Hindawi Publishing Corporation
Journal of Chemistry
Volume 2016, Article ID 8329650, 7 pages
http://dx.doi.org/10.1155/2016/8329650

Research Article

Comparative Study on Adsorptive Characteristics of Diazinon and Chlorpyrifos from Water by Thermosensitive Nanosphere Polymer

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Received 6 July 2016; Revised 7 September 2016; Accepted 15 September 2016

Academic Editor: José M. G. Martinho

Diazinon and chlorpyrifos are two common organophosphorus poisons to fight the pests in Iran. The removal of these poisons from water by thermosensitive nanosphere polymer (TNP), synthesized from the copolymerization of N-isopropylacrylamide and 3-allyloxy-1,2-propanediol, was investigated. The effect of pH, contact time, and the initial concentration on the removal amount was studied. The highest removal amount of these poisons by TNP occurred at pH 7. The contact time increase improves the removal amount and the equilibrium contact time for diazinon and chlorpyrifos was 10 and 18 min, respectively. For low concentration of less than 50 mgL^{-1} it was shown that removal capacity remains above 95%. The initial concentration above 50 mgL^{-1} decreased the removal amount, in which chlorpyrifos showed a greater decrease. The kinetic data has been checked using pseudo first-order, pseudo second-order, and intraparticle diffusion equations. The intraparticle diffusion model had the best conformability for the adsorption process.

1. Introduction

Today, due to the growing number of population and the lack of natural resources, an increase in the agricultural products along with their better qualitative conditions seems really integral. To do so, using poisons is unavoidable [1, 2]. The poisons used in gardens and fields include organochlorine, organophosphorus, carbamates, and pyrethroids, among which organophosphorus pesticides are the commonest [3]. According to the yearly report by Agricultural Jihad Organization of Guilan province, diazinon and chlorpyrifos are the most commonly used poisons of organophosphorus classification [4]. This is why they were considered in this study. Poisons move into the surface water resources or can penetrate into the soil layers and reach underground water reservoirs and contribute to their pollution [5]. In addition to these poisons' direct effects on human's well-being, they can enter human and other beings' food chains [6]. Organophosphorus pesticides can be easily absorbed through skin and digestive and respiratory systems [7]. There have been many reports through the years on poisons' effect on human immune system along with their carcinogenicity symptoms. So many people are exposed to a variety of diseases due to poisoning [8]. Because of the uncontrolled consumption of poisons and their entry into water resources, there should be a study on how to remove them from water. Different methods have been investigated to remove poisons, among which the commonest include oxidation [9, 10], ozonation [11–13], activated carbon adsorption [14–17], nanofilteration [18–20], irradiation techniques [21], biological method [22, 23], photocatalysis [24], Fenton treatment [25], and ultrasonic treatment [26–28].

Recently, noticeable improvements in smart polymers with diverse applications and qualities are achieved [29].

Smart polymers are synthetic polymers with unique physical and chemical characteristics which have lots of scientific and trade applications [30, 31]. The performed studies show that, in addition to their application in medical industries [32, 33], electrochemical industries [34, 35], and agricultural industries [36], smart polymers have newly attracted many scientists to examine their applications in environmental engineering. The removal of pollutants like nickel [37, 38], heavy metals [39–41], metal cations [42], calcium [43], and gold ion [39] is among the reported applications of smart polymer in environmental engineering.

Thermosensitive polymers are a group of smart polymers which generally show two types of behaviors toward temperature change. The first type of polymers becomes soluble with the temperature increase, which possess the upper critical solution temperature (UCST), and the second type is the thermosensitive polymers that become insoluble to the temperature increase, which possess lower critical solution temperature (LCST) [44, 45].

Of the thermosensitive polymers, N-isopropylacrylamide (NIPAM) is the commonest whose chemical structure includes amide and isopropyl belonging to hydrophilic and hydrophobic groups, respectively. This polymer has LCST around 32°C [46, 47]. At the temperature below LCST, water is considered as a proper solvent, in which polymer is expanded and the polymeric chains are in the form of a coil. At the temperature above LCST, water is considered insoluble for this polymer, in which water hydrogen bonds with amide groups are disturbed and the polymer starts to get shrunk and forms globules. LCST can be increased and decreased using NIPAM copolymerization with monomers of hydrophilic and hydrophobic groups, respectively [48].

Among all the thermosensitive copolymers and according to the previous work, the polymerization of NIPAM with 3-allyloxy-1,2-propanediol (APD) was introduced as an absorbent to adsorb and remove diazinon pesticide from water. This absorbent successfully removed a high percentage of diazinon poison from water. Furthermore, it exhibited a good reusability and was introduced as an environmentally friendly adsorbent [49].

In this study, the removal of chlorpyrifos, a halogenated organophosphorus pesticide, was investigated by (NIPAM-co-APD) adsorbent. Its removability was compared with that of diazinon which is a nonhalogenated poison under different environmental conditions. This paper also describes the diazinon and chlorpyrifos adsorption kinetics behaviors. The kinetic parameters of these poisons' adsorption process were determined and compared with each other.

2. Experimental

2.1. Reagents and Solutions. NIPAM, APD, ammonium peroxodisulfate (APS), N,N,N,N-tetramethyl ethylenediamine (TEMED), methanol, acetonitrile, all the inorganic acids (acetic acid, boric acid, and phosphoric acid), NaOH, and NaCl came from Merck (Darmstadt, Germany). To adjust pH between 5 and 9, a magic buffer was prepared with the combination of three acids (acetic acid, boric acid, and phosphoric acid) and NaOH with the concentrations of 0.04 and 0.1 moles/litre, respectively. Diazinon and chlorpyrifos pesticides were purchased from Sad Gol Gostar Asia Co., Tehran, Iran. The stock solutions of diazinon and chlorpyrifos were prepared in methanol (500 mgL^{-1}).

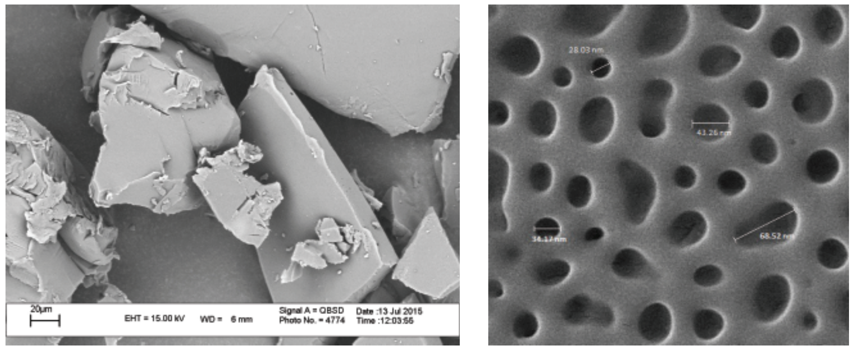
2.2. Synthesis of Sorbent. In order to synthesize this thermosensitive copolymer, 2 g NIPAM and 3 mL APD with 40 mL double distilled water were exposed to nitrogen gas for 15 min. The solution was degassed, put in an ice bath for 30 min, and, then, exposed to nitrogen gas for 15 min. After that, 450 mg APS and 60 mL TEMED were added and the solution was again put in the ice bath for 6 hours. Then, 5 mL of 0.6 molar NaCl was added to the achieved light yellow clear solution which was then placed in the 70°C hot bath. Further details on copolymer synthesis (NIPAM-co-APD) are available in previous study [49]. The residues in the achieved milky solution were separated by a centrifuge device (Hettich Zentrifugen, made in Germany) at 6000 rpm. The resulting residues were dried and powdered and the desired adsorbent was prepared.

2.3. Adsorption Procedure. 10 mL sample solutions with the desired concentration for each of diazinon and chlorpyrifos poisons were prepared out of their primary stocks (500 mgL^{-1}), being poured in separate tubes. Afterwards, 0.05 g TNP was added to the solutions. The desired pH was adjusted, using magic buffer. Having passed the time required to adsorb poisons by TNP, the tubes were placed in the hot bath at 70°C for 15 min. The solutions were centrifuged at 6000 rpm for 1 min and the supernatants were separated from the residues. The concentration of diazinon and chlorpyrifos in supernatants was measured by UV/visible scanning spectrophotometers (obtained by JENWAY spectrometer model 7315, Staffordshire, UK). According to the results, the removal amount of diazinon and chlorpyrifos was calculated.

3. Result and Discussion

3.1. Characterization of Copolymer. The structure of the copolymer was confirmed by elemental analysis Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer and Fourier transform infrared spectrometer (Bomem MB-Series Fourier transform infrared spectrometer, Quebec, Canada) tests. The study of elemental analysis results proved the presence of one unit of APD for every two units of NIPAM in each copolymer chain unit. Moreover, SEM images (Figure 1) of this copolymer show that there exist lots of nonmetric cavities at its surface. This is why this copolymer is known as a thermosensitive nanosphere polymer (TNP). According to the previous studies, NIPAM copolymerization with APD, which is a hydrophilic compound, increases the transition temperature from 32°C to 37°C [49].

3.2. Effect of pH. The adsorption amount of diazinon and chlorpyrifos by TNP was experimented at a range of pH = 5 to pH = 9 and the stable poisons concentration of 25 mgL^{-1} and 0.05 g TNP. All the tests were done with 30 min contact time



(a) (b)

Figure 1: SEM images of copolymer.

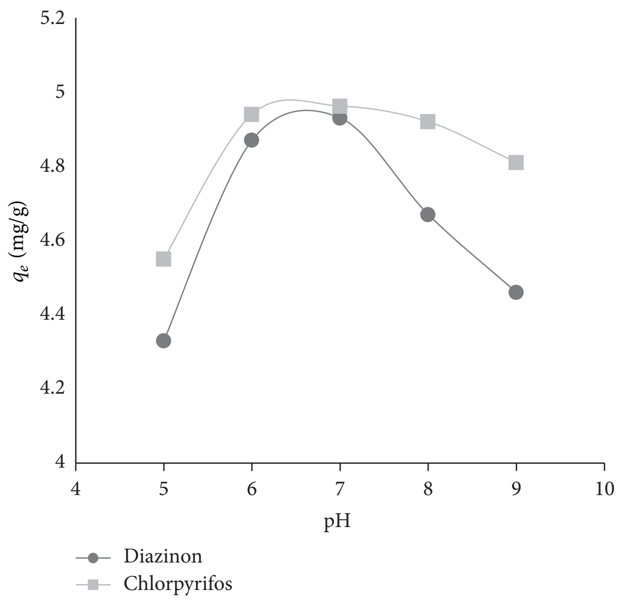


Figure 2: Effect of pH on adsorption of diazinon and chlorpyrifos by TNP.

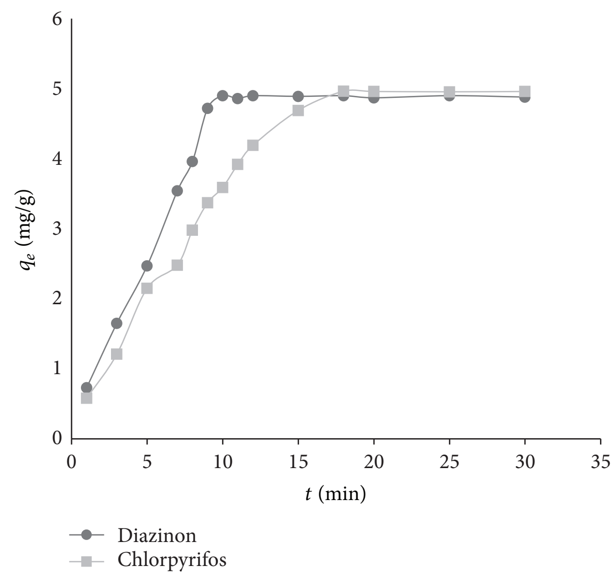


Figure 3: Effect of contact time on adsorption of diazinon and chlorpyrifos by TNP.

at the temperature around 25°C according to the previous report [49], the synthesized copolymer showed a better adsorption under LCST temperature, and, furthermore, the highest amount of adsorption was achieved at 20–25°C temperature domain [49]. The pH of solutions was adjusted at 5, 6, 7, 8, and 9 by the magic buffer. The procedure of poison adsorption from water was followed according to earlier discussions. As illustrated in Figure 2, higher poison removal is attained in acidic medium but the trend is reversed when pH increases above 7 (basic solution). The optimum removal capacity for both poisons is achieved when pH is 7 (neutral condition). This happens because of the power increase of hydrogen bonding for both these poisons at this pH. Therefore, in the next experiments, pH 7 was applied.

3.3. Effect of Time. The contact time is one of the essential parameters in the removal of pollutants. In this study, a series of sample solutions of each poison were considered at 25 mgL^{-1} concentration. 5 mgL^{-1} TNP was added to the solution at pH 7 and different contact times of 1 to 30 min were examined. Figure 3 shows the effect of contact time variation on the removal capacity of diazinon and chlorpyrifos poisons by TNP.

The results showed that the increase in the contact time increases the removal capacity of both poisons under study and the highest amounts of diazinon and chlorpyrifos adsorption were achieved at the contact times of 10 and 18 min, respectively. After the given times, the removal amount does not show any change. The results showed that this synthesized copolymer is able to adsorb the whole amount of poison which can be removed in a short time span. As can be seen in SEM images (Figure 1), these proper kinetics are due to the many nanometric cavities on the surface of the synthesized adsorbent which makes the quick adsorption of these poisons.

3.4. Effect of Initial Concentration. In order to investigate the initial concentration of the poisons on their removal capacity,

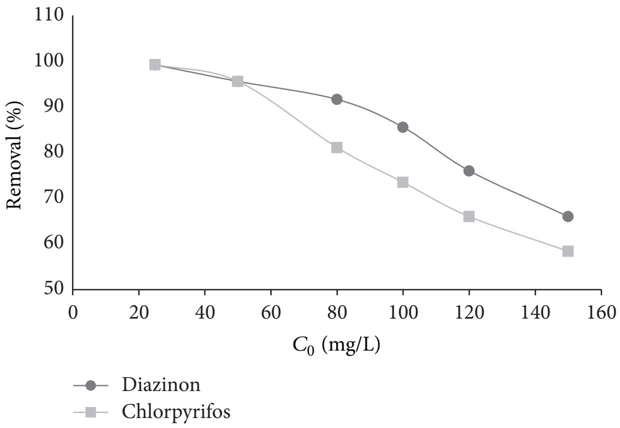


Figure 4: Effect of initial concentration on removal percentage of diazinon and chlorpyrifos by TNP.

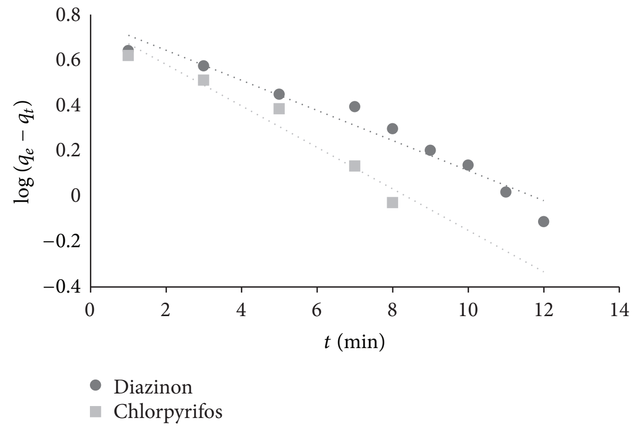


Figure 5: Pseudo first-order kinetic model for adsorption of diazinon and chlorpyrifos by TNP.

a series of sample solutions of diazinon and chlorpyrifos with the concentration of 25, 50, 80, 100, 120, and 150 (mgL^{-1}) were prepared out of their primary stocks (500 mgL^{-1}). These experiments were carried out with 0.05 gr TNP, at pH 7 and at the room temperature. The contact time was considered 10 and 18 min for diazinon and chlorpyrifos, respectively, which is the equilibrium contact time for the adsorption of these poisons by TNP. The effects of the initial concentration of the poisons on their removal amount by TNP are shown in Figure 4. The results show that, up to 50 mgL^{-1} of concentration, the removal amount for both poisons is above 95%; however, at higher concentrations, the removal amount decreases for both poisons. The decrease amount is more for halogenated chlorpyrifos in comparison to nonhalogenated diazinon which can be due to their molecular formation and chemical structure.

3.5. Adsorption Kinetics. In order to study the adsorption processes of diazinon and chlorpyrifos by TNP, three kinetic models, the pseudo first-order, pseudo second-order, and intraparticle diffusion models, were employed to describe the mechanism of adsorption.

The pseudo first-order kinetic model is expressed as

$$\frac{dq_t}{dt} = k_1 (q_e - q_t). \tag{1}$$

The linear form can be written as

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \tag{2}$$

and the pseudo second-order kinetic model is expressed as

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2. \tag{3}$$

The linear form can be written as

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

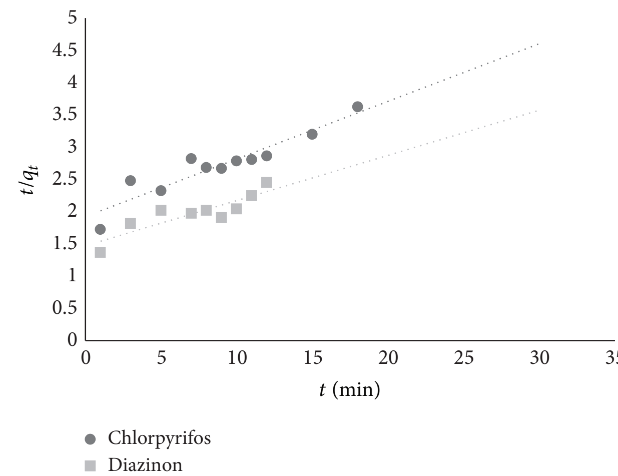


Figure 6: Pseudo second-order kinetic model for adsorption of diazinon and chlorpyrifos by TNP.

The intraparticle diffusion model is expressed as

$$q_t = k_{\text{dif}} t^{0.5} + C, \tag{5}$$

where q_t and q_e are the amount of pesticide adsorbed by the absorbent $(\mathrm{mg\,g}^{-1})$ at any time and at equilibrium, respectively. In these equations k_1 (min^{-1}) and k_2 $(\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1})$ are the equilibrium rate constants for the pseudo first-order kinetic and pseudo second-order kinetic model, respectively, and k_{dif} $(\mathrm{mg}\,(\mathrm{g\,min}^{0.5})^{-1})$ is the intraparticle diffusion rate constant.

The validity of the three models can be assessed from the linear plots of $\log(q_e - q_t)$ versus t (Figure 5), t/q_t versus t (Figure 6), and q_t versus $t^{0.5}$ (Figure 7).

Table 1 shows the predicted values of k_1, k_2, and k_{dif} from regression analyses and the correlation coefficient (R^2) for adsorption of diazinon and chlorpyrifos by TNP. Since the intraparticle diffusion model conforms well with the experimental data, this approach suggests that the adsorption of diazinon and chlorpyrifos by TNP is diffusion-controlled.

Table 1: Comparison of kinetic parameters for the adsorption of diazinon and chlorpyrifos by TNP.

Poisons	k_1 ($\min^{-1}$)		k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$)		k_{dif} ($\mathrm{mg\,(g\,min^{0.5})^{-1}}$)			
	k_1	R^2	k_2	R^2	k_{dif1}	${R_1}^2$	k_{dif2}	${R_2}^2$
Diazinon	0.2103	0.9545	0.0033	0.7693	2.1355	0.988	0.5615	0.9634
Chlorpyrifos	0.1524	0.9514	0.0042	0.874	1.6748	0.9844	0.5269	0.932

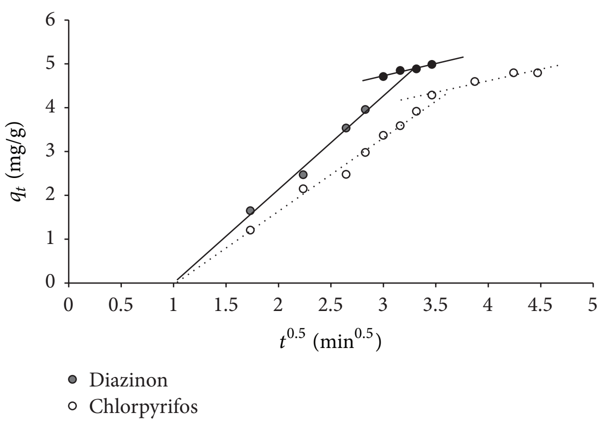


Figure 7: Intraparticle diffusion model for adsorption of diazinon and chlorpyrifos by TNP.

From Table 1, it can be seen that the adsorption rate was bigger in the first stage (k_{dif1}) than in the second stage (k_{dif2}) for both poisons (diazinon and chlorpyrifos), for which the slope of the plot had a significant change. Initially, the poisons are adsorbed by the external micropore sites of the TNP particles, so the adsorption rate was very high. When the adsorption of the microporous structure reached saturation, the molecules of poison were diffused in the nanopore structure within the particles and then were adsorbed by the internal surface of the TNP particles. When the poison is diffused in the nanopores of the particle, the diffusion rate decreased due to the increase of the diffusion resistance. In the final stage, the poison concentration was decreased and the diffusion rate became lower and the diffusion processes attained the equilibrium state. Thus, the changes in k_{dif1} and k_{dif2} are related to the adsorption phases of the external surface, internal surface, and the equilibrium stage.

4. Conclusion

This paper focuses on and compares the removals of two organophosphorus poisons, diazinon and chlorpyrifos, from water by synthesized copolymer. The results showed that TNP has a high ability to remove both of these poisons. High efficiency, ease of handle, and the short time of the removal process are of the advantages of this method. The removal amount of both these poisons by TNP has an increase with pH up to neutral condition. Furthermore, the increase in the contact time to the equilibrium state (10 min for diazinon and 18 min for chlorpyrifos) proved effective in the increase of the poisons removal and after the equilibrium contact time, the removal amount stayed approximately stable. The removal amount of these two poisons up to their initial concentrations of 50 $\mathrm{mgL^{-1}}$ was above 95%. However, the removal efficiency of these poisons decreased for concentrations above 50 $\mathrm{mgL^{-1}}$ and this decrease was more for chlorpyrifos. The study on the overall adsorption capacity and the comparison of the kinetic models was best described using the intraparticle diffusion model. Moreover, the obtained k_{dif} showed that diazinon had faster and more adsorption in comparison to chlorpyrifos.

Competing Interests

The authors declare that they have no competing interests.

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