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Removal of diazinon and 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solutions by granular-activated carbon

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ABSTRACT

In this paper, batch removal of diazinon and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution by granular-activated carbon was investigated. The required concentrations of toxins were prepared by appropriate dilution of the stock standard solution. There was a significant relationship between chemical oxygen demand (COD) and toxins concentration and that COD was measured instead of direct analysis of toxins. For all the concentrations tested, removal efficiency increased by increasing contact time for both toxins. The highest removal efficiency of 90% for 2,4-D and 88% for diazinon obtained in 50-min contact time. The highest value of toxin removal for both toxins occurred at pH=6. Based on the results obtained, one can conclude that granular-activated carbon has high efficiency in 2,4-D and diazinon removal from aqueous solution.

Keywords: Granular-activated carbon; Diazinon; 2,4-Dichlorophenoxyacetic acid; Adsorption; Aqueous solutions

1. Introduction

Increasing use of pesticides and improper sewage disposal may cause water resources pollution and extremely damaging effects on the environment [1,2]. The pesticides considered as persistent organic pollutants (POPs) are found in effluent of pesticide-producing industries and drainage of agricultural activities [3]. Used pesticides may percolate into water sources as a result of direct washing and irrigation [4,5]. 2,4-Dichloro phenoxyacetic acid (2,4-D) is a commonly used herbicide from phenoxyacetic acid category with weak aromatic characteristics. Its soluble derivatives have been extensively applied to eliminate broadleaf weeds in agriculture, parks, and pastures worldwide. 2,4-D toxin may endanger human and animal health through exposure to polluted air, earth, food, and water [6,7]. Diazinon is a type of organophosphate pesticides and volatile insecticide greatly applied to eliminate flies and ticks, especially O. tholozani tick. This toxin is widely used in farms and its residue could be found in underground waters and rivers [8–12]. Entering these pollutants into drinking water supply sources may cause human health and environment concerns. The incidence of their harmful

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effects varies depending on chemical material type, duration, exposure time, input concentration, and the amount of venom, [13,14]. Though 2,4-D toxicity is widely concerned, no study has confirmed its carcinogenic, mutagenic, and genetic side effects. Other symptoms on the central nervous system, however, may appear as motor incoordination, weak reflexes, and muscle stiffness as well as the coma and death probably due to increasing accumulation of the toxin in humans and animals [15–17]. Experimental studies have also confirmed hepatotoxicity of 2,4-D [18]. 2,4-D is known as endocrine venom [19] and different studies emphasized that the presence of hormonally active chemicals in municipal, industrial, and agricultural waste as well as their potential in turning back to the environment especially drinking water [20]. Some investigations have shown that pesticides causes abortion, mental retardation, teratology effects, and some defects in body tissues and actions. Organophosphate toxins like diazinon affect acetyl cholinesterase and lead to severe nervous side effects [10,12]. In addition, diazinon easily absorbed through the skin and holds a synergic characteristic with other toxins such as pyrethrines [21]. Thus, removing these pollutants from water sources seems indispensable. To achieve this aim, different methods such as adsorption processes [22,23], advanced oxidation processes including Fenton [24], photo Fenton [25], UV/H_2O_2 [26,27], UV/Tio [28,29], and anodic Fenton [30,31] adsorption have been applied to remove 2,4-D from water sources. Nowadays, adsorption method has in large extent been applied to treat surface water and groundwater. Activated carbon is derived from carbonation of different materials such as charcoal, wood, coconut bark or sawdust and exists in powder and granule forms [32]. In activated carbon, the adsorption process might not happen on a flat surface, but it is observable on thin-walled cavities distributed inside activated carbon [33]. Important factors affecting activated carbon efficacy include molecule weight, pH, pollutant concentration, particle size, flow rate, and temperature [34]. Activated carbon adsorbs taste and odor-producing organic compounds, synthetic organic compounds, humic materials, THMs, chlorine, and viruses [35]. In water supply systems (specifically water treatment plants), many strategies must be taken into consideration to remove these toxins where their quantities exceeds maximum allowed for drinking. Limited number of researches investigated the effectiveness of activated carbon on toxin removal and they also have paid attention to few practical factors affecting toxin removal process [22,23]. On the other hand, no such studies have been carried out in this area. This paper, thus, aims to survey effectiveness of granular-activated carbon in removing 2,4-D and diazinon from aquatic environments and elucidate practical effective factors of adsorption process.

2. Materials and methods

2.1. Preparation of toxins

Thousand milligram per litre of 2,4-D and diazinon were prepared using 98% pure reincarnation of 2,4-D with 1.2 g/cm^3 density and 60% solution of diazinon with 1.03 g/cm^3 density from Sigma Corporation, USA. Activated carbon of 2.5 mm in diameter was of analytical grade and obtained from Merck, Germany. Required concentrations of toxins were prepared by appropriate dilution of the stock standard solution and chemical oxygen demand (COD) was determined for all the samples.

2.2. Experimental procedures

Optimum pH was determined for the adsorption of 0.5, 1, 1.5, and 2 g of granular-activated carbon and analyte concentrations of 100 and 150 mg/l. For modification of the pH, 0.1 N HCl or NaOH were applied. For determining optimum contact time, each toxin at concentrations of 50, 100, and 150 mg/l was added into six beakers and mixed up with 3grams granular-activated carbon with contact times of 5, 10, 20, 30, 40, and 50 min. Finally, the content of beakers was completely blended. COD was measured for all 375 samples prior and after each experiment.

Each parameter in test conditions (e.g. pH=6 in certain concentration of toxin or absorbent dose) was examined three times and the results presented as means. COD was measured using Closed Reflex method by HACH COD reactor. pH was measured using pH-meter based on standard methods [36]. Data were analyzed by Pearson's correlation coefficient and ANOVA tests.

3. Results and discussion

3.1. Effect of concentration on COD of 2,4-D and diazinon samples

COD of both toxins increased with increasing the toxin concentration (Fig. 1). The maximum and minimum remaining COD concentration for 2,4-D were obtained at 150 mg/l (COD = 1,350 mg/l) and 1 mg/l (COD = 13 mg/l), respectively. Respective values COD for diazinon at 150 and 1 mg/l were 1,846 28 mg/l.

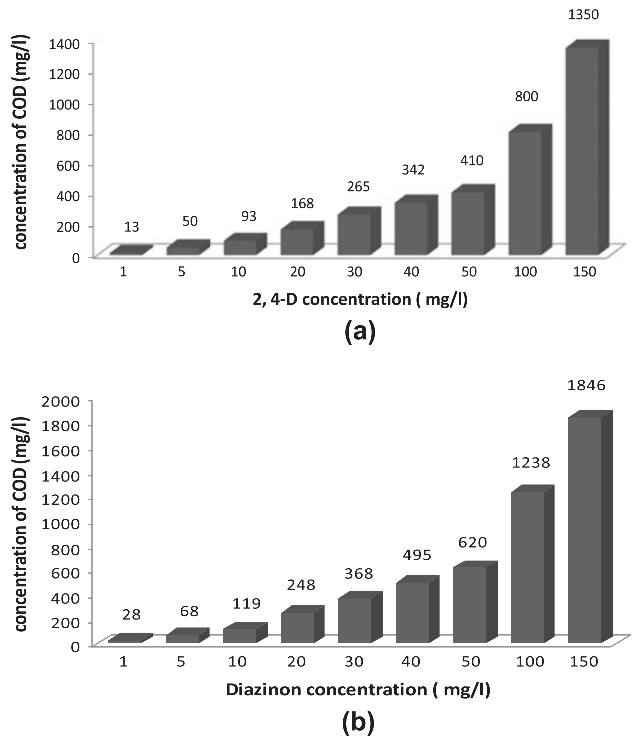

Fig. 1. Effect of 2,4-D (a) and diazinon (b) concentration on COD.

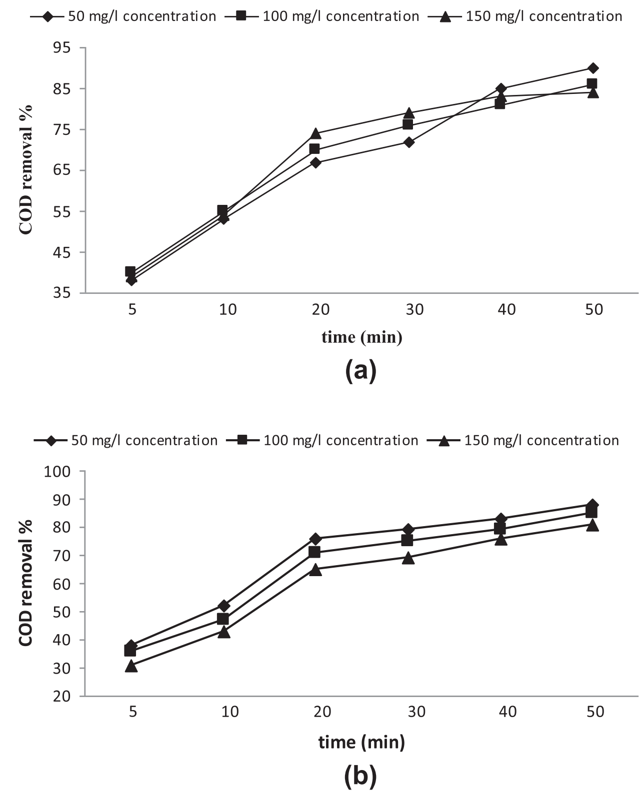

Fig. 2. The effect of contact time on COD removal in different concentrations of 2,4-D (a) and diazinon (b) by granular-activated carbon.

3.2. Effect of contact time

The effect of contact time on COD removal at different concentrations of toxins by granular-activated carbon is shown in Fig. 2. COD removal increased with increasing the contact time but the removal of COD decreased by increasing the toxin concentration. The maximum and minimum COD removal for 2,4-D occurred in contact time of 50 min and concentration of 50 mg/l (90%) and contact time of 5 min and concentration of 150 mg/l (38%), respectively. The highest COD removal for diazinon was in contact time of 50 min and 50 mg/l concentration (88%) and the lowest occurred in contact time 5 min and concentration of 150 mg/l (31%).

3.3. Effect of pH

COD adsorption was studied as a function of pH over a pH range of 5–9 on granular-activated carbon with adding constant concentration of 100 mg/l toxins as shown in Fig. 3. Moreover, the rate of COD removal by granular-activated carbon was determined at toxins concentration of 150 mg/l at pH of 6 and 7 with adding 1, 2, and 3 grams of activated carbons (Fig. 4). The highest value of toxin removal occurred at pH=6.

3.4. Effect of adsorbent dose

COD removal at different toxin concentrations increased by increasing adsorbent dose from 1 to 10 g/l (Fig. 5). Maximum COD removal efficiency for 2,4-D was observed on analyte concentration of 10 mg/l and activated carbon mass of 10 grams (83%) and the minimum efficiency occurred at 1 gram activated carbon and 50 mg /l toxin concentration (6%). Similarly, the maximum and minimum efficiency of COD removal for diazinon related to 10 grams activated carbon at 10 mg/l toxin and activated carbon of 1 gram at 50 mg/l toxin concentration, respectively.

3.5. Correlation between COD and 2,4-D and diazinon concentration

There were significant relationships between COD and toxins concentration ($r = 99.8$), and therefore, direct measurement of the toxin concentrations could be altered by COD quantification (Fig. 6). ANOVA test showed significant differences between obtained efficiencies at different experiment conditions (pH, toxin concentration, adsorbent dose, and contact time)

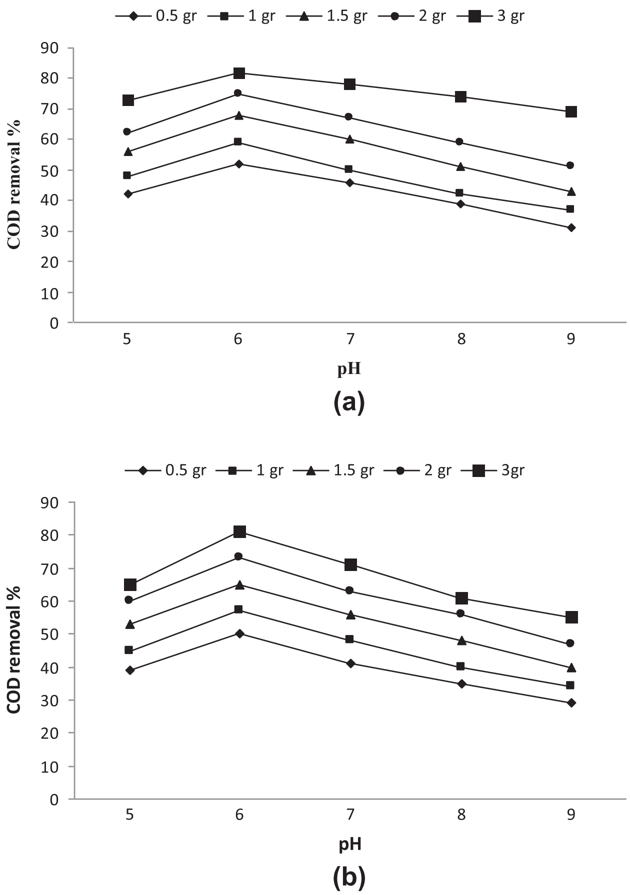

Fig. 3. COD removal in pH range of 5–9 by different dosages of granular-activated carbon at constant concentration of 100 mg/l 2,4-D (a) and diazinon (b).

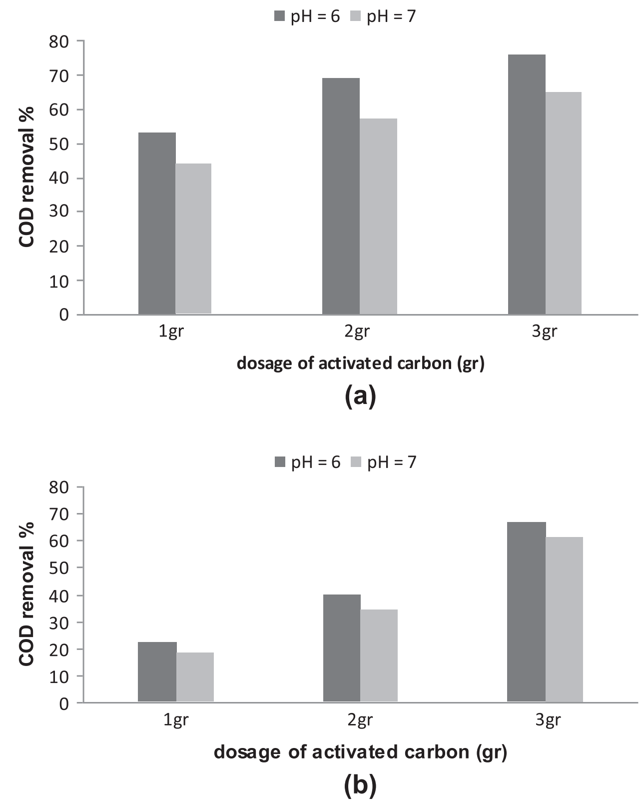

Fig. 4. COD removal in pH of 6 and 7 by different dosages of granular-activated carbon at constant concentration of 150 mg/l 2,4-D (a) and diazinon (b).

($p < 0.05$) and Pearson's correlation coefficient between toxin concentration and value of COD was 99.8%.

Results indicated that by increasing mass of 2,4-D and diazinon, COD concentration increases that approves a direct and positive correlation between COD and toxins concentration. Thus, test of COD can be used to measure remaining toxin. Contact time considered as an important parameters in removing pollutants. Removal efficiency of activated carbon was increased by increasing contact time for all the toxin levels. As the highest removal efficiency was observed in 50 min contact time, at this contact time, removal efficiency at 50 and 150 mg/l concentration of 2,4-D and diazinon were 90 and 88%, and 84 and 81%, respectively. Daneshvar et al. found that the efficiency of diazinon removal by UV/ZnO increases by rising contact time [37]. Buenristro also concluded that the efficiency of 2,4-D removal by membrane bioreactor increases when contact time increases which is in agreement with findings of present study [38]. The ANOVA results showed significant difference ($p < 0.05$) in efficiency of adsorbent in removing toxin at initial concentration of 100 mg/l and different pH by different mass of activated carbon. The optimum pH of 6 was found for removing 2,4-D in all masses of granular-activated carbon where the maximum removal of 2,4-D and diazinon with 3 grams adsorbent were 82 and 81%, respectively. Buenrostro-Zagal et al. studied 2,4-D removal by membrane bioreactor with filled bed of granular-activated carbon at pH 6, 7, 8 and reported the highest removal efficiency to occur at pH=8 [38].The reason for such salient difference may refer to the differences in removal method.

In a membrane bioreactor, toxins are removed biologically and microbes biodegrade organic materials significantly at neutral and slightly alkali pH. Evaluation of combined effect of toxin concentration and granular-activated carbon mass on removal efficiency of toxins by adsorption system showed that increasing toxin concentration traced no outstanding effect in adsorption rate in certain mass of added activated carbon. However, when the mass of granular-activated carbon increased the rate of toxins adsorption was also increased. Therefore, the highest removal for variable toxin concentration achieved at granular-activated

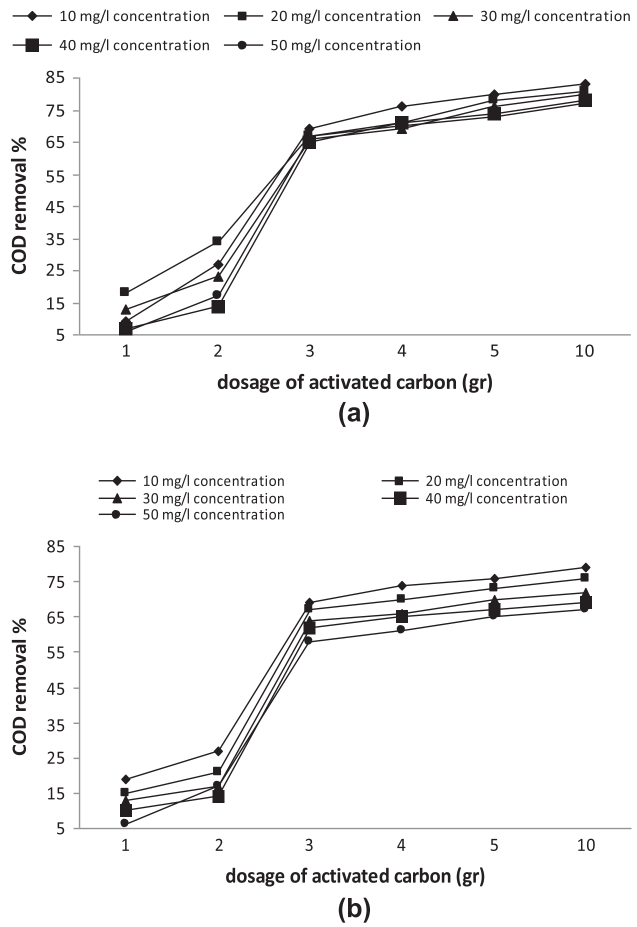

Fig. 5. COD removal at different concentrations for 2,4-D (a) and diazinon (b) at different granular-activated carbon dose (pH=6).

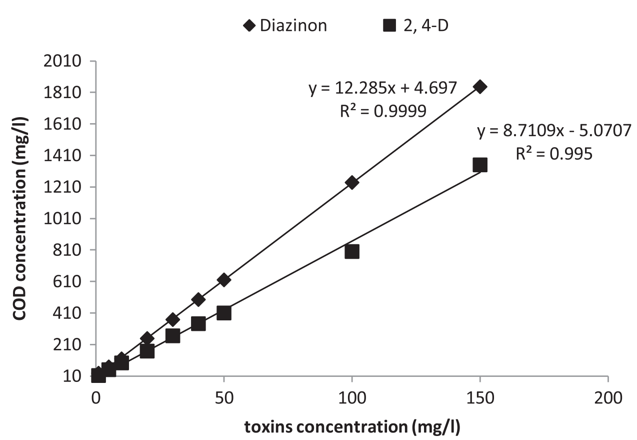

Fig. 6. Correlation between 2,4-D and diazinon concentration and COD concentration.

carbon mass of 10 grams. Samadi et al. examined diazinon removal by UV/O3 at pH 6, 7, 9 and found the maximum removal of toxin to occur at pH=9 [39]. The removal method applied may explain the reason for the difference observed for in these studies. In UV/O3 method, the production of hydroxyl radicals rises in alkali environments [40], while in adsorption system, H + ion production which itself known as an adsorbent agent resulted at acidic condition. Bazrafshan showed toxin removal to increase significantly by electrocoagulation process at pH=3 and contact time of 60 min [41]. Aksu and Kabasakal, and Chingombe et al. used activated carbon for 2,4-D adsorption from water and found that activated carbon to adsorb efficiently these toxins [22,23]. Koichi et al. findings indicated that activated carbon seems to be a proper choice in removing diazinon from water [42]. These results are in good agreement with the findings of current study. Generally speaking, activated carbon absorbs 2,4-D more efficiently than diazinon.

4. Conclusion

Survey of combined effect of toxins concentration and granular-activated carbon on removal efficiency of 2,4-D and diazinon toxins by adsorption system showed that increasing concentrations of toxins did not significantly increase the toxin adsorption at specified activated carbon dose. If the amount of granular-activated carbon increases, the elimination of toxins increases which is due to increasing adsorption process. So the highest removal rates of toxins in their initial concentration happened at the activated carbon mass of 10 g and pH: 6. Also, this study demonstrated a significant correlation between COD measurement and 2,4-D and diazinon concentrations. Therefore, COD measurement can be used instead of direct measurement of toxin concentration. Generally, activated carbon removes 2,4-D more efficiently than diazinon.

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