liquid interface play a significant role, and according to the literature reports (Hamdaoui & Naffrechoux 2007; Busca et al. 2008; Jung et al. 2002) the possible interactions between the carbon surface and phenols involve electron donor–acceptor interactions between the aromatic phenolic ring and the basic surface oxygens such as carbonyl groups, dispersion forces between $\pi$-electrons in phenols and $\pi$-electrons in activated carbon or electrostatic attraction and repulsion when ions are present.

According to the FTIR and carbon content analyses, the MNM is covered with some organic residues involving carbon–oxygen groups. Consequently, the adsorption mechanism of phenol and PCP might be controlled by the dispersion force between the $\pi$-electrons on the carbon

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**Table 2** Kinetic parameters for the pseudo-first-order model at different initial concentrations of PCP and the correlation coefficient ($R^2$) for the pseudo-first-order and pseudo-second-order

<table>
<thead>
<tr>
<th>Pseudo-first-order Adsorbate</th>
<th>Initial concentration $C_0$ (mg L⁻¹)</th>
<th>$k_1 \cdot 10^3$ (min⁻¹)</th>
<th>$R^2$</th>
<th>$q_e$ (mg g⁻¹) Experimental</th>
<th>$q_e$ (mg g⁻¹) Calculated</th>
<th>Pseudo-second-order $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>25</td>
<td>1.89</td>
<td>0.9785</td>
<td>2.536</td>
<td>2.938</td>
<td>0.2517</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.00</td>
<td>0.9734</td>
<td>9.371</td>
<td>10.171</td>
<td>0.8905</td>
</tr>
<tr>
<td>$p$-Chlorophenol</td>
<td>25</td>
<td>1.87</td>
<td>0.9832</td>
<td>4.449</td>
<td>5.112</td>
<td>0.3005</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.33</td>
<td>0.9407</td>
<td>21.013</td>
<td>24.773</td>
<td>0.9007</td>
</tr>
</tbody>
</table>

**Figure 5** Isotherm plots for phenol and PCP adsorption onto MNM adsorbent.
surface and those in phenols and also by the hydrogen bonding between the hydrogen atoms of the hydroxyl groups of phenol and PCP and the oxygen atoms of the carbon–oxygen functional groups present on the adsorbent surface.

It can be also observed the better adsorption capacity for PCP (46.1 mg g\(^{-1}\)) than those for phenol (13.5 mg g\(^{-1}\)), in agreement with the results reported in the literature. Hamdaoui & Naffrechoux (2007), studying the adsorption of phenol and chlorophenols onto granular activated carbon, reported also a better adsorption capacity for PCP (310 mg g\(^{-1}\)) as compared with phenol (210 mg g\(^{-1}\)). This behavior can be explained by the lower solubility and pK\(_a\) value of PCP compared with phenol and is in full agreement with the proposed mechanism, given that the chloro-group in PCP, which is a strong electron-withdrawing group, reduces the overall electron density of the aromatic ring, enhancing attraction with the surface of carbon, which leads to an increase in adsorption capacity.

Compared with other values reported in the literature, the adsorption capacity of MNM is higher than those reported by Subramanyam & Das (2009) for phenol and much higher than those reported by Li et al. (2012) for PCP.

Considering the facile and inexpensive MNM synthesis method, the simplicity and efficiency of magnetic separation, the adsorbent used in this study could be considered as a versatile and promising candidate for the removal of phenol and PCP from wastewater.

**CONCLUSIONS**

MNM was prepared by a new technique of combustion method which allows us to directly obtain magnetic nanopowder covered with some organic residues resulting from the fuel combustion, which increases its adsorption capacity.

The MNM demonstrated better adsorption capacity for p-chlorophenol than for phenol, explained by the lower solubility and pK\(_a\) value of PCP compared with phenol.

The kinetic studies indicated that the adsorption of phenol and PCP onto MNM adsorbent followed the pseudo-first-order model and the equilibrium adsorption data were correlated by the Langmuir isotherm.

The MNM exhibited high adsorption efficiency for both phenol and PCP and can be easily separated by using a magnetic field, suggesting its potential application in removal of phenolic pollutants from wastewater.

**ACKNOWLEDGEMENT**

This work was partially supported by the strategic grant POSDRU 107/1.5/S/77265 (2010) of the Ministry of Labor, Family and Social Protection, Romania, co-financed by the European Social Fund – Investing in people.

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First received 5 July 2013; accepted in revised form 21 October 2013. Available online 5 November 2013