A new Fe₃O₄/CuO/AC Nanocomposite for Imidacloprid Removal: Characterization, Optimization, and Adsorption Modeling

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A new Fe₃O₄/CuO/AC nanocomposite for Imidacloprid removal: Characterization, optimization, and adsorption modeling

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Abstract

A new magnetic adsorbent ($\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$) composed of magnetite (Fe_3O_4) and copper oxide (CuO) nanoparticles Impregnated with activated carbon (AC) has been fabricated and used for the first time to remove imidacloprid (IMCP) insecticide from the aqueous solutions. This composite was characterized using field emission scanning electron microscopy, Fourier transform infrared spectroscopy, x-ray diffraction, energy dispersive x-ray diffraction, and vibrating sample magnetometer. The main influential factors such as the solution pH, the adsorbent amount, temperature, agitating time, and initial pesticide concentration were also tested to evaluate the optimized condition. Based on the results obtained from isotherm and kinetic modeling, the adsorption mechanism of IMCP on $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ is a combination of physisorption and chemisorption phenomena. The experimental data fitted best to the Freundlich isotherm model revealing the presence of heterogeneous sites for IMCP adsorption. Besides, the kinetics results revealed that the adsorption process well fitted with pseudo-second-order model, implying that the chemisorption was determining step in adsorption process. Thermodynamic results showed the spontaneous and exothermic nature of the adsorption process. Under optimal conditions (pH 7; contact time, 10 min; initial pesticide concentration, 10 mg L^{-1}), IMCP removal efficiency was 99.6%, indicating the excellent ability of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite for the adsorption of this pesticide from water solutions.

Keywords: Imidacloprid, Neonicotinoids, Magnetic adsorbent, Fe_3O_4 nanoparticles, CuO nanoparticles, activated carbon.

1. Introduction

Imidacloprid (IMCP) with chemical name of [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine] (Fig. 1) is a member of neonicotinoids as a relatively new class of insecticides which are widely used for control of sucking and chewing insects including aphids, thrips, plant hoppers, diamondback moths, and whiteflies. They act via binding to postsynaptic nicotinic receptors in the central nervous system of insect(1) (2, 3). IMCP is utilized for insects control in various crops such as cereals, maize, vegetables, citrus fruit and pome fruit, because of its high effectiveness and low toxicity to mammalian. However, due to the extensive consumption of the IMCP in agricultural production, its high solubility in water (500 mg L^{-1}), and half-life in soil is (48–190 days), occurring of its residues in surface waters and plant foods can pose a serious risk to human health because of their interactions with acetylcholinesterase receptors and proteins (2, 4-7). Besides, recent studies showed that IMCP and other neonicotinoids represent the significant risk to honeybees, aquatic beings, and birds (8-10). They are categorized in persistent contaminants, and therefore, they can transport into aquatic ecosystems through drainage of agricultural areas (10). The levels of neonicotinoids, especially IMCP, have been monitored in some countries including Netherlands with highest reported concentration of 0.32 mg L^{-1} (11-14). The maximum residual levels of these insecticides in honey and other related products have been announced by the European Union in the range of 50 to $200 \text{ } \mu\text{g kg}^{-1}$ (15).

During the past decade, a number of methods such as membrane process (16), ionexchange (17), chemical precipitation (18), coagulation-flocculation (19), photocatalytic reduction (20), biological (21), and adsorption (22) methodologies have been exploited for the removal of contaminants from the polluted water bodies. However, most of these methods have high operational costs, chemical consumption, and sludge production as well as low efficiency (23-25). Among these methodologies, the adsorption strategy has been widely exploited for the treatment of various contaminated food and environmental samples. This process is proven as suitable method for the removal of pollutants including pesticides, heavy metals, and other poisons from water solutions (26-28).

So far, some strategies have been developed for the removal of neonicotinoids including biopurification (29), microbial degrading (30), oxidation processes (31), and adsorption

technique (6). The use of adsorption process in order to remove these pesticides from polluted water solutions was rarely reported (6, 7, 32). However, some efforts has been performed for the extraction and/or preconcentration procedures of neonicotinoids (including IMCP) using an adsorbent via solid phase extraction (SPE) method (5, 15, 33-38),

Activated carbon is known as standard and effective adsorbent for the purification of municipal and industrial wastewaters for more than decades (22, 28, 39). However, its turbidity creation and separation from effluents in removal process is a challenging issue. In this regard, cost-effective, simple and rapid separation of Fe_3O_4 (magnetite) nanoparticlces as a biocompatible adsorbent introduces it as a suitable candidate for composite formation with activated carbon to solve the turbidity problem (38, 40). The easy separation of the magnetic adsorbent from aqueous solution is simply performed using an external magnetic field (41). On the other hand, owing to the presence of amine groups in IMCP molecule, the attraction between copper and these groups can be exploited by the use of CuO nanoparticles in the fabrication of the effective adsorbent (1, 42). Therefore, the scope of current work, is to focus on the development of new effective adsorbent namely $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite due to the important role of the adsorbent materials in adsorption process. Copper oxide nanoparticles, activated carbon, and magnetite nanoparticles were selected to increase the selectivity, adsorption power, and the easy separation of the adsorbent from solution, respectively. This new nanocomposite was used to effective removal of IMCP from water solutions.

2. Experimental

2.1. Reagents and standards

All the used chemicals were of analytical grade. All the solutions were prepared using the double distilled water (DDW) throughout the experiments. Standard of IMCP and copper (II) oxide (nanopowder) were obtained from Merck Company (Germany). Iron (III) chloride anhydrous, iron (II) chloride tetrahydrate, hydrochloric acid solution (HCl), sodium hydroxide (NaOH), and methanol were obtained from Samchun chemicals company (Korea). Activated carbon powder was obtained from Sigma-Aldrich. 100 mg L⁻¹ stock solution of IMCP was used to prepare the standard solutions with different concentrations.

2.2. Apparatus

A Perkin Elmer UV-VIS double beam spectrophotometer was applied to record the UV-Vis absorbance measurements and spectra. A Bruker spectrometer (model Tensor 27, Germany) was used to obtain Fourier transform infrared (FT-IR) spectra. The magnetic properties of the synthesized Fe_3O_4 nanoparticles and $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite were recorded using a MDK-VSM instrument (Meghnatis Daghigh Daneshpajouh Co., Iran). The morphology and elemental composition of nano-composite were evaluated by Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray Diffraction (EDX) using a Tescan model Mira3-XMU instrument (Czech Republic). The pattern of the nanocomposite x-ray diffraction (XRD) was recorded using an X'Pert Pro MPD instrument (PANalytical, Netherlands). The pH values were adjusted by use of a Metrohm pH-meter model 623 (Switzerland).

2.3. Synthesis of Fe_3O_4 nanoparticles

The co-precipitation of Fe(II) and Fe(III) chloride as the iron oxides (FeO and Fe_2O_3) in the presence of ammonia solution was exploited for the preparation of Fe_3O_4 nanoparticles at room temperature as described previously (25). In brief, 5 mL of a solution composed of Fe(II) and Fe(III) with 1:2 molar ratio, was vigorously stirred while 50 mL of ammonium hydroxide solution (1.5 M) was added drop-wisely. A black suspension identified the formation of magnetite nanoparticles. The mixture was stirred at 500 rpm for another 10 min at this condition. An external magnetic field was applied to collect Fe_3O_4 nanoparticles. Then, the collected nanoparticles were thoroughly washed with DDW to eliminate excess ammonia and dried in oven at 80 °C.

2.4. Preparation of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ magnetic adsorbent

1 g of each CuO and Fe_3O_4 nanoparticles were mixed with 0.5 g of AC powder and suspended in 50 ml of DDW, homogeneously. After adjusting the suspension pH at 8 by use of HCl and NaOH solutions, it was heated to 80 °C for ten min. Then the prepared nanocomposite was dried at 80 °C in oven.

2.5. Design of IMCP adsorption experiments

For the adsorption studies the batch procedure was used. A beaker containing 10 mL of IMCP solution was used in all the removal experiments. The effects of some influencing experimental parameters including pH of solution, the adsorbent amount, contact time,

temperature, and initial pesticide concentration were examined on the performance of adsorption.

2.5.1. pH effect

To check the effect of pH on the adsorption process, 5 mg of the adsorbent was mixed with 10 mL of 10 mg L⁻¹ IMCP solutions in the pH range of 4-10. By additions of dilute NaOH or HCl solutions, the pH value of the suspension remained constant throughout the removal process. The mixture was stirred at room temperature (20 °C) with the rate of 500 rpm for 5 min.

2.5.2. The effect of adsorbent amount

The influence of the adsorbent amount on the adsorption was examined with 10 mg L⁻¹ IMCP solutions (10 mL) containing 2-30 mg of the adsorbent at pH 7, and agitating at room temperature (20 °C) with the rate of 500 rpm for 5 min.

2.5.3. The influence of contact time

For kinetic studied, 20 mg of the adsorbent with 10 mg L⁻¹ IMCP solutions (10 mL) at pH 7 were mixed. The suspensions were shaken at room temperature (20 °C) in the fixed intervals including 1, 2, 5, 10, 20, 30, 40, 50, 60, and 90 min with the rate of 500 rpm.

2.5.4. The influence of initial concentration of IMCP on adsorption

The effect of initial concentration of the pesticide on adsorption equilibrium was studied by mixing 20 mg of the adsorbent and IMCP solutions (10 mL) with varying initial concentrations in the range of 5 to 30 mg L⁻¹. These prepared suspensions were stirred for 10 min at pH = 7 and 20 °C with the rate of 500 rpm.

2.6. Analysis of IMCP

In all adsorption experiments, after separating of the adsorbent by the external magnetic field, IMCP concentration in solution was measured by spectrophotometry at the maximum wavelength of the analyte (270 nm). The UV-Vis. spectrum of IMCP was obtained within the wavelength region from 200 to 350 nm for the selection of maximum wavelength. The spectra related to IMCP solution before and after agitating with Fe₃O₄/CuO/AC are depicted in Fig. 2. In each adsorption experiment, the removal

efficiency and the equilibrium adsorption capacity were obtained by the following equations:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\text{Removal (\%)} = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where C_0 and C_e (mg L^{-1}) are IMCP initial and equilibrium (residual) concentrations, respectively. In equation (2), q_e (mg g^{-1}), m (g), and V (L) are the adsorption capacity, adsorbent amount, and solution volume, respectively. All the experiments were conducted in triplicate, and the mean values of the measurements were reported as results.

2.7. Modeling of the adsorption process: isotherms and kinetics

To design a proper adsorption unit, the kinetic studies showing the removal rate of poison from the aqueous solutions is necessary. For modeling the adsorption process of IMCP on $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$, four common and widely used kinetic models including pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich were exploited. The linear equations of these models are given in Table 1.

Generally, the adsorption behavior of molecules onto the surface of adsorbent is revealed by the isotherm studies. In this way, to fit the experimental data of adsorption process, four common theoretical isotherm models including Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (D-R) were examined. The parameters and equations related to these models are presented in Table 2.

2.8. The influence of temperature on adsorption

To check the temperature influence on the equilibrium of adsorption, a series of experiments was performed by mixing 20 mg of the adsorbent with 10 mg L^{-1} IMCP solutions (10 mL) at pH 7. The suspensions were shaken for 10 min with the rate of 500 rpm at the temperature range of 20-60°C.

3. Results and Discussion

3.1. Characteristics of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite

As can be seen from Fig. 3A, FESEM image of the prepared Fe_3O_4 nanoparticles shows the diameter distribution of around 25 nm with spherical shape. Moreover, Fig. 3B shows the

morphology of nanocomposite with the large number of cavities, and the presence of a mixture of metal nanoparticles and layered carbon particles. The EDX spectrum of Fe₃O₄/CuO/AC (Fig. 3C) exhibits the peaks for iron, copper, carbon, and oxygen indicating the successful synthesis of the adsorbent.

As can be seen from Fig. 4A, the FTIR spectra of Fe₃O₄ nanoparticles, Fe₃O₄/CuO/AC nanocomposite, IMCP, and Fe₃O₄/CuO/AC@IMCP are obtained in the wavenumber range of 400-4000 cm⁻¹. The strong and sharp peak at 576.82 cm⁻¹ can be related to the Fe–O vibration in Fe₃O₄ nanoparticles (Fig. 4A-a) (43). The strong absorption peaks in Fig. 4A-b at 576.12 cm⁻¹ (with some shoulders) and 3433.99 cm⁻¹ can be ascribed to the vibrations of metal oxide bands (Fe–O and Cu–O), and O–H band of surface adsorbed water molecules in Fe₃O₄/CuO/AC nanocomposite, respectively. Fig. 4A-c presents the nanocomposite spectrum after adsorption of IMCP revealing almost all characteristic peaks of the constituents with slight shift due to physicochemical mechanism of the adsorption process. These shifts can be seen in metal oxide (579.13 cm⁻¹) and N–H or O–H vibrations (3412.53 cm⁻¹).

XRD pattern of Fe₃O₄/CuO/AC nanocomposite in position at 40 kV and 30 mA with Cu anode over the 2θ: 4-70° is presented in Fig. 4B. The diffraction peaks related to Fe₃O₄, CuO, and AC in this XRD spectrum indicated the successful synthesis of the adsorbent without any phase change.

A vibrating sample magnetometer (VSM) was exploited to study the magnetic properties of Fe₃O₄ and Fe₃O₄/CuO/AC nanocomposite. As seen in Fig. 4C, the super-paramagnetic property of the prepared Fe₃O₄ and Fe₃O₄/CuO/AC was indicated by the absence of magnetic hysteresis loops in their curves, (44). Furthermore, the saturation magnetization of Fe₃O₄ (69.1 emu g⁻¹) was higher than that Fe₃O₄/CuO/AC (42.8 emu g⁻¹), revealing the existence of non-magnetic CuO and AC in the nanocomposite structure. Despite the reduction in the magnetic property, this adsorbent was efficiently and rapidly eliminated from aqueous solutions using a magnet due to its relatively high saturation magnetization value.

3.2. Experimental conditions

3.2.1. The influence of pH

In adsorption studies, the solution pH is of vital importance in the ionization and surface charge of adsorbent functional groups. The influence of solution pH on the removal efficiency of IMCP (section 2.5.1) is presented in Fig. 5a. As seen, the adsorption efficiency (removal percentage) of IMCP increases substantially with increase in the solution pH from 4.0 to 7.0, and then decreases in higher pH values. According to these results, the maximum percent of IMCP removal (56.0%) was achieved at pH value of 7.0, and the adsorbent exhibits the best function neutral media. This observation is in agreement with the other reports which show the maximum adsorption potential of IMCP in pH 7 probably owing to its neutral molecular structure in this pH (5, 15, 37, 38). At acidic media the lower uptake of adsorbent may be related to the protonation of the amine groups of IMCP molecules as well as surface of magnetite and CuO nanoparticles of the adsorbent. This phenomenon, on one hand, reduces the tendency between IMCP and the adsorbent because of the electrostatic repulsion between the moieties with positive charges, and on the other hand, a vigorous competition between proton ions and the poison takes place for the adsorption on the active sites of the adsorbent (24, 25). However, the observed decrease in the removal rate at alkaline environments ($\text{pH} > 7$) might be correlated to the existence of the large number of hydroxide ions and their competition with IMCP for the active sites of the adsorbent. Considering the maximum removal of IMCP, pH 7 was chosen for the subsequent experiments.

3.2.2. The effect of adsorbent amount

The influence of adsorbent amount on the adsorption extent of IMCP on $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite was tested in the range of 2-30 mg under conditions that is described in section 2.5.2. As depicted in Fig. 5b, the uptake of IMCP enhances with by increasing the adsorbent quantity and the removal percentage reaches to 96.7% using 20 mg of the adsorbent. Besides, the removal trend shows direct relationship with the adsorbent amount up to 20 mg which means that the greater surface area and more active sites provide the adsorption with more efficiency at fixed IMCP initial concentration. Thereafter, increasing the adsorbent dosage cannot cause further adsorption and thus, the removal rate levels off. The aggregation of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ particles at higher amounts and therefore, the lower usage of the adsorbent active sites might be the reasons for this observed phenomenon (25). Based on these results, 20 mg of $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ nanocomposite was chosen as the optimal adsorbent amount for further tests.

3.2.3. Kinetic modeling: contact time effect

At optimal conditions of pH and the adsorbent amount, the influence of stirring time on the adsorption efficiency was evaluated at 90 min period as describes in section 2.5.3. As can be observed from Fig. 6a, the equilibrium state and nearly the complete removal of IMCP (99.6%) from the test solution take place in the first 10 min. This rapid increase in the removal percentage in the initial contact times and reaching to equilibrium state in very short time can be explained in the context of fast kinetic of adsorption reaction (fast occupation) and saturation of reactive sites of the adsorbent. The previous studies have reported the similar trends (26, 45). According to the findings, the subsequent experiments were carried out in the optimum contact time of 10 min. Besides, based on these experiments, the plots and parameters of four widely used kinetic models including pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich were obtained and are given in Fig. 6b and Table 3. In Table 3, q_t , is the adsorption capacity at a given time t , and q_1 , and q_2 are the adsorption capacity at equilibrium state at pseudo-first-order and pseudo-second-order kinetic models, respectively. The rate constants of pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models are K_1 , K_2 , and K_{ip} are, respectively.

Firstly, the correlation coefficients (R^2) obtained from the linear form of equations related to the kinetic models (Figs S1-S4) were compared with each other. Then, the highest value of R^2 was used to choose the most proper kinetic model fitting the IMCP adsorption on $Fe_3O_4/CuO/AC$ nanocomposite. As can be seen from Table 3, the R^2 obtained for the pseudo-second-order kinetic model ($R^2 = 0.9991$) is the highest compared to the other models, indicating that this model has a better fit with the adsorption of IMCP on the adsorbent. The plots of various kinetic models (Fig. 6b), also confirms that the experimental data of IMCP adsorption onto $Fe_3O_4/CuO/AC$ nanocomposite is in agreement with the pseudo-second order model, implying that the determining step is chemisorption. Furthermore, the calculated $q_{2, cal.}$ value (5.076 mg g^{-1}) is closer to the experimental $q_{e, exp.}$ (4.688 mg g^{-1}) than those of the other models, which is another confirmation for this model. According to this finding it can be concluded that the adsorption on IMCP onto the adsorbent is performed by chemisorption (27, 46, 47). The adsorption process probably involves the electron sharing between IMCP molecules via nitrogen free electrons and the binding sites of the adsorbent, specially, CuO nanoparticles (23).

The other models showed lower R^2 values revealing their lesser role in the removal process. Besides, for intra-particle diffusion model the value of $C_i > 0$ indicates that linear parts of the curve (q_t vs. $t^{0.5}$) do not pass through the origin (Table 3). This observation reveals that although this model can control the adsorption process to some extent by diffusion in boundary layer, but is not the only rate-controlling step (24, 47, 48).

3.2.4. Isotherm modeling: IMCP initial concentration effect

The effect of initial concentrations of IMCP ranging from 5-30 mg L⁻¹ on its adsorption by Fe₃O₄/CuO/AC (section 2.5.4) is depicted in Fig. 7a. As seen, the removal efficiency decreases by increasing IMCP concentration from 99.7% to 67.1% mg L⁻¹ for 5 and 30 mg⁻¹, respectively, probably owing to the fixed number of active sites on the adsorbent as reported in previous studies (24). However, the adsorption capacity increases with the rise in initial IMCP concentration due to the increase of its adsorption per mass unit of the adsorbent (from 2.47 to 14.61 mg g⁻¹). This observation might be owing to the increase of the driving force to overcome the mass transfer resistance of IMCP molecules between the solid and aqueous phases (45).

Under the optimal conditions, the linear equations of four isotherm models including Freundlich, Langmuir, Temkin, and D-R were used to explain the adsorption of IMCP in the concentration range of 5-30 mg L⁻¹ (Figs S5-S8). The obtained graphs for these isotherm models and also values for the equilibrium isotherm parameters are presented in Fig. 7b and Table 4. In this Table, K_L , K_F , and K_T are Langmuir, Freundlich, and Temkin constants, respectively. Besides, in D-R model, ϵ (kJ mol⁻¹) is the Polanyi potential and can be determined via $\epsilon = RT \ln (1 + (1/C_e))$ equation. The q_m , n , R_L , and E parameters are the maximum adsorption capacity, Freundlich adsorption heterogeneity factor, the separation parameter, and the mean free energy of adsorption, respectively (48).

As shown in Fig. 7b and Table 4, based on the R^2 values, the isotherm models are fitted to the experimental results in the following order: Freundlich > Langmuir > Temkin > D-R. The correlation coefficient of 0.9924 for Freundlich model suggests the presence of heterogamous conditions in adsorption process.

Langmuir and Freundlich isotherms show the single-layer (homogeneous) and multi-layer (heterogeneous) mechanisms of the adsorption process, respectively. In addition, the indirect

interactions between the adsorbent and the adsorbate are considered in Temkin model, and D-R isotherm model shows a surface area with the homogeneous adsorption energy (25, 49).

In D-R model the E value of is obtained by use of the following equation:

$$E = \frac{1}{\sqrt{-2D}} \quad (3)$$

The desirability of IMCP adsorption onto the adsorbent was studied using R_L ($1/(1 + C_0/K_L)$) as a dimensionless parameter which is derived from Langmuir model (Table 4). Generally, the adsorption process will be favorable if R_L lies within 0 and 1 ($0 < R_L < 1$). For $R_L = 0$, $R_L > 1$, and $R_L = 1$, the adsorption is irreversible, unfavorable, and linear, respectively (49). A favorable behavior of IMCP onto the adsorbent surface was confirmed by the R_L value (0.060) as shown in Table 4.

The $1/n$ value in Freundlich model shows the favorability of IMCP adsorption on $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$. The small value of $1/n$ (0.318), between 0 and 1, and the large value of K_F (5.974 mg g^{-1}) confirms the effective adsorption of IMCP molecules on the adsorbent.

The E value in D-R model gives an idea about either chemical or physical adsorption according to its magnitude. With the E values of $8\text{--}16 \text{ kJ mol}^{-1}$ the mechanism of adsorption can be chemical process, while with the values of $E < 8 \text{ kJ mol}^{-1}$ shows that the physical adsorption mechanism is predominant (24). As can be seen from Table 4, the E value for IMCP adsorption on $\text{Fe}_3\text{O}_4/\text{CuO}/\text{AC}$ ($4.784 \text{ kJ mol}^{-1}$) was found to be lower than 8 kJ mol^{-1} , indicating that the dominant mechanism is the physical adsorption. Generally, in adsorption process, the chemisorption mechanism is the slowest step, while the physisorption is the main mechanism in the system, as mentioned before (section 3.2.3) (25).

3.2.5. Determination of the thermodynamic parameters: the effect of temperature

The effect of solution temperature was studied in the range of $20\text{--}60^\circ\text{C}$ under conditions described in section 2.7, and the optimal temperature for IMCP adsorption as well as the related thermodynamic parameters was obtained. The results revealed that in the temperatures higher than 20°C , the removal efficiencies of IMCP slow down, gradually, showing that the lower temperatures are favorable in adsorption process (Fig. S9). The thermodynamic parameters including standard entropy change standard enthalpy change (ΔH^0 , kJ mol^{-1}), (ΔS^0 , $\text{kJ mol}^{-1}\text{K}^{-1}$), and Gibbs energy (ΔG^0 , kJ mol^{-1}) were calculated from Van't Hoff equation (50):

$$\Delta G = -RT \ln K_d \quad (4)$$

In Eq. (4), R is the gas constant (8.3145 Jmol⁻¹K⁻¹), and distribution coefficient of K_d (Eq. 5) is the ratio of the adsorbed IMCP concentration (C_s) to the aqueous phase IMCP concentration (C_e) at the defined temperature (T) at equilibrium state (51).

$$K_d = \frac{C_s}{C_e} \quad (5)$$

The ΔG value was calculated by use of Eq. (4). In addition, ΔH^0 and ΔS^0 values were determined using slope and intercept of $\ln K_d$ versus $1/T$ plot from another form of Van't Hoff equation according to Eq. (6), respectively (Fig. S10).

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

In Table 5 the calculated parameters and their values are presented. As seen, all the three values of thermodynamic parameters (ΔH^0 , ΔS^0 , and ΔG^0) are negative in standard condition (25°C and 1 atm pressure). The negative ΔH^0 value indicates the exothermic behavior of the adsorption process and describes the decrease in the sorption ability of the adsorbent with an increase in the solution temperature. Furthermore, the negative value of ΔS^0 confirms the affinity of the adsorbent for IMCP, and also, reveals that the randomness decreased at the solid–solution interface during the sorption phenomenon. As seen from Table 5, the ΔG value for all the examined temperatures is negative demonstrating the spontaneous nature of adsorption process. Besides, with an increase in the temperature, the value of ΔG^0 increases indicating that lower temperatures are favorable for the IMCP adsorption and the enhancing in temperature reduces the spontaneity of the removal reaction. According to ΔG^0 value, the adsorption process is categorized to chemisorption (-80 to -400 kJ mol⁻¹) or physisorption (0 to -20 kJ mol⁻¹). From Table 5, it can be concluded that the sorption process has a physical nature ($\Delta G^0 = -7.756$ kJ mol⁻¹), and the physical adsorption is the mechanism is predominant in this system. This result is consistent with the data documented in Table 4, as E value refers to the physisorption phenomenon.

4. Conclusion

Herein, a selective and effective approach for IMCP elimination from water solutions has been developed with the removal efficiency of about 99% by use of Fe₃O₄/CuO/AC via

adsorption process. The experimental results showed that operating factors such as initial concentration of IMCP, pH, temperature, and adsorbent amount remarkably influence on the adsorption efficiency. Fe₃O₄/CuO/AC nanocomposite exhibited a better performance with the initial concentration level of 10 mg L⁻¹ and 25°C at pH 7. The optimum contact time of 10 min implied that the adsorption process reaches the equilibrium state in very short time which can be related to the high tendency of the adsorbent to IMCP. The pseudo-second-order kinetic model and Freundlich isotherm model were consistent with the adsorption process. According to these results it was proved that both chemisorption and physisorption mechanisms were involved in the adsorption process. The synthesized adsorbent presented the high saturation magnetization (42.8 emu/g), demonstrating its rapid and easy isolation from water solution. This inexpensive adsorbent composed of metal oxides nanoparticles and activated carbon showed rapid removal process in soft conditions in terms of pH and temperature with the high adsorption performance, and the excellent capability for water remediation.

Declarations

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Caption to the figures:

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Figures

Figure 1

Molecular structure of Imidacloprid.

Figure 2

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b

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