Comparative Study for Removal of Imidacloprid and Oxamyl Pesticides by Cement Kiln Dust: Kinetics and Equilibrium Studies

Ahmed A. El-Refaey¹, Hamza S. Abou-Elnasar²

ABSTRACT

This study investigated the removal of imidacloprid (IMI) and oxamyl (OX) pesticides by cement kiln dust (CKD) as industrial by-products. CKD was identified by elements composition, Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM). Effects of initial concentration (100–2000 mg/L), and contact time (10–360 min) were investigated. The kinetic results of IMI and OX pesticides were fitted to pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations. The pseudo-second-order kinetic model fitted well for IMI removal, while pseudo-first-order kinetic model fitted to OX removal results. Isotherm results were examined by different isotherm models (Freundlich, Langmuir, and Temkin equations). The results fitted well with the Langmuir isotherm model (R²=0.988 and 0.999) with maximum adsorption capacity of 142.85 and 100.00 mg/g for IMI and OX pesticide removal by CKD, respectively. The obtained results indicated the potential of using CKD as an efficient and, low-cost adsorbent for the removal of IMI and OX pesticides from aqueous solutions.

Keywords: Cement kiln dust; Imidacloprid; Oxamyl; Adsorption isotherm; kinetics.

INTRODUCTION

Besides pests, pesticides are toxic compounds to other organisms and should be consumed safely and rightly disposed of in the environment. Over 1000 various pesticides are applied all over the world (WHO, 2022). Due to their persistence, they have a reciprocal influence on the ecosystem and accumulate in the food chain (Thakur and Pathania, 2020).

Imidacloprid (IMI) is neonicotinoids group pesticide and is applied as an insecticide for controlling agricultural pests and other applications. Because of its capability to accumulate in the ecosystem, IMI could become a threat to the ecosystem, aquatic organisms, and human health (Singh et al., 2021; Wang et al., 2022). However, exposure to imidacloprid may influence the cardiovascular, hematological, liver, and thyroid (Rodriguez et al., 2015).

Oxamyl (OX) is a systemic pesticide that belongs to the carbamate group and is applied in many agricultural activities as an insecticide and nematicide with vegetables, bananas, pineapple, peanut, cotton, and other crops (Tomlin, 2002; Minnis et al., 2004). Hence, the application is directly onto plants or to the surface of the soil. The possibility of its pollution hazard increased due to its low sorption coefficient with soil, and high water solubility. Besides its effect on the ecosystem and aquatic organisms, exposure to oxamyl could cause abdominal pain, nausea, unclear vision, and osteoporosis (Taha et al., 2014; Duan et al., 2016).

Therefore, seeking an efficient and low-cost method for its remediation is a major concern for environmental issues. Among the applied method for remediation of pesticides, adsorption is still the most applied methods due to its effectiveness, simplicity, and low-cost method (Maneerung et al., 2016; Mohammad and El-Sayed, 2021). Many recent studies focused on using activated carbon derived from agricultural wastes, and clay minerals are pesticide removal from polluted water (Liu et al., 2015; Tran et al., 2015; Mojiri et al., 2020).

Cement kiln dust (CKD) is a by-product of the cement manufacturing process. Because of its properties as adsorbent, CKD has been used effectively for removing heavy metals, and organic pollutants such as dyes (El Refaey, 2016 & 2017; Magdy & Altaheer, 2018; El Refaey & Mohamed, 2019; El Refaey, 2021). Also, CKD has been consumed for the disposal of obsolete pesticides in numerous developing countries (Karstensen et al., 2006; Li et al., 2014).

The current study aims to investigate the ability to remove imidacloprid (IMI) and oxamyl pesticides by cement kiln dust as an industrial by-product from aqueous solutions. Cement kiln dust was characterized by elements composition and surface area. Fourier transform infrared (FTIR) and surface morphology of CKD were inspected before and after the adsorption experiment. Isotherm and Kinetic studies were conducted and the equilibrium results were fitted by Langmuir and, Freundlich isotherm models, while kinetic results by pseudo-first-order, pseudo-second-order, and Elovich models.

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**MATERIALS AND METHODS**

**Adsorbates and adsorbent characterization**

The used pesticides in these experiments are Imidacloprid and oxamyl. Characterization of the two pesticides and their chemical structure are recorded in Table (1). Standard concentration solutions stocks of each pesticide were prepared (100, 200, 500, 1000, 1500, and 2000 mg/L using distilled water.

CKD samples were collected from El-Amerya cement plants, Alexandria, Egypt. Total carbon, nitrogen, hydrogen, and sulfur of CKD contents were conducted by a CHNS analyzer (Elementar, Vario EL, Germany). For metals concentration (Cd, Pb, Ni, Cu, Fe, Mn, and Cr) of CKD was determined by the fusion method (Pansu and Gautheyrou, 2003). The metals concentrations were measured by Atomic Absorption Spectrophotometer Varian Spectra (model 220).

FTIR spectra was recorded before and after adsorption experiments for the two pesticides by KBr pellet method at 400 – 4,000 cm⁻¹ range using a Fourier transforms infrared spectrometer (Infra-Red Bruker Tensor 37, German).

CKD surface morphology was examined using a Jeol IT-200 scanning electron microscope (SEM). CKD samples were coated with gold in a sputter-coating unit (JFC-1100E) before the examination. SEM images were acquire d at various magnification scales before and after the sorption experiments.

**Adsorption experiments**

Isotherm experiments were conducted by batch technique to study the removal of the two pesticides (OX and IMI) on CKD from aqueous solutions. A 0.40 g of CKD was added to 40 ml of initial pesticide concentrations (100, 200, 500, 1000, 1500, and 2000 mg/L in 100 mL plastic jars, and agitation was conducted at 120 rpm for 6 hours to reach equilibrium at room temperature (25°C). After filtration (with 0.45 μm), the supernatants were analyzed for the determination of the residual pesticides concentration at the end of the equilibrium period. All of the experiments were replicated. For Kinetic studies, 2.00g of CKD was added to 250 mL glass Erlenmeyer flasks containing 200 mL of 200 mg/L concentrations of pesticides solution (OX or IMI). Withdrawn samples (10-20 ml) at various intervals of time were taken, filtered with 0.45 μm, and analyzed for residual pesticide concentration.

The residual concentrations of imidacloprid and oxamyl were measured in the supernatant by HPLC. Pesticide concentrations in the solutions were measured by an Agilent HPLC 1260 infinity series (Agilent Technologies) with a quaternary pump, a variable wavelength diode array detector (DAD), and an auto sampler. Samples (5µl) were injected into Agilent Zorbax SBC18 column.

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**Table 1. Some characteristics of imidacloprid and Oxamyl.**

<table>
<thead>
<tr>
<th></th>
<th>Imidacloprid</th>
<th>Oxamyl</th>
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<tbody>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Imidacloprid Chemical Structure" /></td>
<td><img src="image" alt="Oxamyl Chemical Structure" /></td>
</tr>
<tr>
<td>IUPAC name</td>
<td>N-[1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl]nitramide</td>
<td>Methyl 2-(dimethylamino)-N-[(methylcarbamoyl)oxy]-2-oxoethanimidothioate</td>
</tr>
<tr>
<td>Pesticide group</td>
<td>neonicotinoids</td>
<td>carbamate</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₉H₁₀ClN₅O₂</td>
<td>C₇H₁₃N₃O₃S</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>255.66</td>
<td>219.26</td>
</tr>
<tr>
<td>Solubity in water (g/L)</td>
<td>0.61</td>
<td>280</td>
</tr>
</tbody>
</table>
The mobile phase was water: methanol (50:50, v/v) with a 1 ml/min flow rate. Agilent Open LAB CDS Chem Station software (C.01.07 version) was used in collecting and processing data. The standard calibration curve has proceeded as described by Yang et al. (2014) and Devan et al. (2015).

The adsorption amount (qt), and the removal percentage of imidacloprid or oxamyl (R %) were determined by the following equations:

\[ q_t = (c_0 - c_t) \frac{V}{m} \quad (1) \]
\[ R\% = \left( \frac{c_0 - c_t}{c_0} \right) \times 100 \quad (2) \]

Where

c0, c: Pesticides initial and final concentration, respectively; V: Volume of pesticides solution; m: CKD mass.

**RESULTS AND DISCUSSION**

**CKD Characterization**

Some chemical characteristics of CKD were listed in Table (1). The CKD total CaCO\textsubscript{3} content was 47.60 % (Table. 2). Calcite is the main mineral in CKD structure and CaO equals 43.42% as reported by El Refaey (2021). The chemical behavior of CKD seems to be affected by calcium content with some other alkali oxides (El-Refaey, 2016, 2017, and 2019). The carbon content was 6.35 % more than other elements content (such as S, Cd, Cu, Fe, Mn, Pb, and Zn) as expected of the presence of high calcium carbonates.

**FTIR analysis**

FTIR spectrum is a helping tool in identifying the present functional groups that control the adsorption behavior and mechanism (Zheng and Ewarand, 2004). The FTIR spectra of CKD before and after adsorption experiments are shown in Fig. (1). The peaks at 3394.68, and 1796.55 cm\textsuperscript{-1} are related to O–H (hydroxyl) (Saraya and Aboul-Fetouh, 2012; El-Refaey, 2016). The peaks at 2981.38, and 2873.24 cm\textsuperscript{-1} are attributed to C–H stretching while the peak at 2515 related to CC stretching vibration in the alkyne group (Meziti & Boukerroui, 2012; El Refaey & Mohamed, 2019). The peaks at 1425.07, and 874.27 cm\textsuperscript{-1} indicated the carbonate existence group (Saleem & Velayi, 2012; El-Refaey, 2016, 2017, and 2021). The peaks at 1136.30, 1013.35, 712.04, and 451.511 cm\textsuperscript{-1} indicated the presence of silicate stretching vibration (Saraya & Aboul-Fetouh, 2012, El Refaey 2021). The peak at 613.30 cm\textsuperscript{-1} is attributed to K–O vibration (Saleem et al., 2012; El-Refaey & Mohammad, 2019; El Refaey, 2021). CKD functional group peaks shifts and appearance bands after adsorption of IMI and OX confirm the adsorption of pesticides onto CKD and the role of this functional group in the process (Fig.1).

**SEM analysis**

The SEM examination gives knowledge about morphological aspects of the surfaces of CKD particles before and after pesticide removal reactions (Fig. 2). The finest particle sizes of CKD were remarked and the particles morphological and size changes after adsorption experiments for two pesticides. CKD particles after adsorption reactions were wrapped by complex formations. These formations were a little more condensed in oxamyl pesticide reactions than in imidacloprid reactions (Fig. 2). This may indicate the CKD removal capacity for the two pesticides and the different mechanisms involved in removal reactions.

**Removal of IMI and OX pesticide by CKD**

The removal of IMI and OX pesticide with different initial concentrations, and contact time were investigated (Fig. 3). Batch experiments of different initial concentrations showed the affinity of removing IMI and OX pesticide by CKD especially with the examined low concentrations (100 mg/L), 91.0 and 82.0% for IMI and OX respectively (Fig. 3A). As expected, the removal percents decreased with increasing the initial concentrations to 2000mg/L to reach 7.05 and 9.85% for IMI and OX, respectively with privileges for OX than IMI in all examine concentration (Fig. 3A). The removal of IMI and OX could be devoted to adsorbent properties (CKD) such as high surface area, calcium oxide contents, and other oxide content which enhanced sorption and/or precipitation (Mackie et al., 2012; El Zayat et al., 2014; El Refaey, 2016; 2017, and 2021). Also, the contained calcium could have a role in non-covalent interactions with groups in pesticide molecule composition such as nitro and chloro (NO\textsubscript{2} & Cl), especially imidacloroprid (Singh et al., 2021).

The adsorption of IMI and OX pesticides removal by CKD were conducted for different contact times with an initial concentration of 200 mg/L at room temperature (25°C) and normal pH (Fig. 3A). Removal of IMI pesticide by CKD increased to reach 37.5 % after two hours and showed stability increase to 45.0 % after 6 h (Fig. 3B). On the other hands, removal of OX pesticide by CKD showed small increase tend in first 2h (18.5) and increased sharply to reach 72.5% after 6 h of the removal reaction (Fig. 3B).
Table 2. Some chemical characteristics of CKD

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Cd</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Pb</th>
<th>Zn</th>
<th>Total CaCO₃</th>
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<tr>
<td>pH</td>
<td>10.20</td>
<td>6.350</td>
<td>0.190</td>
<td>Nil</td>
<td>0.840</td>
<td>0.0001</td>
<td>0.004</td>
<td>0.113</td>
<td>0.018</td>
<td>0.010</td>
<td>0.005</td>
</tr>
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</table>

Fig.1. FTIR spectra of cement kiln dust (CKD) before and after of imidacloprid (IMI) and oxamyl (OX) pesticides removal reactions.
Fig. 2. SEM images of cement kiln dust (CKD) before and after imidacloprid (IMI) and oxamyl (OX) pesticides removal reactions.
Fig.3. Removal percent of imidacloprid (IMI) and oxamyl (OX) pesticides with different initial concentrations (mg/L) (A), and time (min) (B) by cement kiln dust (CKD).
Kinetic studies

For describe and understand the removal of IMI and OX pesticide by CKD, different kinetics models, pseudo-first-order, pseudo-second-order, and intra-particle diffusion, were examined. The linear form equations as reported by El Refaey (2021):

Pseudo-first-order:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303$$  \(3\)

Pseudo-second order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \(4\)

Intra-particle diffusion:  

$$q_t = k_i t^{1/2} + C$$  \(5\)

Where:

$q_e$ and $q_t$ are the adsorbed pesticide by CKD (mg g$^{-1}$) at equilibrium and time (t), respectively; $k_1$ and $k_2$ are rate constants of pseudo-first (min$^{-1}$), and second-order models (g$^{-1}$ min$^{-1}$), respectively; $k_i$ (gmg$^{-1}$ min$^{1/2}$) represents intra-particle diffusion rate constant; C is constant (mg g$^{-1}$) related to the boundary layer thickness.

Kinetic parameters of the imidacloprid (IMI) and oxamyl (OX) pesticide removal by cement kiln dust (CKD) are represented in Table (3). The obtained results for IMI adsorbed by CKD were correlated well with the second-order equation, while OX adsorbed by CKD was correlated well with the first-order equation (Fig. 4). The regression coefficients($R^2$) for the two pesticides regarding pseudo-second order model for IMI pesticide was 0.956 and 0.932 regarding pseudo-first order model for OX pesticide (Table 3). This agreement of the results with pseudo-first and second-order equation indicated the chemical nature of the removal process with different rate of reaction (Fig.4).

Isotherm studies

The isotherm results help in discovering the relation between adsorbates and adsorbent and their adsorption capacity (Salleh et al., 2011). The results of the isotherm experiments were examined by Freundlich, Langmuir, and Temkin isotherm models as follows (El Refaey, 2021):

Freundlich: $q_e = K_F C_e^{1/n}$  \(6\)

Langmuir: $q_e = q_{max}(K_L C_e / 1 + K_L C_e)$  \(7\)

Temkin: $\theta = RT/\Delta Q \ln K_0 C_e$  \(8\)

Where:

$q_e$: adsorbed pesticide (mg g$^{-1}$), $C_e$: pesticide equilibrium concentration (mg L$^{-1}$), $K_F$: constant related to adsorption capacity (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$), n: a constant, $q_{max}$: maximum adsorption capacity (mg g$^{-1}$), $K_L$: constant correlated to adsorption free energy (L mg$^{-1}$), $\theta$: fractional coverage, R: universal gas coefficient (kJ mol$^{-1}$ K$^{-1}$), T: temperature (K), $\Delta Q$: $(\Delta H)$ adsorption energy difference (kJ mol$^{-1}$), and $K_0$: coefficient of Temkin (L mg$^{-1}$). The isotherm parameters of the imidacloprid (IMI) and oxamyl (OX) pesticides removal by cement kiln dust (CKD) are represented in Table (4).

The data were fitted very well to Langmuir according to regression coefficients values ($R^2$) for both adsorbates (Table 4). The regression coefficients ($R^2$) for the removal of imidacloprid (IMI) and oxamyl (OX) pesticide by CKD were 0.988 and 0.999, respectively (Fig.4B). The Langmuir isotherm was well-known to represent the chemisorption. The maximum sorption capacity for removal of imidacloprid by CKD (142.85 mgg$^{-1}$) was significantly higher than that for removal of oxamyl (OX) pesticide by CKD (100.00 mgg$^{-1}$) (Table 4). This may be denoted by the difference in adsorption rates.

The obtained results indicated higher adsorption capacity compared to other sorbents derived from agricultural waste for both pesticides (Mohammad et al., 2014; Urbainet al., 2017; Mohammad and El-Sayed, 2021).

| Table 3. Kinetic parameters for imidacloprid (IMI) and oxamyl (OX) pesticides removal by cement kiln dust (CKD). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | Pseudo-first-order |                  | Pseudo-second-order |                  | Intra-particle diffusion |                  |
|                                 | $q_e$  | $k_1$  | $R^2$   | $q_e$  | $k_2$  | $R^2$  | $k_i$ | $C$ | $R^2$ |
| IMI                             | 4.07   | 0.0051 | 0.710   | 15.673 | 0.00098| 0.277  | 0.326 | 3.608 | 0.822 |
| OX                              | 18.44  | 0.0051 | 0.932   | 26.110 | 0.00011| 0.956  | 0.879 | 2.562 | 0.872 |
Fig. 4. Pseudo-first-order(A), pseudo-second-order(B), and intra-particle diffusion(C) kinetic models for removal of imidacloprid (IMI) and oxamyl (OX) pesticides by cement kiln dust (CKD).
Table. 4. Adsorption isotherm parameters of imidacloprid (IMI) and oxamyl (OX) pesticides removal by cement kiln dust (CKD).

<table>
<thead>
<tr>
<th></th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Temkin</th>
</tr>
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<tr>
<td></td>
<td>$K_F$ (mg(^1) L(^{(1/n)}))</td>
<td>$q_m$ (mg g(^{-1}))</td>
<td>$K_L$ (mg L(^{-1}))</td>
</tr>
<tr>
<td>IMI</td>
<td>5959.51</td>
<td>0.106</td>
<td>0.897</td>
</tr>
<tr>
<td>OX</td>
<td>8793.94</td>
<td>0.113</td>
<td>0.710</td>
</tr>
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</table>

Fig. 5. Freundlich isotherm (A), Langmuir (B), and Temkin (C) isotherm models for removal of imidacloprid (IMI) and oxamyl (OX) pesticides by cement kiln dust (CKD).
CONCLUSION

The results indicated affinity of CKD for removal of imidacloprid (IMI) and oxamyl (OX) pesticides with privileges for OX pesticide than IMI. Different kinetic models, pseudo-first-order, pseudo-second-order, intra-particle diffusion, were applied to examined the obtained results. The results were the best fitted to the pseudo-second-order model for IMI removal onto CKD with $R^2$ equals 0.956, while pseudo-first-order was the best fitted for OX pesticide onto CKD with $R^2$ equals 0.932. That could suggest, that the adsorption of two pesticides by CKD is chemisorption. Isotherm models, Freundlich, Langmuir, and Temkin, were used to examine the obtained isotherm data and the Langmuir isotherm fitted well to the experimental results for both pesticides. The maximum adsorption capacity for removal of imidacloprid (IMI) and oxamyl (OX) pesticides were 142.85 mg g$^{-1}$ and 100.0 mg g$^{-1}$, respectively. The results indicated the high potential of using CKD as an adsorbent for the two pesticides.

REFERENCES


الملخص العربي

دراسة مقارنة لإزالة مبيدات الآفات من نوع إيميداكلوربيد وأوكساميل imidacloprid وأوكساميل oxamyl بواسطة التراب الأسمنتي: دراسة حركية واتزان الادمصاص

أحمد عبد الخالق الرفاعي، حمزة سمير أبو النصر

في هذه الدراسة تم إجراء مقارنة لإزالة مبيد الآفات إيميداكلوربيد IMI (imidacloprid) وأوكساميل OX (oxamyl) بواسطة التراب الأسمنتي CKD (Calcium Bentonite) کناتج ثانوية من عملية تصنيع الأسمنت. وقد تم تشخيص ودراسة خواص التراب الأسمنتي والتعرف على مكونات العناصر الكيميائية به و كذلك دراسته بواسطة التحليل الطيفي بالأشعة تحت الحمراء FTIR و تحت الميكرسكوب الإلكتروني قبل وبعد تجربة الادمصاص. وقد تم دراسة تأثير التغير في التركيز الأولي للمبيد من 100 إلى 2000ملج/لتر وكذلك التغير في إزالة المبيد مع الوقت (من 10-30 دقيقة). كما تم دراسة حركة الأدمصاص لكلا المبيدتين من خلال النماذج المختلفة وهي نموذج الاتزان الأولى والثانية وكذلك نموذج الانتشار intra-particle. واظهرت النتائج تطابق النموذج الحركي من .diffusion