

Adsorption of Imidacloprid on Powdered Activated Carbon and Magnetic Activated Carbon

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The adsorptive characteristics of imidacloprid on magnetic activated carbon (MAC12) in comparison to powdered activated carbon (PAC) were investigated. Adsorption of imidacloprid onto powdered activated carbon and magnetic activated carbon was studied as a function of time, initial imidacloprid concentration, temperature and pH. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models for both carbons were used to describe the kinetic data. The adsorption equilibrium data were analyzed using the Langmuir and Freundlich models. For powdered activated carbon the isotherm was 'H' type, and 'L' type for magnetic activated carbon. Equilibrium data fits well to the Langmuir model in the studied concentration range of imidacloprid. It was found that both the boundary layer and intraparticle diffusion for both adsorbents play an important role in the adsorption mechanisms of imidacloprid. The adsorption of imidacloprid on PAC and MAC12 followed a pseudo-second-order kinetic model rather than pseudo-first-order model. A decrease in the adsorption of imidacloprid on powdered activated carbon and magnetic activated carbon was observed with the increase in temperature. The pH of the solutions had no effect on the adsorption capacity of the adsorbents.

Key words:

Pesticides, adsorption, powdered activated carbon, magnetic activated carbon, imidacloprid, environmental pollution, adsorption kinetics

Introduction

The removal of pesticides from water is one of the major environmental concerns these days. One of the environmental concerns is that the nature of these substances is toxic. Moreover, degradation products of pesticides make these chemical substances a potential hazard to the environment. Imidacloprid [1-(6-chloro-3-pyridinylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] is an insecticide used for seed treatment and flea-control. It kills the insects by disrupting their nervous system.¹ Imidacloprid is considerably soluble in water (500 mg L⁻¹) and its half-life in soil is 48–190 days, however breaking down is faster with plant ground cover than in fallow soils.^{2,3} Due to its high solubility and mobility, it has the potential to leach into ground water and surface water through dissolution in run-off.³ Imidacloprid is a potential environmental hazard due to its persistent nature, while its concentration does not decrease for a year following treatment. In addition, its ability to move in soil has been demonstrated by a variety of studies, so it is considered by the US Environmental Protection Agency (EPA) to be a potential water contaminant.^{4,5} Imidacloprid is slightly toxic to fish, moder-

ately toxic to aquatic invertebrates and is highly toxic to bees and house sparrow.⁶

It is necessary to protect human health and the environment from the potential effects that can be caused by pesticide exposure. If the effluents containing pesticides are treated before they disperse throughout the environment, pesticide pollution could be controlled.⁷

The various methods used for pesticide removal are: photocatalytic degradation,^{8,9} combined photo-Fenton and biological oxidation,¹⁰ advanced oxidation processes,¹¹ aerobic degradation,¹² nanofiltration membranes,¹³ ozonation¹⁴ and adsorption.^{15–23} These adsorption processes are the most widespread technologies, offering the possibility to remove a wide range of compounds. Various adsorbents have been used by authors for the removal of pesticides from waters. Mahramanlioglu *et al.* (2003) used acid activated spent bleaching earth for the removal of MCPA (4-chloro-2-methyl phenoxyacetic acid) and 2,4-D from aqueous solutions.^{24,25} Powdered activated carbon has been the standard adsorbent for the reclamation of municipal and industrial wastewaters for almost three decades.^{26,27} Soc'is-Viciano *et al.* (2003) reported the adsorption of imidacloprid on heat-treated kerolites with best fit to Freundlich adsorption isotherm.²⁸ In spite of the intensive use of imidacloprid world-

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wide, physicochemical parameters for its adsorption onto powdered activated carbon have not been evaluated.

On the other hand, magnetic adsorbents have been used to remove organic and inorganic pollutants and after their use in treatment systems, they can be separated from the medium by a simple magnetic process.²⁹ The easy separations of magnetic activated carbons from the medium have caused a lot of studies on magnetic activated carbons.^{29–36}

Although, in our previous work, magnetic activated carbon was prepared and used for dyestuff removal from aqueous solutions.³⁷ However, in this study, in order to avail further insights, our basic aim is to investigate the adsorptive parameters of the prepared iron oxide/PAC composite in comparison to that of PAC.

Material and methods

Chemicals

Imidacloprid (analytical grade) was obtained from Fluka. Iron chloride, iron sulphate and sodium hydroxide (analytical grade) were purchased from Merck. Powdered activated carbon was obtained from Norit.

Preparation of magnetic activated carbon

Iron oxide/PAC composite was prepared as described previously.^{29,37}

An iron chloride and iron sulphate suspension was prepared by mixing 200 mL each of solutions of FeCl₃ (28 mmol) and FeSO₄ (14 mmol). The suspension was stirred at 70 °C and NaOH solution (100 mL, 5 mol L⁻¹) was added dropwise to precipitate the iron oxide.²⁸ The same procedure was repeated for the preparation of iron oxide-powdered activated carbon composite but with the addition of powdered activated carbon. The amount of powdered activated carbon was adjusted in order to obtain iron oxide-powdered activated carbon mass ratio of 1 : 2 (MAC12). The final product was washed to pH 6.5 using distilled water, filtered, and dried in an oven at 100 °C for six hours. Under the process conditions, four iron oxides are formed including magnetite, maghemite, hematite and goethite. Among these iron oxides, only magnetite and maghemite show the magnetic properties.

The prepared MAC12 composite and iron oxide were characterized by XRD (Ni filtered Cu K_α, λ = 1.5418). The BET surface area of PAC, MAC12 and iron oxide were determined by surface area analyzer QS-7 by standard N₂ adsorption at 77K.

Batch experiments

Equilibrium experiments were carried out in order to determine the adsorption capacity of the adsorbent. Stock solution of known concentration of imidacloprid (25 mg L⁻¹) was prepared in distilled water. Test solutions were prepared by diluting the stock solutions to the desired concentration. The pH of the test solutions was measured (7.40) and there were no appreciable changes in pH after 8 hours. Adsorption experiments were carried out using routine batch technique. All experiments were carried out at 20 °C. Known amount of test solutions (50 mL) were taken in 250 mL stoppered plastic bottles and known amount of adsorbates (0.01 g) were added to each. The samples were shaken at a 300 rpm constant rate for 12 hours in thermostat cum shaking assembly. Samples were centrifuged twice at 10000 rpm for ten minutes and were analyzed by UV-Visible spectrophotometer at 270 nm.

The kinetics experiments were carried out in a specially designed cylindrical vessel. The vessel was charged with 3 L aqueous solution of imidacloprid and constant amount of adsorbent (0.6 g). Mixing was provided by a blade. A motor was used to drive impeller. The top surface of the vessel was open to atmosphere. Experiments were taken out at the agitation rate of 300 rpm. Samples withdrawn at different time interval using a syringe were analyzed by UV-Visible spectrophotometer after centrifugation at 270 nm.

Results and discussions

The surface areas of powdered activated carbon, iron oxide and the magnetic activated carbon are given in Table 1. Table 1 reveals that magnetization processes affected the surface area and the value of micropores structure. Powdered activated carbon, magnetic activated carbon and iron oxide were also characterized by XRD. Fig. 1 shows the presence of maghemite and magnetite. In Fig. 2, the XRD patterns show the presence of goethite in PAC structure. This goethite peak was also observed in the iron oxide/PAC composite structure (Fig. 3).

Table 1 – Surface area of the powdered activated carbon, magnetic activated carbon and iron oxide

Material	Surface area/ m ² g ⁻¹	Microporous volume/ cm ³ g ⁻¹	Mesopore volume/ cm ³ g ⁻¹
powdered activated carbon	1040	0.308	0.070
magnetic activated carbon	868	0.202	0.065
iron oxide	64	0.07

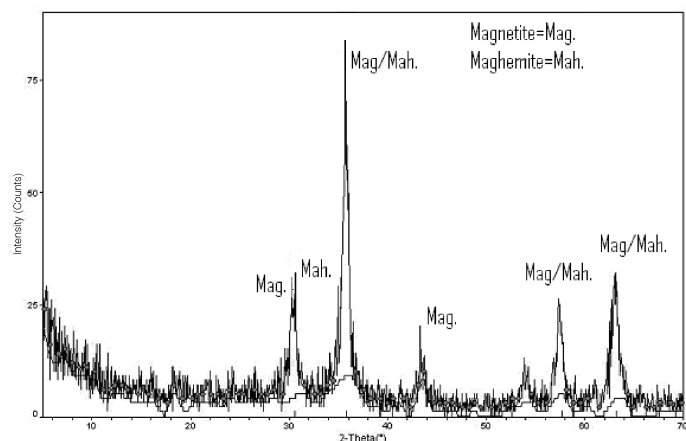


Fig. 1 – X-Ray patterns of Iron oxide sample

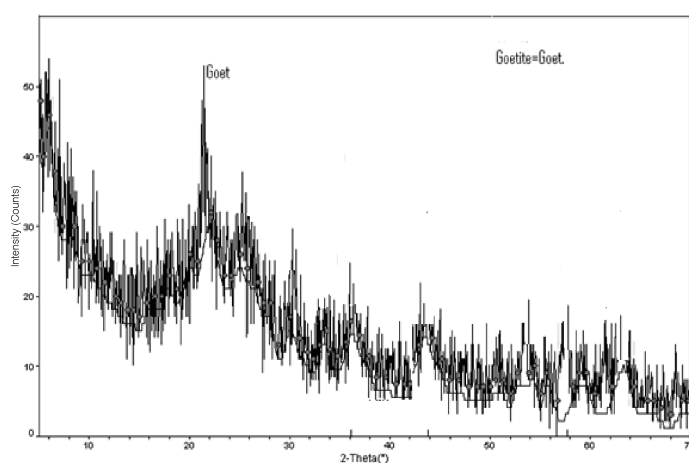


Fig. 2 – X-Ray patterns of powdered activated carbon

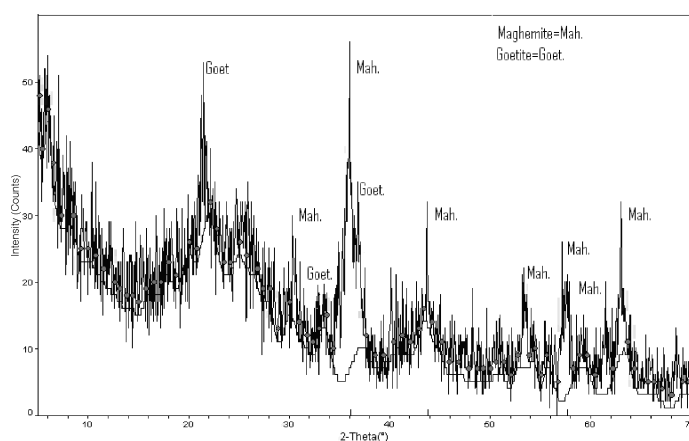


Fig. 3 – X-Ray patterns of 1 : 2 iron oxide, carbon composite

Adsorption isotherms

The adsorption capacity of any adsorbent for the removal of substances from aqueous solutions is generally calculated from Langmuir and Freundlich isotherms. The data obtained from equilibrium studies were used to calculate the value of the Langmuir and Freundlich isotherm constants.

The Langmuir isotherm

The Langmuir adsorption isotherm has been used by many authors for the adsorption of inorganic and organic substances. The Langmuir adsorption model³⁸ is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules. The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{C}{q} = \frac{C}{Q_0} + \frac{1}{Q_0 b} \quad (1)$$

Where q is the amount adsorbed (mg g^{-1}), C is the equilibrium concentration of the adsorbate (mg L^{-1}) and Q_0 and b are Langmuir constants related to maximum adsorption capacity and energy of adsorption respectively.

C/q was plotted against c and straight line with slope $1/Q_0$ was obtained (Figs. 4–5). The values of Q_0 and b for powdered activated carbon and magnetic activated carbon calculated from the slope and intercept of the straight line are given in Table 2.

Table 2 – Isotherm parameters for adsorption of Imidacloprid on PAC

Isotherm	Powdered activated carbon	Magnetic activated carbon
Langmuir:		
$Q_0/\text{mg g}^{-1}$	110.59	94.89
$b/L \text{ mg}^{-1}$	2.0	2.28
R^2	0.997	0.995
Freundlich:		
$K/\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$	71.08	53.9
$1/n$	0.26	0.37
R^2	0.86	0.65

The results show that magnetic activated carbon has lower capacity than powdered activated carbon. This can be explained by the fact that the decrease in the surface area of the adsorbent decreases the adsorption capacity.

Freundlich isotherm

The adsorption data for imidacloprid was also analyzed by the Freundlich model. The Freundlich isotherm³⁹ is an empirical equation employed to describe heterogeneous systems. The logarithmic

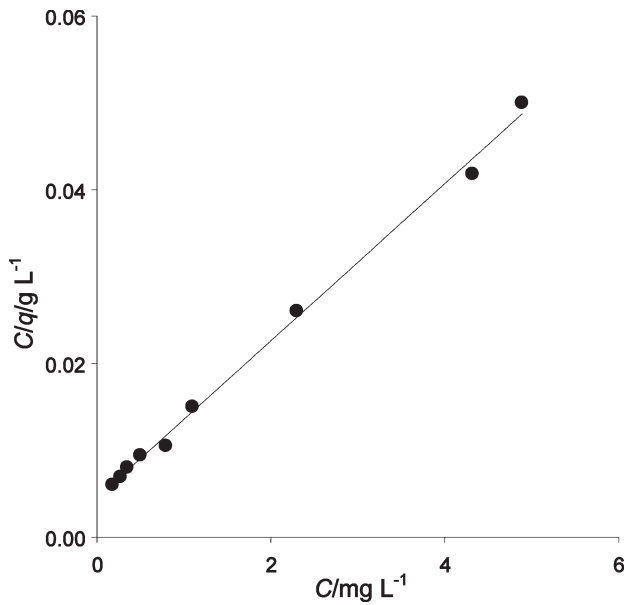


Fig. 4 – Langmuir plot for the adsorption of imidacloprid on powdered activated carbon

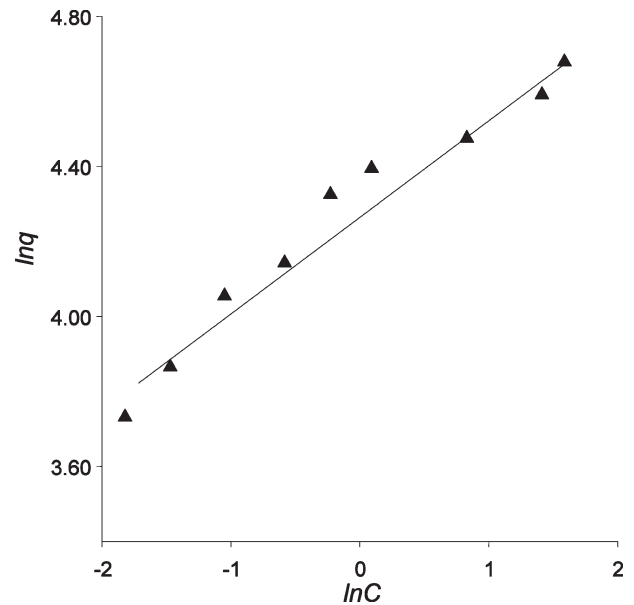


Fig. 6 – Freundlich plot for the adsorption of imidacloprid on powdered activated carbon

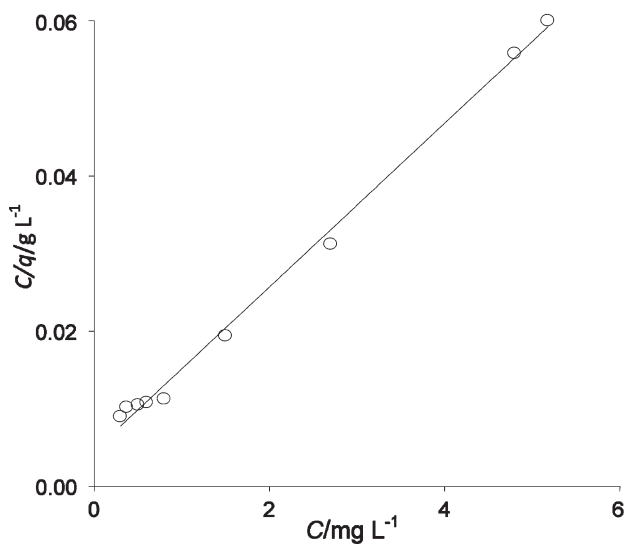


Fig. 5 – Langmuir plot for the adsorption of imidacloprid on magnetic activated carbon

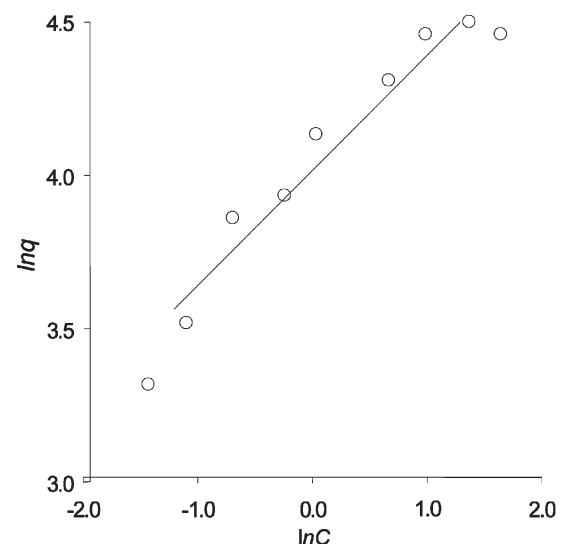


Fig. 7 – Freundlich plot for the adsorption of imidacloprid on magnetic activated carbon

form of the Freundlich model can be written by the following equation:

$$\ln q = \ln K + \frac{1}{n} \ln C \quad (2)$$

Where C is the equilibrium concentration (mg L^{-1}), q is the amount adsorbed (mg g^{-1}). K and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. $\ln q$ was plotted against $\ln C$ for the equilibrium data of imidacloprid and given in Figs. 6 and 7. The Freundlich constants, K and n for both adsorbents calculated from slope and intercept of the plot are given in Table 2. The correlation coefficients for

both adsorbents in Table 2 are too low and therefore the values of K and n cannot be compared. The best fit was observed with the Langmuir model. The determination coefficient values for this model is higher than that of Freundlich model.

The Giles isotherm

Figs. 8 and 9 show the Giles isotherm⁴⁰ for imidacloprid. In Fig. 8, the isotherm may be classified as H type. H type is the particular case of L type isotherm. Initial slope is very high. This can be distinguished from the other types of isotherm due to high affinity between solute and adsorbent.

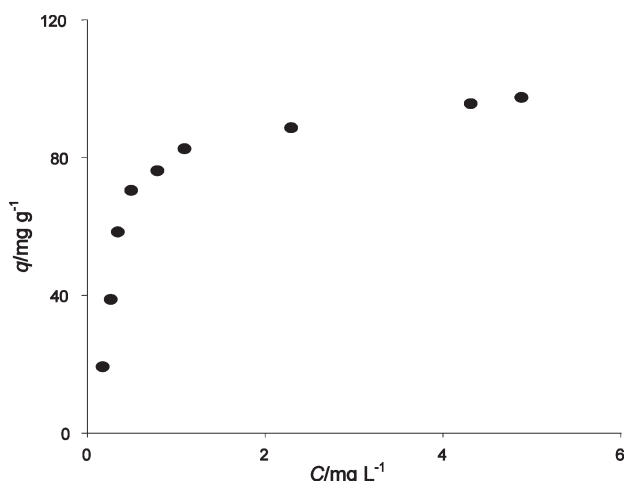


Fig. 8 – Giles isotherm for the adsorption of imidacloprid on powdered activated carbon

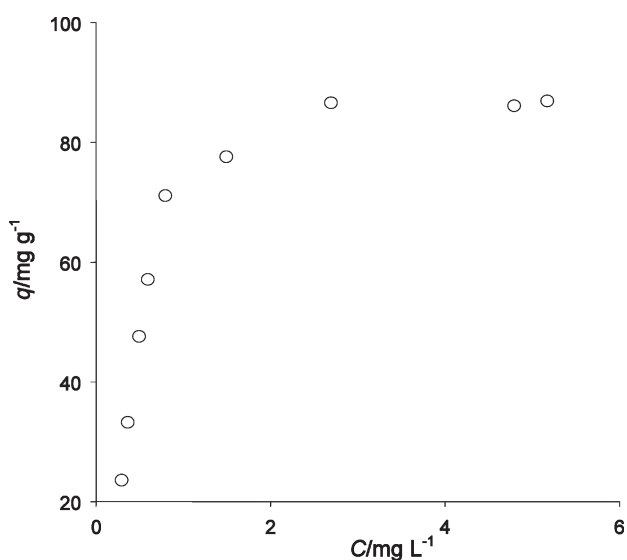


Fig. 9 – Giles isotherm for the adsorption of imidacloprid on magnetic activated carbon

From Fig. 9, the isotherm may be classified as L type isotherm. It is seen that the curve reaches a plateau. L curves are the most common and best known. L curve occurs probably in the majority of cases of adsorption from dilute solution.

Effect of pH on adsorption of imidacloprid

pH of solutions has an important effect on adsorption processes. Olivia *et al.* (2003) showed that pH of the solution affects the iron oxide content of the magnetic activated carbon.^{29,32} Therefore, the effect of pH on the iron oxide content of the magnetic activated carbon produced in this study was examined between pH = 1 and 8. A significant change was observed in iron oxide content of the composite in the pH range 1 to 4.80. At pH 4 there was about 7 % loss in magnetization of the compos-

ite, which was due partial attack of acid on iron oxide. At pH 3 and 2, the loss in magnetization was 12 % and 32 % respectively, while at pH 1 the magnetization was totally lost due to dissolution of iron oxide by the acid. There were no significant changes in iron oxide content in the pH range 4.8 to 8. Therefore, the rest of the experiments were carried out in the pH range 4.8–8.0.

The effect of pH on the adsorption of imidacloprid was studied using 25 mg L⁻¹ of initial concentrations. Fig. 10 shows the variation of concentration with pH of the solutions. It is evident from Fig. 10, that there is no significant change in the concentrations of imidacloprid with pH. Similar results were reported by Daneshvar *et al.* (2007) for the adsorption of imidacloprid (pH = 4 and 7) from aqueous solutions on granular activated carbon.⁴¹

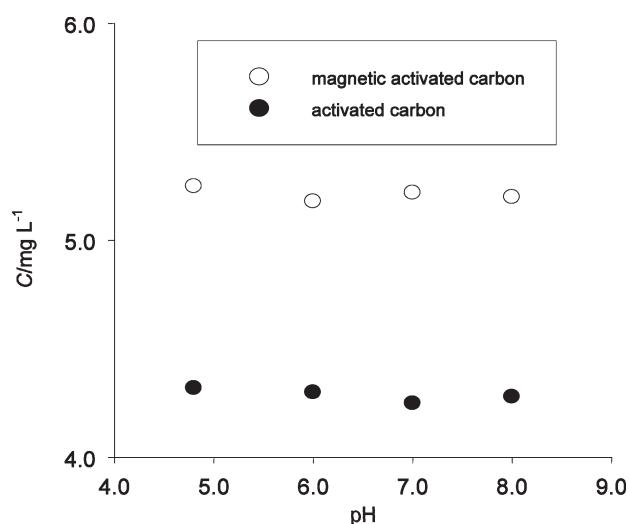


Fig. 10 – Effects of pH on adsorption of imidacloprid on powdered activated carbon and magnetic activated carbon

Adsorption kinetics

Effect of contact time

The variations of concentration with time for both adsorbents are seen in Figs. 11 and 12. The figures show the variation of the initial concentration of 25 and 50 mg L⁻¹ as a function of time. The equilibrium times for both initial concentrations are 45 and 50 minutes, while for MAC12 it is 35 and 40 minutes, respectively. It is clear from these values that the equilibrium time increases with the increase in initial concentration.

Adsorption kinetic model

The knowledge of adsorption kinetics is very important for the removal of pollutants from waters. In order to evaluate the values of the kinetic experi-

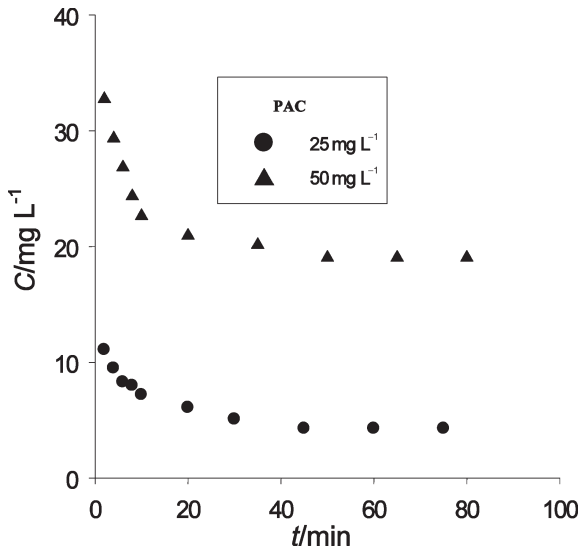


Fig. 11 – The variation of concentration of imidacloprid with time

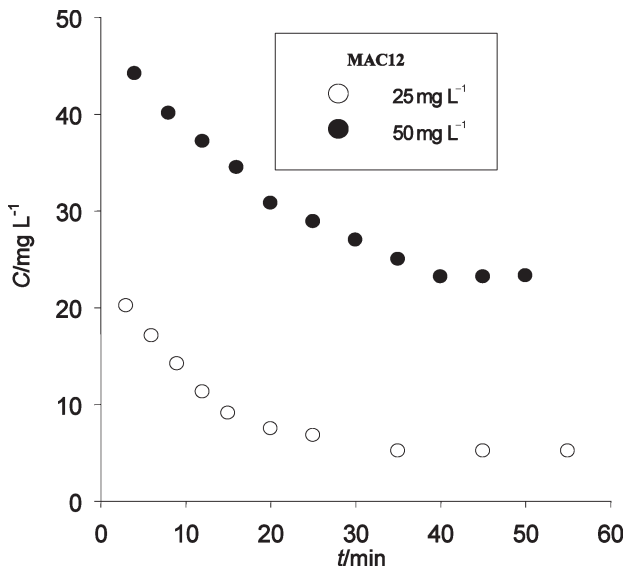


Fig. 12 – The variation of concentration of imidacloprid with time

ments, the Lagergren first-order⁴² and pseudo-second-order^{42,43} models were used. The best fit was obtained for pseudo-second-order equation. The pseudo-second-order equation can be expressed by the relation:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \left(\frac{1}{q}\right)t \quad (3)$$

Where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of adsorption, q (mg g^{-1}) is the amount of imidacloprid adsorbed at equilibrium, and q_t is the amount of imidacloprid adsorbed at time t .

The plots of t/q_t versus t are straight lines (Figs. 13, 14). The values of k_2 and q were calcu-

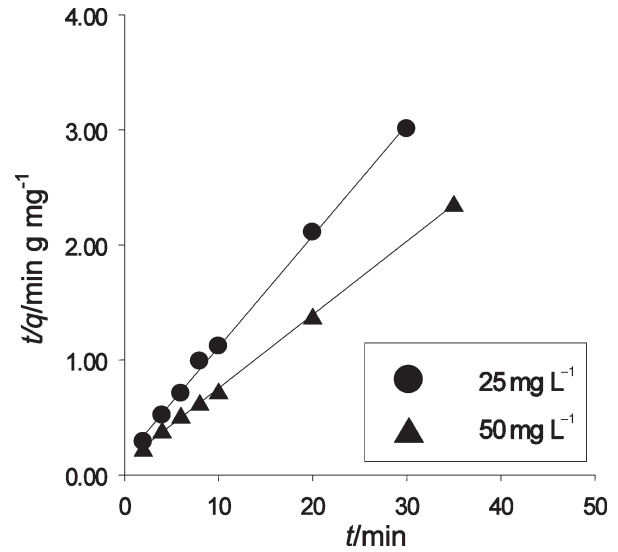


Fig. 13 – Second order kinetics plots for imidacloprid adsorption on PAC

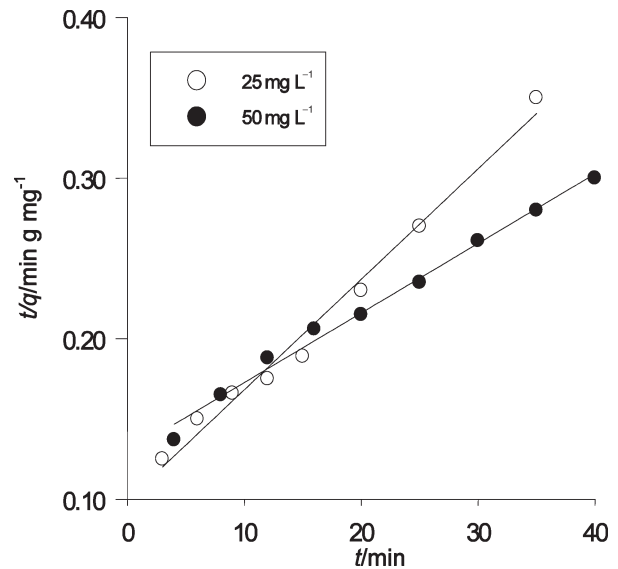


Fig. 14 – Second order kinetics plots for imidacloprid adsorption on MAC12

lated from slope and intercept of the straight line respectively. The values of k_2 and R^2 for the two adsorbents are given in Table 3.

Table 3 – Pseudo-second-order adsorption rate constants and correlation coefficients

Adsorbent	Initial concentration/ mg L^{-1}	Pseudo-second-order kinetic model	
		$k_2/\text{mmol}^{-1} \text{min}^{-1}$	R^2
Powdered activated carbon	25	0.064	0.99
	50	0.038	0.99
Magnetic activated carbon	25	0.043	0.99
	50	0.0129	0.99

Adsorption mechanism

The main steps in the removal of adsorbate by adsorbent in the adsorption process are: Transport of ingoing particles to the external surface of the adsorbent, transport of the adsorbate through the pores of adsorbent except for a small amount of the adsorption which occurs on the external surface (inter particle diffusion) and adsorption of the ingoing particles (adsorbate) onto the interior surface of the adsorbent. Among these, the rate-controlling step, which affects the overall removal rate, is the key step.

In order to determine the rate-controlling step, the kinetic experimental results were fitted to the Weber's intraparticle diffusion model:⁴⁴

$$q_t = k_{id}t_{1/2} + C \quad (4)$$

Where C is the intercept and k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intraparticle diffusion rate constant, which can be evaluated from the slope of q_t versus $t^{1/2}$ plot, as shown in Figs. 15 and 16. If the linear part of the curves passes through the origin, it can be considered that intraparticle diffusion is not the only rate-controlling process. The figures show an initial curve followed by the linear relationship. The initial curve can be explained by the boundary layer effect while the linear part corresponds to the intraparticle diffusion. The linear portions of the curves for both adsorbents do not pass through the origin; indicating that intraparticle diffusion is not the only rate-controlling step for the adsorption of imidacloprid in the system.

Thermodynamic parameters

Heat of adsorption (ΔH^0) and the change in entropy (ΔS^0) were calculated by Van't Hoff equation.

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

Where R is the universal gas constant, T is the absolute temperature, K is the distribution coefficient.

A plot of $\ln K$ against $1/T$ for each adsorbent yields a straight line (Fig. 17). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the straight lines, and are given in Table 4.

The Gibbs free energy change (ΔG^0) is related to the change in entropy ΔS^0 and the heat of adsorption (ΔH^0) at constant temperature as follows.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

It can be seen from Table 5, that ΔH^0 and ΔS^0 for both adsorbents have negative values, and ΔG^0

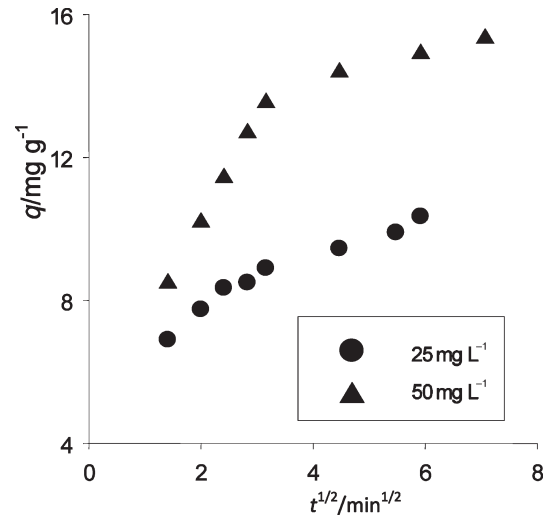


Fig. 15 – Plots of intraparticle diffusion for imidacloprid adsorption on PAC

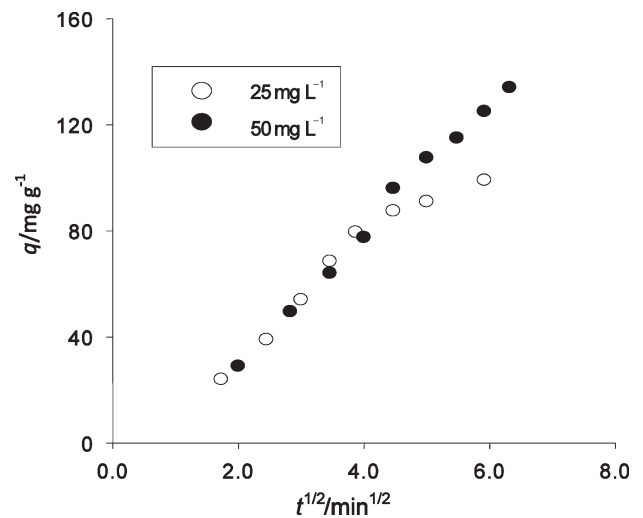


Fig. 16 – Plots of intraparticle diffusion for imidacloprid adsorption on MAC12

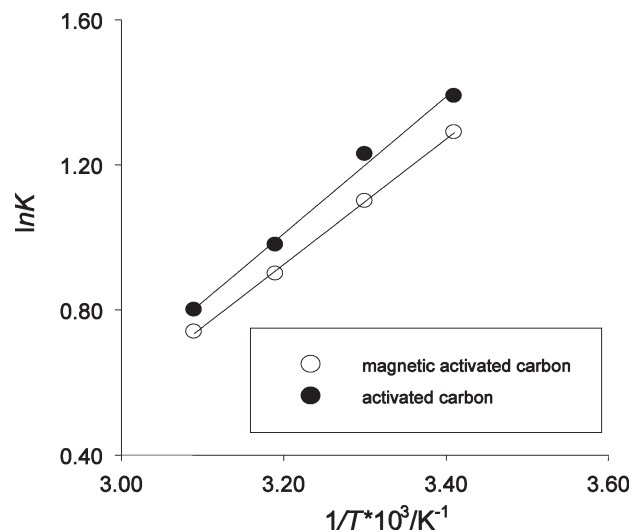


Fig. 17 – Van't Hoff plot for the determination of thermodynamic parameters

Table 4 – Thermodynamic parameters for both adsorbents

Adsorbent	$\Delta H^0/\text{J mol}^{-1}$	$\Delta S^0/\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta G^0/\text{J mol}^{-1}$			
			20 °C	30 °C	40 °C	50 °C
Powdered activated carbon	–15697	–41.73	–3470	–3053	–2635	–2218
Magnetic activated carbon	–14383	–38.33	–3141	–2769	–2386	–2002

also has negative values. The negative ΔH^0 value shows the exothermic nature of the overall sorption process. The negative value of ΔS^0 shows decreased randomness at the adsorbent and solution interface i.e. an increase in the order of the system. The negative values of ΔG^0 for both adsorbents indicate the spontaneity of the adsorption process. The negative values of ΔG^0 , ΔH^0 , and ΔS^0 were also reported for the adsorption of reactive red 189 on cross-linked chitosan,⁴⁵ lac dyeing on silk⁴⁶ and bromophenol blue adsorption by a mesoporous hybrid gel.⁴⁷

Conclusion

In this study, magnetic activated carbon was prepared from powdered activated carbon and iron oxide, and the adsorption capacity of the magnetic activated carbon for imidacloprid was measured. Measurements indicated that the surface area and micropores volume of powdered activated carbon were higher than that of magnetic activated carbon. The study shows that the equilibrium time for adsorption of imidacloprid on powdered activated carbon and magnetic activated carbon decreases with the decrease in concentration. The kinetics data fit well to pseudo-second-order kinetics model, while the equilibrium data fits well to Langmuir adsorption isotherm rather than the Freundlich model. The thermodynamic parameters for both adsorbents showed the feasibility of the adsorption process. Powdered activated carbon showed an H type curve, while magnetic activated carbon showed an L type. The pH of the solutions had no effect on the adsorption capacities of both adsorbents. However, at low pH the magnetic components of the iron oxide/PAC composite were lost due to dissolution of iron oxide. Magnetic activated carbon can be used to remove imidacloprid in treatment systems since they have high adsorption capacities and they can be separated easily from the medium by application of a magnetic field.

ACKNOWLEDGMENTS

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List of symbols

- q – amount of adsorbate adsorbed at equilibrium, mg g⁻¹
- q_t – amount of adsorbate adsorbed at time t , mg g⁻¹
- C – equilibrium concentration of the adsorbate, mg L⁻¹
- Q_0 – Langmuir constants related to maximum adsorption capacity, mg g⁻¹
- b – Langmuir constants related to energy of adsorption, L mg⁻¹
- K – Freundlich constants related to adsorption capacity
- n – Freundlich constants related to adsorption intensity
- k_2 – pseudo-second order rate constant of adsorption, g mg⁻¹ min⁻¹
- R^2 – correlation coefficient
- k_{id} – the intraparticle diffusion rate constant, mg g⁻¹ min^{-0.5}
- ΔH^0 – heat of adsorption, kJ mol⁻¹
- ΔS^0 – change in entropy, J mol⁻¹ K⁻¹
- ΔG^0 – Gibbs free energy change, kJ mol⁻¹
- R – universal gas constant, JK⁻¹mol⁻¹
- T – absolute temperature, K

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