Surfactant modified kaolinite (MK-BZK) as an adsorbent for the removal of diazinon from aqueous solutions

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A B S T R A C T

This paper presents the adsorption potential of natural kaolinite (NK) and kaolinite modified with benzalkonium chloride (MK-BZK) for the removal of the diazinon pesticide from contaminated water. Batch experiments were carried out with various experimental conditions such as pH (3, 7, and 11), adsorbent dosage (1, 5, and 10 g/L), initial diazinon concentration (5–100 g/L) and contact time (0–40 min). Based on the experimental data, the removal efficiency of MK-BZK was slightly higher (97%) than that of NK (93%) operating at pH 3 and optimum contact times of 10 and 15 min, respectively. The adsorption rate followed a pseudo-second-order kinetics model and the equilibrium adsorption fitted well the Freundlich adsorption isotherm model. The maximum adsorption capacity of diazinon on NK and MK-BZK was 0.86 and 2.25 mg/g, respectively. Overall, MK-BZK has potential as a local and cost-effective adsorbent to remove diazinon from aqueous solutions.

Keywords: Adsorption; Aqueous solution; Diazinon; Kaolinite

1. Introduction

Organophosphate compounds (DDVP, diazinon, chlorpyrifos, parathion, etc.) are common pesticides that have been extensively used in the agriculture industry worldwide [1]. Diazinon is one of the most important and hazardous pesticides which has been identified on the Environmental Protection Agency National Priorities List [2]. Diazinon is released to the environment by agricultural runoff during pesticide applications [3]. The toxicity of diazinon to humans was documented [4]. Thus, epidemiologic studies reported that diazinon was linked to cancer risk and had neurotoxicity effects in humans [5]. Diazinon is mostly non-biodegradable in the environment and its toxic effects on surface and groundwater quality cause World Health Organization concern which has classified it as “moderately hazardous” class II [6]. Although the diazinon application was banned in the USA, it is still used in many developing countries [7]. Several methods have been developed for diazinon removal from aqueous solutions such as adsorption, advanced oxidation processes, coagulation, membrane filtration, and biodegradation [8–11]. However among the...
different developed methods, adsorption has received more attention due to its flexibility, simplicity design, ease of operation, and low-cost [12]. Cost is an important parameter when comparing adsorbent materials. Adsorption is a chemical process that takes place on the surface of an adsorbent and whose performance depends on its surface area, porosity, and a number of surface active sites [13]. Clay minerals have been widely used in several technological processes [14,15]. In recent years, several types of researches have improved the adsorption capacity of clay materials by modification [16–18]. Kaolinite is a type of clay mineral that has hydrophilic properties in nature, high cation exchange capacity (CEC) charge on the layer, and interlayer. Among the above-mentioned properties, CEC has an important role in the modification [19–21]. However, the specific surface area and the interlayer space of kaolinite can also be improved by modification. Moreover, modified kaolinite is able to adsorb both ionic and non-ionic substances [22]. Change in the surface of clay helps to improve the interaction between the surface of the clay and the molecules of water. Surfactants are long-chain molecules with hydrophilic and hydrophobic properties and among them; benzalkonium chloride (BZK) is a cationic surfactant. Some documents reported that the presence of surfactants on montmorillonite and kaolinite affected their adsorption behavior [23,24]. In recent years, modified clay was used for the removal of different pollutants such as organic chemicals [25], synthetic dyes [26], Eriochrome Black T [27] and heavy metals [28] but there is no paper about the modified kaolinite efficiency on dyes [26], Eriochrome Black T [27] and heavy metals [28] but.

2. Materials and methods

2.1. Chemicals

Diazinon (C₂₁H₂₇N₅O₅PS, chromatography grade) and BZK were purchased from Sigma-Aldrich (St Louis, MO). Reference Kaolinite (Al₂Si₂O₅(OH)₄, KGa-1) was supplied by ZEOLYST International, Inc., (China) (Table 1). All analytical standards (>99.99% purity), the high-performance liquid chromatography (HPLC) analytical grade chemicals, including acetonitrile, methanol, water, dichloromethane, anhydrous sodium sulfate, and sodium chloride and the syringe filters (PTFE) 0.45 μm were purchased from Merck (Germany). Stock solutions (1,000 mg/L) were prepared by dissolving 0.05 g of solid diazinon.

2.2. Instruments

HPLC was used to analyze diazinon. The instrument was equipped with a variable-length UV/VISIBLE detector (SPD 10 AVP) and columns, SUPELCO discovery reversed-phase C₁₈ (25 cm × 4.6 mm i.d., particle size 5 μm). HPLC working conditions were binary gradient, eluent solvent (acetonitrile: water 70:25), and a flow rate of 0.8 mL/min. The surface morphology of the adsorbent was examined by scanning electron microscopy. Moreover, Fourier-transform infrared spectroscopy (FT-IR) was carried out to characterize the modified kaolinite. All experiments were run according to ASTM [29]. The pH of the solutions was measured by dual-channel pH-ion meter pH 5500.

2.3. Adsorbent preparations

The adsorbent of natural kaolinite (NK) was washed with doubly distilled water and dried at room temperature for 24 h. A conical flask containing the BZK-surfactant (50 mL) with kaolinite (10 g) was stirred using a magnetic stirrer for 24 h at 150 rpm for preparing 1 CEC suspension. Afterward, the solution was filtered and the kaolinite modified with benzalkonium chloride (MK-BZK) was subsequently washed for several times with doubly distilled water to remove the surplus surfactant and then, it was dried in an oven at 80°C–85°C for 60 min and placed into US Standard 100 meshes in accordance with the ASTM [29].

2.4. Batch experiments

Adsorption studies were performed on a closed batch system. Batch experiments were carried out at different values of pH (3, 7, and 11), initial diazinon concentration (5, 10, and 50 mg/L) and MK-BZK adsorbent dosage (1, 5, and 10 g/L) for an optimum time of 15 min at a constant temperature (20°C ± 3°C) in a platform shaker (CFL, 3005, Germany). Sodium hydroxide (1.0 M) was used for adjusting the pH of the solutions. The optimum adsorption conditions were obtained by varying each variable while keeping the others constant at each stage of the experiment. In each stage, samples were taken and filtered with 0.45 μm membrane filters. The filtrate was analyzed by HPLC. The adsorption capacity of diazinon by NK and MK-BZK (q,e, g/L) was calculated by the following formula:

\[
q_e = \frac{(C_i - C_e)V}{m}
\]

where \(C_i\) is the initial diazinon concentration (g/L); \(C_e\) is the residual diazinon concentration (g/L); \(V\) is the volume of the solution (L); \(m\) is the mass of the adsorbent (g). Finally, the adsorption isotherms (Langmuir and Freundlich isotherm models) were determined in the obtained optimum experimental conditions.

2.5. Statistical analysis

Experiments were conducted based on the mean ± standard deviation. Adsorption efficiency of diazinon by NK and MK-BZK was analyzed by using SPSS 17.00 windows version and the obtained data were analyzed using the analysis of variance test. Design generation and statistical analysis were performed using the R software by the RSM package.

3. Results and discussion

3.1. Characterization of the adsorbent

In Fig. 1 the morphology of kaolinite before and after modification by BZK is reported. Kaolinite is an expandable clay able to hold inorganic and organic cations into the interlayers. The FT-IR spectra of NK and MK-BZK are shown in Figs. 2a and b. The bands from 3,622 to 3,690 cm⁻¹ can be attributed to OH and the bands at 677–790 cm⁻¹ can be attributed to typical Al–O–Si bending vibrations. In addition,
the absorption bands of Al–OH within the crystal structure appear at 908 cm\(^{-1}\). The vibration band at 995–1,114 cm\(^{-1}\) corresponds to the Si–O. After kaolinite had been treated with BZK, the spectrum showed three new peaks at 1,440; 2,830; and 2,920 cm\(^{-1}\) corresponding to the surfactant vibration related to the symmetric and the asymmetric stretching vibrations of the C–H–C. The chemical composition of NK and MK-BZK samples as determined by the XRF technique (wt. %) are listed in Table 1. The results show that the surface of kaolinite did not change significantly after modification.

3.2. Effect of contact time on diazinon removal

In order to find out the optimum contact time, experiments were carried out for 40 min of contact time. According to Fig. 3 the adsorption of diazinon increased with increasing the contact time. The adsorption rate was different for the two adsorbents used and, thus, the equilibrium was reached within 15 and 10 min for MK-BZK and NK, respectively. Therefore, the adsorption rate of NK was higher than that of MK-BZK. The obtained data indicated that both MK-BZK and NK are cost-effective adsorbents in comparison to previously reported research [30–33]. In addition, the maximum adsorption efficiency for NK and MK-BZK was 29% and 45%, respectively. The rapid adsorption was probably due to the large surface availability of the adsorbent. In addition, the results showed that increasing the contact time led to a higher removal efficiency, the maximum level is reached within 40 min. At the initial stage, a large number of binding sites are available on the adsorbent surface for the pollutant adsorption which is being occupied with time. On the other hand, the adsorption rate of diazinon was higher at the beginning due to a larger surface area of the adsorbent was available for diazinon adsorption. As the surface adsorption sites become occupied, the adsorption rate was controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles [20,34].

3.3. Effect of pH on diazinon removal

In aqueous solutions, pH is an important parameter that affects the adsorption process and directly linked to the surface charge of the adsorbent. To determine the optimal pH value of diazinon adsorption on NK and MK-BZK batch experiments were conducted at different pH values ranging from 3.0 to 11 (Fig. 4). According to the obtained data, the adsorption of diazinon decreased when the pH level increased. Previous literature reported that diazinon hydrolysis was accelerated in acidic solution [35]. Therefore, a high degree of diazinon removal was observed for NK (75%) and MK-BZK (92%). However, at low pH levels (i.e. pH < 6.6) the surface of NK and MK-BZK is positively charged and the anionic species of diazinon are electrostatically attracted [36] while at high pH values (i.e. pH > 6.6) the surface of NK and MK-BZK becomes negatively charged and the diazinon anionic molecules are electrostatically repulsed and, thereby the removal percentage decreases [37].

3.4. Effect of adsorbent dosage on diazinon removal

The influence of the initial adsorbent dosage (MK-BZK and NK) (0.1–10 g/L) at optimum pH (i.e. 3) and contact time (15 and 10 min) was investigated. As shown in Fig. 5, adsorption was increased by increasing the adsorbent dosage from 0.1 to 1 g/L. Thus, diazinon removal percentage varied from 49% to 93% and from 64% to 97% for KN and MK-BZK, respectively. However, MK-BZK (97%) showed higher adsorption efficiency in comparison with NK (93%). According to the obtained results, the optimum dosage was determined to be 0.5 and 1 g for MK-BZK and NK, respectively. Thus, a lower amount of MK-BZK than that of NK was required for maximum adsorption efficiency (93%). Thus, MK-BZK is an efficient and low-cost alternative adsorbent for removing diazinon from contaminated water.

3.5. Effect of initial diazinon concentration

Experiments were carried out to study the effect of varying the initial diazinon concentration ranging from 5 to 100 mg/L on diazinon removal by NK and MK-BZK,
operating at the optimum pH, contact time and adsorbent dosage obtained in the previous experiments. The results indicated that increasing the initial diazinon concentration decreased the adsorption efficiency. Thus, the adsorption efficiency of NK and MK-BZK gradually decreased from 93% to 75% and from 96% to 76.8%, respectively (Fig. 6). The reduction in adsorption efficiency as a function of initial diazinon concentration can be explained by the increase of the mass ratio of adsorbate to the adsorbent. Also, the number of available adsorption sites on the surface of the
adsorbents decreased as the number of diazinon molecules increased, diminishing the removal efficiency [39].

3.6. Adsorption isotherms

The Langmuir and Freundlich isotherms are the most common isotherm models employed to describe the experimental adsorption data [40,41]. Both models were used to describe the relationship between the amount of diazinon adsorbed and its equilibrium concentration in solutions at different adsorbent dosages and pH values (Table 2). For this, linearized equations were used to determine the model parameters and the isotherms. The calculated linear correlation coefficients ($R^2$) (Table 3) and data revealed that the Freundlich isotherm ($R^2 > 0.994$) fitted well the experimental data. The reason for that may be due to the multilayer adsorption nature of the surface sites involved in the diazinon uptake. The Freundlich adsorption isotherms obtained for diazinon adsorption on NK and MK-BZK are presented in Figs. 7a and b. In the Freundlich isotherm model, $K_f$ and $n_f$ are important factors used to distinguish the adsorption performance and indicate the adsorption capacity. According to the Freundlich isotherm, the maximum adsorption capacity ($K_f$) for MK-BZK was higher (2.26 mg/L) than that obtained for NK (0.86 mg/L). Therefore, $K_f$ indicated that MK-BZK

<table>
<thead>
<tr>
<th>Constituent</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>39.3</td>
</tr>
<tr>
<td>MgO</td>
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</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0.4</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.2</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.4</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of contact time on adsorption of diazinon on NK and MK-BZK (initial adsorbent: 0.1 g/100 mL; initial diazinon concentration: 10 mg/L; solution pH: 7).

Fig. 4. Influence of solution pH on diazinon adsorption onto adsorbent (diazinon concentration: 5 mg/L; solution pH: 3–11; MK-BZK concentration: 1 g/L; NK concentration: 1 g/L; contact time: 10 and 15 min, respectively).

Fig. 5. Effect of adsorbent dosage on the removal efficiency of diazinon (initial diazinon concentration: 1 g/100 mL; solution pH: 3; contact time: 10 and 15 min).

Fig. 6. Effect of initial diazinon concentration on the diazinon removal efficiency (NK adsorbent dosage: 1 g/100 mL mg; MK-BZK adsorbent dosage: 0.5 g/100 mL solution pH: 3; contact time: 10 and 15 min).
had a higher affinity for diazinon adsorption than that of NK. Another important parameter is $1/n$ which was found to be between 0 and 1 for both adsorbents (i.e. 0.57 for NK and 0.63 for MK-BZK) indicating favorable adsorption. (Table 3). The value of the adsorption capacity of NK and MK-BZK compared to the adsorption capacity of various low-cost adsorbents for diazinon removal are indicated in Table 4. Thus, NK and MK-BZK are suitable, available, and cost-effective alternative adsorbent materials for removing diazinon from aqueous solutions.

### 3.7. Adsorption kinetics

To evaluate the kinetics of the adsorption process, the linearized form of the pseudo-first-order (PFO) and pseudo-second-order (PSO) models were tested (Table 2). The PFO equation is normally used for describing adsorption in solid–liquid systems based on the adsorption capacity of solids [42], while PSO models are applied for analyzing chemisorption kinetics from liquid solutions [43,44]. However, a close inspection of the linear adsorption kinetics, showed the highest correlation coefficients for the PSO model ($R^2 > 0.99$). Thus, the PSO model was used for interpreting the adsorption kinetics of NK and MK-BZK (Fig. 6). It was suggested that the chemical adsorption rate may be limited by valence forces between the adsorbent and the adsorbate [45]. The values of the parameters $q_e$ and $k_2$ obtained from the PSO equation are summarized in Table 5. The experimental data of the PSO model implied a higher adsorption capacity of MK-BZK ($q_e$) than that of...
NK (Table 5). This revealed that mass transfer was the main controlling step of the diazinon adsorption process. The lower PSO kinetics constant ($k_2$) of MK-BZK suggested a decrease of pore diffusion limitation, which could be related to increased surface availability for the diazinon molecules in the solution and, thus, the competition for the adsorption sites was reduced.

4. Conclusions

The adsorption of diazinon, an organophosphate insecticide, on NK and MK-BZK was tested under various operational conditions of pH, contact time, initial diazinon concentration, and adsorbent dosage. The removal efficiency of MK-BZK was more effective (97%) than that of NK (93%) when operating at an optimum contact time of 10 and 15 min, respectively, and at an optimum pH of 3. The obtained data indicated a higher adsorption rate and a higher adsorption capacity of MK-BZK (2.26 mg/g) than those of NK (0.86 mg/g). Adsorption kinetics followed a PSO model ($R^2 > 0.99$) and indicated that the rate-limiting step may be

![Fig. 8. Pseudo-second-order plot for the adsorption of diazinon on natural kaolinite (NK) and modified kaolinite (MK-BZK).](image)

Table 2

<table>
<thead>
<tr>
<th>Models</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order kinetics</td>
<td>$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$</td>
</tr>
<tr>
<td>Pseudo-second-order kinetics</td>
<td>$\frac{t}{q_t} = \frac{1}{k_2 q_{cal}^2} + \frac{t}{q_{in}}$</td>
</tr>
<tr>
<td>Langmuir equations</td>
<td>$q_t = q_{cal} \left( \frac{k_1 C_e}{1 + k_1 C_e} \right)$</td>
</tr>
<tr>
<td>Freundlich equations</td>
<td>$q_t = k_1 C_e^{1/n}$</td>
</tr>
</tbody>
</table>

Table 3

Parameters of Langmuir, Freundlich isotherms and adsorption kinetics (pseudo-first-order and pseudo-second-order models) for adsorption of diazinon on natural kaolinite (NK) and modified kaolinite (MK-BZK)

<table>
<thead>
<tr>
<th>Adsorption model</th>
<th>Parameters</th>
<th>Kaolinite</th>
<th>MK-BZK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$ (L/mg)</td>
<td>0.0816</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>$q_{in}$ (mg/g)</td>
<td>10.10</td>
<td>19.23</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.817</td>
<td>0.826</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_L$ (L/mg)</td>
<td>0.86</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.63</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.993</td>
<td>0.994</td>
</tr>
</tbody>
</table>

Table 4

Comparison of various low-cost adsorbents for diazinon removal

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Water pH</th>
<th>Concentration range (mg/L)</th>
<th>Model used to calculate adsorption capacity</th>
<th>Capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan/carbon nanotube</td>
<td>5.5</td>
<td>5</td>
<td>Sips</td>
<td>222.86</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Neutral pH</td>
<td>20</td>
<td>Langmuir isotherm</td>
<td>250</td>
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<tr>
<td>Chlorine dioxide</td>
<td>4.6</td>
<td>2–20</td>
<td>First-order kinetics model</td>
<td>0.0047–0.0002</td>
<td></td>
</tr>
<tr>
<td>Thermosensitive nanosphere polymer</td>
<td>7</td>
<td>50</td>
<td>Intraparticle diffusion model</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Granular-activated carbon</td>
<td>6</td>
<td>100 and 150</td>
<td>–</td>
<td>–</td>
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</table>

Table 5

Adsorption kinetics model rate constants for diazinon adsorption on natural kaolinite (NK) and modified kaolinite (MK-BZK)

<table>
<thead>
<tr>
<th>Kinetics model</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (1/h)</td>
<td>$q_{cal}$ (mg/g)</td>
</tr>
<tr>
<td>NK</td>
<td>0.275</td>
<td>2.9</td>
</tr>
<tr>
<td>MK-BZK</td>
<td>0.307</td>
<td>4.5</td>
</tr>
</tbody>
</table>
the chemical adsorption rather than the diffusion adsorption. Both Freundlich and Langmuir isotherms were used for analyzing the experimental data and the results fitted well the Freundlich isotherm. The obtained results show the high potential of MK-BZK as a local and cost-effective adsorbent for the removal of diazinon from aqueous solutions.

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