Effect of Agitation Speed on Adsorption of Imidacloprid on Activated Carbon

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Summary: The adsorptive characteristics of imidacloprid on powdered activated carbon were described. The adsorption experiments were carried out as function of time, initial concentration and agitation speed. The equilibrium data fits well to Langmuir adsorption isotherm, while the kinetic data fits well to Pseudo second order kinetic model. The kinetic experiments were carried out at 200, 250, 300 and 350 rpm and it was found that the equilibrium time increases with increase in initial concentration and decreases with increase in agitation speed. This is due to the increased turbulence and as a consequence, the decrease boundary layer thickness around the adsorbent particles as a result of increasing the degree of mixing. At 300rpm the adsorption capacity was maximum and beyond this there was no significant increase in adsorption capacity. Weber intraparticle diffusion model was used to describe the adsorption mechanism. It was found that both the boundary layer and intraparticle diffusion for both adsorbents played important role in the adsorption mechanisms of the adsorbate. The effects of temperature and pH on adsorption were also studied. It was found that the adsorption capacity of the adsorbent decreases with increase in temperature. There was no significant change in adsorption from pH 2 to 8, however at high pH a decrease in adsorption of imidacloprid on activated carbon was observed.

Introduction

Imidacloprid [1-(6-chloro-3-pyridinylme-thyl)-*N*-nitroimidazolidin-2-ylideneamine] is used as a crop and structural pest insecticide, for seed treatment and for flea-control treatment. It works by disrupting nervous system of insects and kills the insects by contact and ingestion [1]. Imidacloprid has comparatively high water solubility (500 mg/L) and its half-life in soil is 48–190 days, however break down is faster with plant ground cover than in fallow soils [2, 3]. According to the US Environmental Protection Agency (USEPA), imidacloprid has the potential to leach to ground water. In addition to its high solubility and mobility, there are concerns for transport to surface water through dissolution in run-off [3]. Some of these concerns are: Imidacloprid has been shown to be persistent and its concentration did 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 USEPA to be a potential water contaminant [4, 5]. Imidacloprid is slightly toxic to fish, moderately toxic to aquatic invertebrates and is highly toxic to bees and house sparrow [6].

The various methods used for pesticides removal are: photo catalytic degradation [7, 8], combined photo-Fenton and biological oxidation [9], advanced oxidation processes [10], aerobic degradation [11], nanofiltration membranes [12], ozonation [13] and adsorption [14-22]. Amongst these, adsorption processes appear to be the best system for pesticide treatment, offering the possibility to remove a wide range of compounds [23]. Adsorption on activated carbon in natural and industrial systems is common everywhere in the world [24, 25]. Study of adsorption equilibrium and kinetics are important for the selection of suitable adsorbent, design of separation process and economical suitability of a process. Enough data is available for the equilibrium and kinetics in the literature, however little is known about the effects of agitation speed on adsorption [26]. The aim of this study was to determine adsorption parameters for the adsorption of imidacloprid on activated carbon and the effect of agitation speed on its adsorption kinetics.

Results and Discussion

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 model [27] 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 t equation (1):

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

(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 (Fig. 1).The values of Q_0 and b, calculated from the slope and intercept of the straight line are given in Table-1.
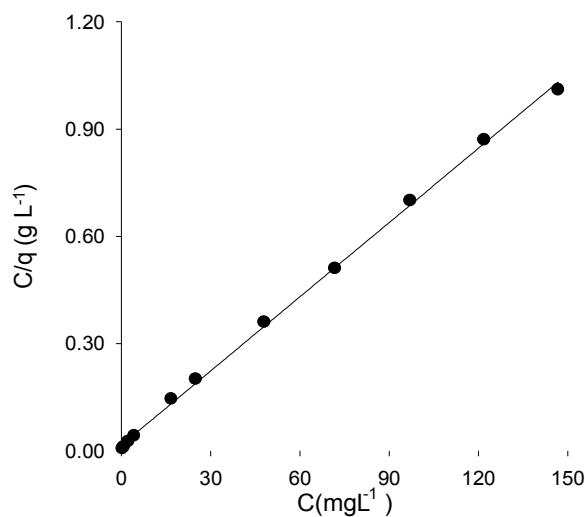

Fig. 1: Langmuir plot for the adsorption of imidacloprid on activated carbon.

Table-1: Isotherm parameters for adsorption of Imidacloprid on Activated Carbon.

Isotherm	Parameters
Langmuir:	
Q_0 (mg g^{-1})	144.93
b (L mg^{-1})	0.43
R^2	0.99
Freundlich:	
K	75.19
1/n	0.15
R^2	0.96

Freundlich Isotherm

The adsorption data for imidacloprid was also analyzed by the Freundlich model. The

Freundlich isotherm [28] is an empirical equation employed to describe heterogeneous systems. The logarithmic form of the Freundlich model can be written by the following equation:

$$lnq = lnK + \frac{1}{n}lnC$$

(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. lnq was plotted against lnC for the equilibrium data of imidacloprid and is given in Fig. 2. The Freundlich constants, n and K were calculated from slope and intercept respectively of the plot and are given in Table-1. The best fit was observed with the Langmuir model. The correlation coefficient value for this model is higher than that of Freundlich model.

The Giles Isotherm

Giles et al [29] classified sorption isotherms based on their initial slopes and curvatures. They distinguished between high affinity (H), Langmuir (L), constant partition (C) and sigmoidal-shaped (S) isotherm classes. Fig. 3 shows the Giles isotherm for imidacloprid. According to Giles classification, the shape of the obtained isotherm shows H2 isotherm. H curve is a special case of the L curve, in which the solute has a high adsorption affinity in dilute solutions. It is completely adsorbed and the first portion of the curve changes abruptly to a flat plateau.
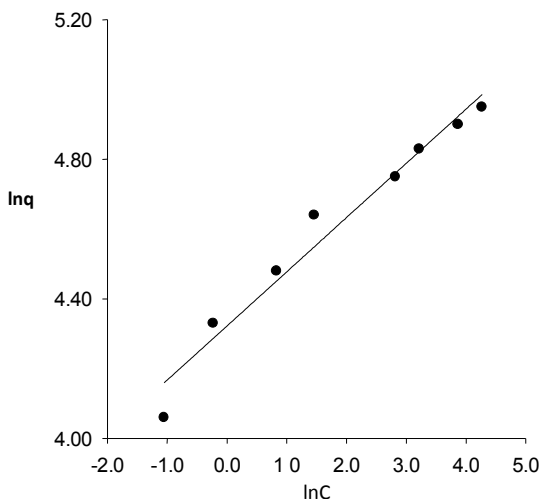

Fig. 2: Freundlich plot for the adsorption of Imidacloprid on activated carbon.

Adsorption Kinetics

Effect of Contact Time

The adsorption experiments were carried out as a function of time and agitation speed. Fig. 4 shows the variation of concentration with time at different agitation rates. The equilibrium time for both initial concentrations at different agitation rates are given in Table-2. It can be seen from the table that the equilibrium time increases with the increase in the initial concentration and decreases with the increase in the agitation speed. This can be explained by the fact that the film resistance to mass transfer surrounding the adsorbent particles is decreased by the agitation rate. The table shows that the equilibrium time for both initial concentrations decreases with the increase in the agitation rate up to 350 rpm. This can be explained by the increase in turbulence with agitation rate.
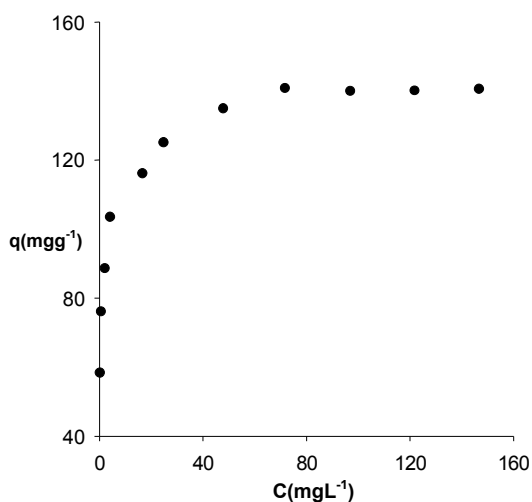

Fig. 3: Giles isotherm for adsorption of imidacloprid on activated carbon.

Table-2: Effect of agitation speed on equilibrium time for 25 and 50 mgL^{-1} imidacloprid solutions on activated carbon.

Agitation speed (rpm)	Equilibrium Time (min)	
	25 mgL^{-1}	50 mgL^{-1}
200	45	75
250	40	60
300	35	50
350	30	45

Effect of Agitation Speed

The effect of contact time on adsorption of imidacloprid on activated carbon at different agitation speed is given in Fig. 5. From Fig. 5 it is clear that the rate of adsorption increases with agitation speed. This is due to the fact that with the increased turbulence, there is a decrease in boundary layer thickness around the adsorbent particles. It can be seen from the figure that at 300 rpm the adsorption capacity of the adsorbent is maximum. Beyond this there is no further increase in the adsorption capacity of the adsorbent and also the equilibrium time increases as shown in Fig. 5. This means that for adsorption process there is optimum speed, which is to be investigated for every adsorbent.

Effect of Temperature

In order to make a comparative study for adsorption of imidacloprid on activated carbon at different temperatures, the adsorption experiments were carried out at 25 °C, 35 °C, 45 °C and 55 °C. The changes in imidacloprid concentration with time during the adsorption process at each temperature are shown in Fig. 6. The figure shows that the adsorption increases with decrease in temperature, indicating that the process is exothermic. The differences in removal efficiency of imidacloprid at different temperature originate from the effect of energy of reaction. The effect of temperature can be explained on the basis of solubility. With increase in temperature solubility increases and, therefore, exhibit lower tendency to go to the adsorbent surface and get adsorbed.

Effect of pH

The pH of the solution is one of the important parameters affecting the adsorption process. The effect of pH on imidacloprid adsorption was studied using 25mgL^{-1} of initial concentration, pH 2-11 at 25 °C (Fig. 7).

As seen, the removal of imidacloprid was almost constant from pH 2 to 8 and decreased with further increase in pH. pH affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. Imidacloprid is stable in acidic and neutral water but more readily hydrolyze in alkaline water [30]. The commercial activated carbons are classified into two groups: the carbon activated at low temperature (200-400 °C) is termed as 'L carbon' while carbon activated at high temperature (800-1000 °C) is termed as 'H carbon'. L carbon generally develop acidic surface sites that can adsorb OH$^-$ ions while H carbon (used in this study) develops basic surface sites consisting of carboxyl, phenolic, alcoholic and quinone groups that can adsorb H$^+$ ions [31]. At high pH imidacloprid hydrolyze and the adsorbent surface is more negative, which reduces the adsorption of imidacloprid.
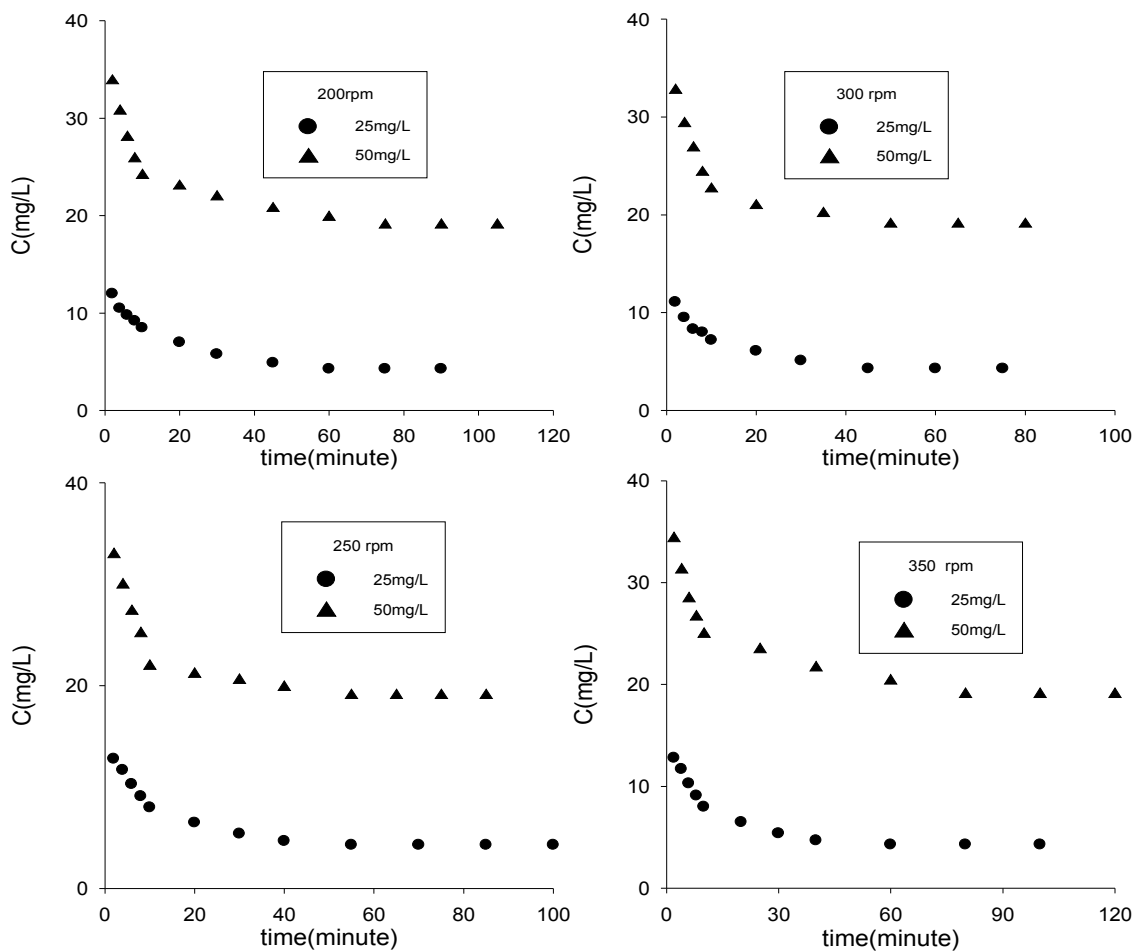
Fig. 4:   Variation of equilibrium concentration of imidacloprid with time at different agitation speeds.
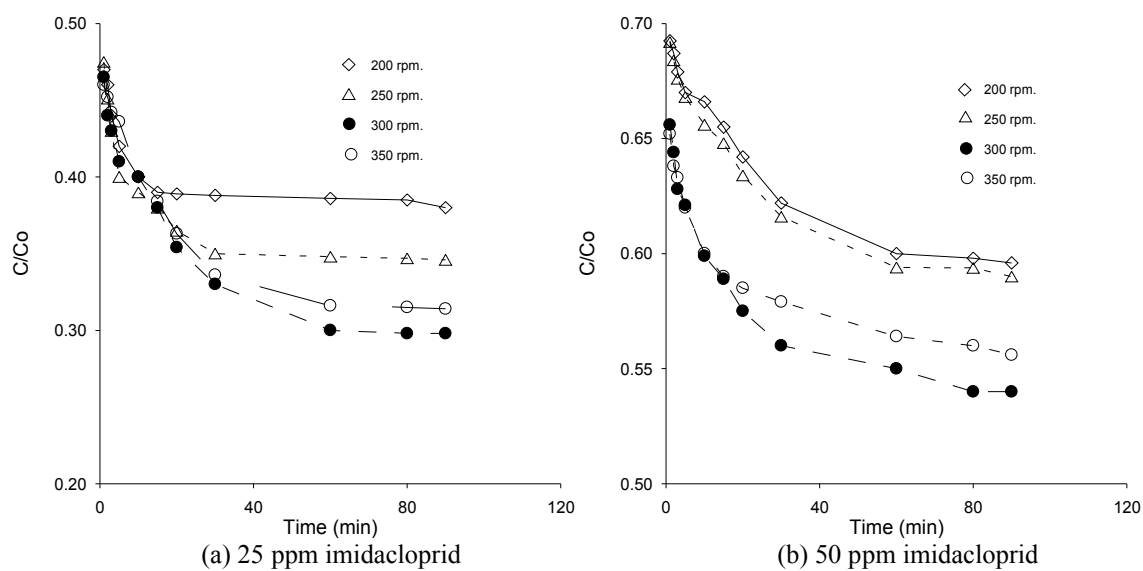

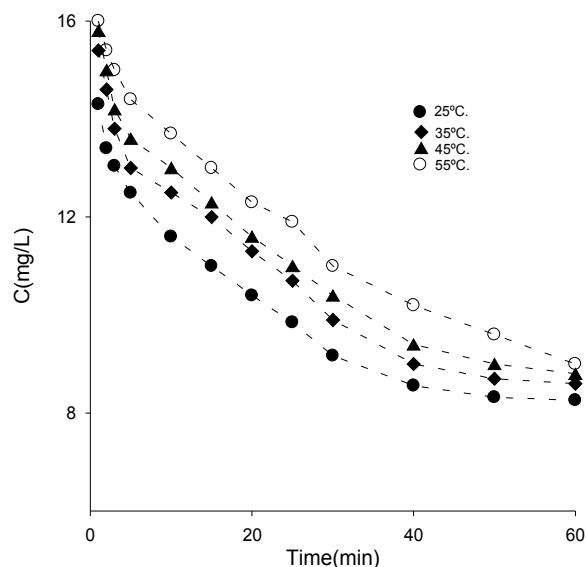Fig. 5. Effect of agitation speed on adsorption of imidacloprid by activated carbon.

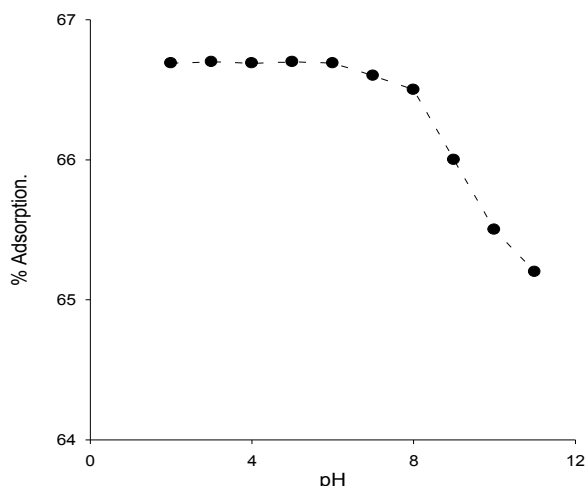Fig. 6: Effect of temperature on adsorption of imidacloprid by activated carbon.

Fig. 7: Effect of pH on adsorption of imidacloprid by activated carbon.

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 experiments, the Lagergren first order and pseudo second order [32, 33] models were used.

The Lagergren equation can be expressed by the equation (3):

$$\ln(q_e - q) = \ln q_e - k_a t \qquad (3)$$

where q_e and q (mg g^{-1}) are the amount of sorbed imidacloprid at equilibrium and time t respectively and k_a (min^{-1}) is the rate constant. This equation shows a linear relationship between ln (q_e –q) and t. The plot of ln (q_e – q) versus t is shown in Fig. 8.

The pseudo second order equation can be expressed by the relation:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \left(\frac{1}{q}\right)t \qquad (4)$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption, q (mg g^{-1}) is the amount of imidacloprid adsorbed at equilibrium and qt at time t.

The plots of t/q_t versus t are straight lines (Fig. 9). The values of k_2 and q were calculated from intercept and slope of the straight line respectively. The values of k_2 are given in Table-3.Table-4 shows that the adsorption kinetics at two different concentrations and agitation rates could be best explained in terms of the pseudo second order rate equation with precision in the correlation coefficients, while the Lagergren rate equation did not reflect the experimental results.

Table-3: Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants.

Initial concentration (mg L^{-1})	Agitation speed (rpm)	Pseudo First order kinetic model.		Pseudo second order kinetic model.	
		K_a	R^2	k_2	R^2
	200	0.039	0.95	0.046	0.998
25	250	0.047	0.92	0.055	0.998
	300	0.15	0.95	0.064	0.999
	350	0.75	0.95	0.039	0.998
	200	0.040	0.95	0.028	0.999
	250	0.051	0.93	0.026	0.994
50	300	0.15	0.96	0.038	0.998
	350	0.038	0.94	0.022	0.998

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) on to interior surface of the adsorbent. Amongst these the rate controlling step, which affect the overall removal rate is the key step.
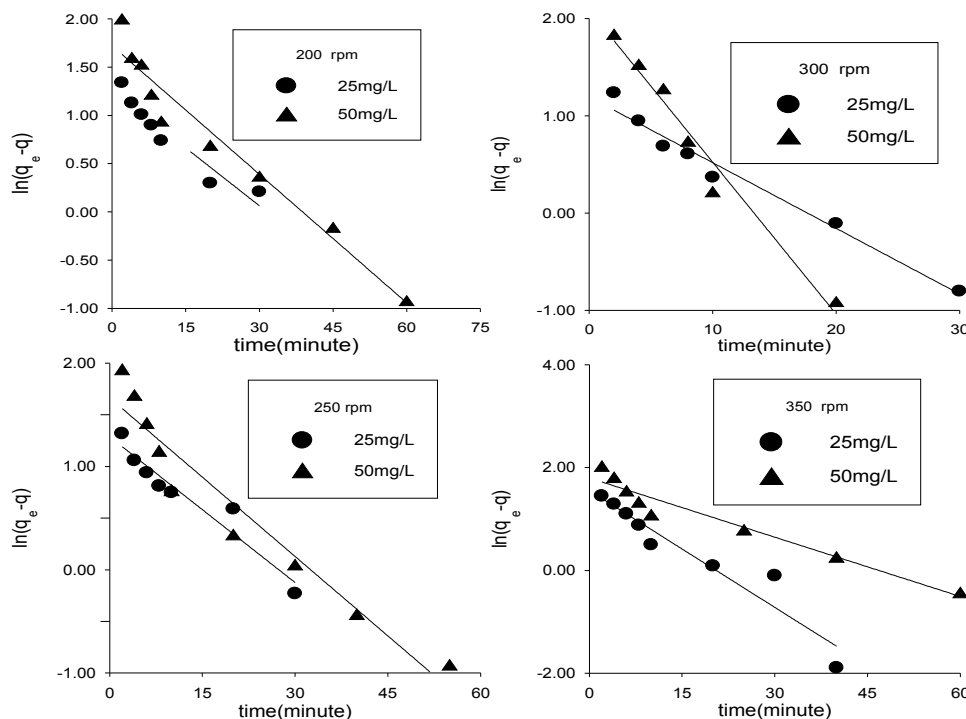
Fig. 8:   Pseudo first order kinetics plots for imidacloprid adsorption on activated carbon at different agitation speeds.
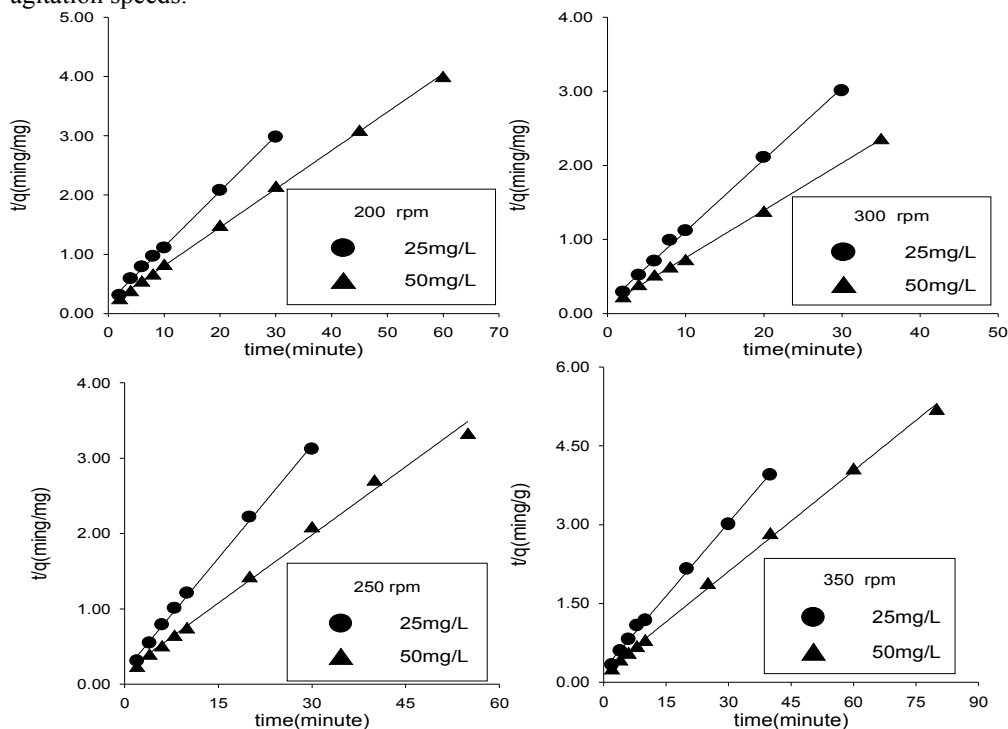

Fig. 9:   Pseudo second order kinetics plots for imidacloprid adsorption on activated carbon at different agitation speeds.

In order to determine the rate controlling step, the kinetic experimental results were fitted to the Weber's intraparticle diffusion model [34]:

$$q_t = k_{id} t_{\frac{1}{2}} + C \qquad (5)$$

where C is the intercept and k_{id} (mg g^{-1} min$^{-0.5}$) is the intraparticle diffusion rate constant, which can be evaluated from the slope of qt versus $t_{1/2}$ plot, as shown in Fig. 10. If the regression of q_t versus $t_{1/2}$ is

linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. In order to understand the kinetic mechanism, the amount of imidacloprid sorbed at time t, was plotted against the square root of time (Fig. 10). 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 do not pass through the origin; indicating that intraparticle diffusion is not the only rate controlling step for the adsorption of imidacloprid.
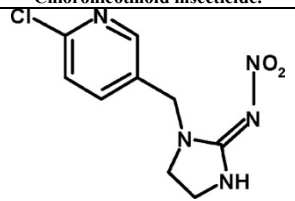
Experimental

A specially designed vessel with 12 L capacity was used. The vessel was charged with 3 L aqueous solution of imidacloprid and constant amount of activated carbon (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 to study the influence of agitation rate, varied from 200 to 350 rpm. Samples withdrawn at different time intervals using a syringe were analyzed by UV-Visible spectrophotometer at 270nm.

In order to determine the adsorption capacity of adsorbent, equilibrium experiments were carried out. Experiments were carried out in triplicate and mean values are presented. The error in the obtained results was within 1%.

Activated carbon (BET surface area 1150 m^2/g) used in the study was obtained from Norit. Activated carbon was washed with distilled water, dried at $105^{\circ}C$ and kept in air tight container. . Imidacloprid was obtained from Fluka and its characteristic properties are listed in Table-4.

Table-4: Properties of imidacloprid.

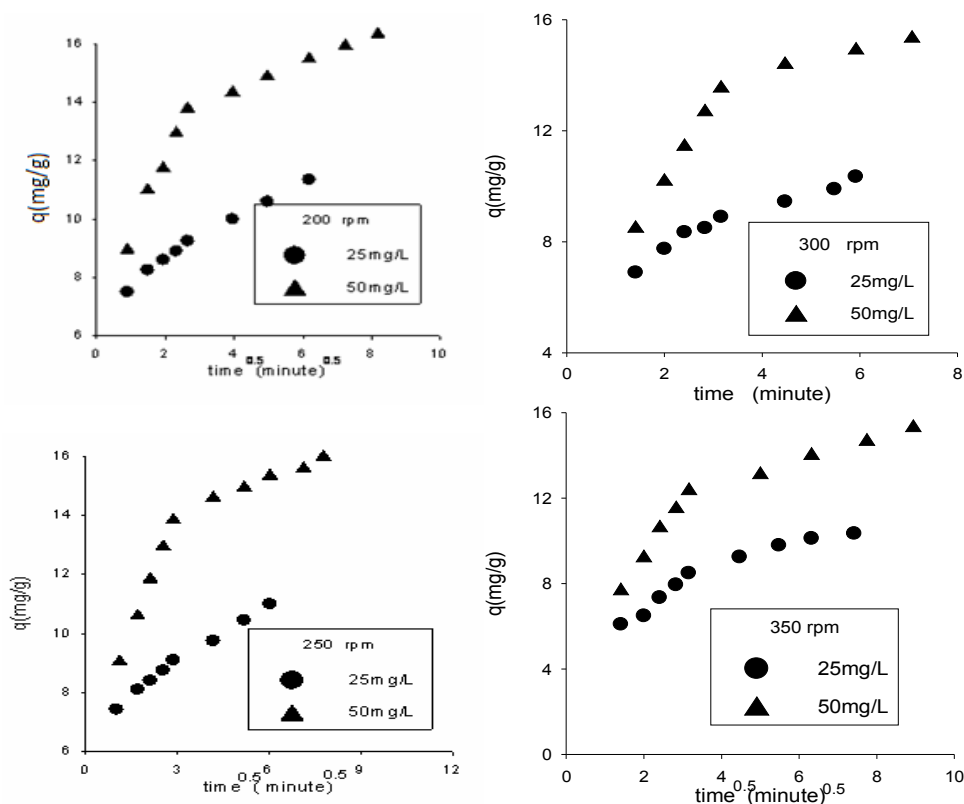| Chemical class.	Chloronicotinoid insecticide.
Chemical structure.	
Molecular weight.	255.7
Color	White (powder)
Water solubility.	5.14 x 102 ppm (20ºC at pH 7)
Rat acute oral LD_{50}	450ppm
λ_{max}	270nm

Fig. 10: Plots of intraparticle diffusion for adsorption of imidacloprid on activated carbon at different agitation rates.

Conclusion

The study shows that the equilibrium time for adsorption of imidacloprid on activated carbon decreases with the increase in the agitation speed of the agitator. The increase in agitation speed results in an increase in turbulence which decreases boundary layer thickness around the adsorbent particles. There is an optimum agitation speed for adsorption at which the adsorption capacity is maximum. Beyond that limit there is no further increase in the adsorption capacity. The kinetics data fits well to pseudo second order kinetics model and the equilibrium data fits well to Langmuir adsorption isotherm rather than Freundlich model. With the increase in temperature the adsorption of imidacloprid on activated carbon decreases. The pH of solution from 2 to 8 does not significantly affect the adsorption of imidacloprid on activated carbon. However at high pH the adsorption capacity of the adsorbent reduces.

Acknowledgement

References

1. L. Lagadic, B. Ludovic and L. Wolfgang, *Pesticide Science*, **4**, 29 (1993).
2. K. Scholz and M. Spiteller, *Brighton Crop Protection. Conference. Pests and Diseases*, **2**, 883 (1992).
3. USEPA, *EFGWB review of imidacloprid*, Washington, DC, (1993).
4. A. S. Felsot, W. Cone, J. Hu and J. R. Ruppert, *Bulletin of Environmental Contamination and Toxicology*, **60**, 363 (1998).
5. USEPA. Imidacloprid Pesticide Fact Sheet. Washington, D.C. (1994).
6. US Geological Survey. Circular 1225, Reston VA; USGS, 60(1999).
7. T. Aungpradit, P. Sutthivaiyakit, D. Martens, S. Sutthivaiyakit and A. A. F. Kettrup, *Journal of Hazardous Materials*, **146**, 204 (2007).
8. M. Mahalakshmi, B. Arabindoo, M. Palanichamy and V. Murugesan, *Journal of Hazardous Materials*, **143**, 240 (2007).
9. M. M.Ballesteros, J. A. Sánchez, J. L. García, L. Montes, J. L. Casas, I. Oller and S. Malato, *Journal of Hazardous Materials*, **155**, 342 (2008).
10. P. Saritha, C. Aparna, V. Himabindu and Y. Anjaneyulu, *Journal of Hazardous Materials*, **149**, 609 (2007).
11. H. M. Rajashekara and H. K. Manonmani, *Journal of Hazardous Materials*, **149**, 18 (2007).
12. A. L. Ahmad, L. S. Tan and S. R. A. Shukor, *Journal of Hazardous Materials*, **151**, 71 (2008).
13. M. I. Maldonado, S. Malato, L. A. Pérez-Estrada, W. Gernjak, I. Oller, X. Doménech and J. Peral, *Journal of Hazardous Materials*, **38**, 363 (2006).
14. C. F.Chang, C. Y. Chang, K. E. Hsu, S. C. Lee and W. Höll, *Journal of Hazardous Materials*, **151**, 295 (2008).
15. P. C. Mishra and R. K. Patel, *Journal of Hazardous Materials*, **152**, 730 (2008).
16. F. Li, Y. Wang, Q. Yang, D. G. Evans, C. Forano and X. Duan, *Journal of Hazardous Materials*, **125**, 89 (2005).
17. V. K. Gupta and I. Ali, *Environmental Science and Technology*, **42**, 766 (2008).
18. V. K.Gupta and I. Ali, *International Journal of Environment and Pollution*, **27**, 204 (2006).
19. V. K. Gupta, I. Ali, S. Suhas and V. K. Saini, *Journal of Colloid and Interface Science*, **299**, 556 (2006).
20. V. K. Gupta, C. K. Jain, I. Ali, S.Chandra and S. Agarwal, *Water Research*, **36**, 2483 (2002).
21. V. K. Gupta and I. Ali, *Water Research*, **35**, 33 (2001).
22. I. Ali and V. K. Gupta, *Natural Protocol*, **1**, 2661 (2006).
23. G. Crini, *Bioresource Technology*, **97**, 1061 (2006).
24. I. Langmuir, *Journalo f the American Chemical Society*, **40**, 1361 (1918).
25. S. Alam, F. Mabood, M. Sadiq, Noor-Ul-Amin and F. K. Bangash, *Journal of the Chemical Society of Pakistan*, **32**, 695 (2010).
26. S. Alam and F. K. Bangas, *Journal of the Chemical Society of Pakistan*, **31**, 705 (2009).
27. M. Ilyas and M. Saeed, *Journal of the Chemical Society of Pakistan*, **31**, 526 (2009).
28. H. Z. Freundlich, *The Journal of Physical Chemistry*, **57**, 384 (1906).
29. C. H.Giles, T. H. Macewan, S. N. Nakhwa and D. Smith, *Journal of Chemical Society*, **30**, 3973 (1960).
30. W. Zheng and W. Liu, *Pesticide Science*, **55**, 482 (1999).
31. Z. Aksu and E. Kabasakal, *Separation and Purification Technology*, **35**, 223 (2004).
32. S. Lagergren, *Handlingar*, **24**, 1 (1898).
33. Y. S. Ho and G. McKay, *Chemical Engineering Journal*, **70**, 115 (1998).
34. W. J. Weber and J. C. Morris, *Journal of the Sanitary Engineering Division Proceedings of the American Society of Civil Engineers*, **89**, 31 (1963).