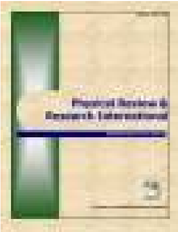

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Adsorption of 2,4-D on Carbonized Chest Nut Shell

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Authors' contributions

This work was carried out in collaboration between all authors. Author JG designed the study, and wrote the first draft of the manuscript. Author SA managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

The adsorption of 2,4-D (dichlorophenoxyacetic acid) in $4x10^{-4}$ and 10^{-3} mol/l aqueous solutions on carbonized chest nut shell (CCS) was studied at 25ºC. The effect of temperature was also studied at 25 and 35ºC for the concentration of 10^{-3} mol/l. The adsorption data was modelled by using Langmuir and Freundlich isotherms. The adsorption data fit well with Freundlich isotherm that indicates the pesticide adsorption is heterogeneous type and multi layer characteristics.The effect of pH on adsorption was also studied. The adsorption capacity is quite high in acidic medium (pH=3). Different pesticide concentrations were studied at this pH from the point of pesticide removal. The carbonized chest nut shell was a good and cheap adsorbent which can be utilized in the place of active carbon.

Keywords: Active carbon; 2,4-D; isotherm; pH.

1. INTRODUCTION

Pollution of surface and ground waters causes risk to human health in the case of the potential health hazards of their constituents of anorganic and organic compounds. Pesticides are like hazardous compounds that cause water pollution due to their extensive application for rodenticides, insecticides, acaricides, repellants, fungicides, algicides,

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herbicides, etc. The common usage of these chemicals has some undesirable effects such as toxicity, carcinocity and mutagenity [1,2,3]. Among the numerous agrochemicals, the herbicide 2,4-D has been applied to control plants in gardens and in agriculture. It is used for low cost and good selectivity. The maximum allowable 2,4-D concentration must be under 100 ppb in drinking water due to toxic effect and poorly biodegredable characteristics. It is extremely diffucult for applying a single method for pesticide disposal due to wide range usage. Adsorption on solid substances such as soils, clays, microorganisms or activated carbon can be used for removing pesticides from waters [4-10].

Adsorption is a fast, inexpensive and universal method. The development of low cost adsorbents has led to the rapid growth of research interests in this field. Gupta nad Ali [11] describes salient features of adsorption and details experimental methodologies for the development and characterization of low cost adsorbents, water treatment and recycling using adsorption technology including batch processes and column operations. They describes the development of inexpensive adsorbents from waste materials, which takes only 1-2 days, and an adsorption process taking 15-120 min for the removal of pollutants. The applications of batch and column processes are presented, along with suggestions to make this technology more popular and applicable.

Adsorption process is efficient for the removal of colors, odors, organic and biologic materials from process. Activated carbons are the most widely used adsorbents from the point of their excellent adsorption abilities [12]. The high adsorption capacities of activated carbons are mostly related to their high surface area, pore volune and porosity [13]. The activation method and the nature of source materials play the important role for removing the undesired materials efficiently [14,15]. Imran Ali used the nanoparticles for removal of toxic metal ions like As, Cr (III), Cd, Cu, Se, etc. from waste water [16,17]. Imran Ali et al. discussed the low cost adsorbents like fly ash, sugar industry wastes, rice husk, fertilizer wastes, peat moss, red mud, zeolites, sediment, etc. for the removal of organic pollutants from waste water [18]. He also mentioned the column operations for water treatment purposes for the removal of inorganic and organic pollutants [19].

There has been an increasing interest for removal of undesired molecules on activated carbons. This is due to the importance of discharging the pollutants from water streams and the atmosphere [20]. The adsorption process depends on several factors such as the nature of adsorbent, adsorbate and adsorption conditions. Adsorbent characteristics include the surface area, pore size distribution, ash content, hydrohobicity, the density and type of functional groups present on the surface. The nature of adsorbate depends on its polarity, its hydrohobicity, the size of the molecule and its acidity or alkalicity. The alkalicity is determined by the nature of the functional group present. Adsorption conditions include several factors such as temperature, the polarity of solvent, pH, concentrations, etc [21].

The aim of this work was to remove of 2,4-D by activated carbon made of chest nut shell with the effects of several factors such as temperature, concentration, pH, pesticide dose, etc.

2. MATERIAL AND METHODS

2.1 Materials

The 2,4-D was supplied in powder form by Hektas chemical company in Turkey. The chemical formula of 2,4-D is shown in Fig. 1 below. The molecular weight of 2,4-D (2,4-

diclorofenoxyacetic acid) is 221.04 g/mol. It is a solid organic substance which comes as a white powder with a melting point of 140.5ºC. Its solubility in water is 900 mg/dm³ and it is used on weeds with broad leaves. It is the most widely used herbicide in the world [22].

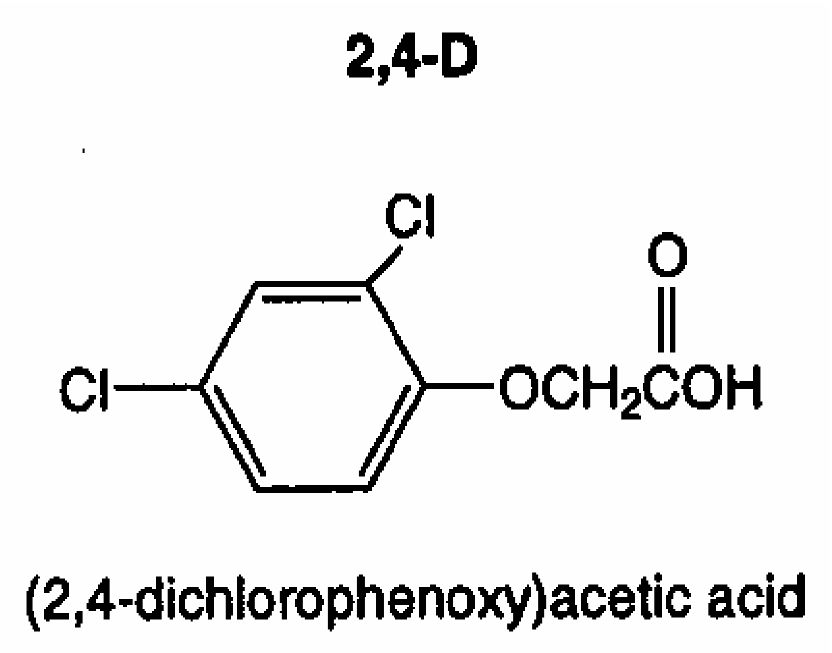

Fig. 1. 2,4-D [23]

2.2 Preparation of the Adsorbents

Carbonized chest nut shell (CCS) was used in the experiments. The chest nut shell was carbonized in an oven at 900ºC. 20 gr of shell were placed in the oven and carbonized under a stream of nitrogen. At the end of the heating period, the product was cooled to room temperature under nitrogen stream and the reactor was opened. Following this procedure, the carbonized material was ground and passed through 0.250 microns. Fig. 2 shows the SEM graphics of CCS at the beginning (a), after carbonization stage (b) and after the experiment (c). The surface area of CCS was 280.42 m^2/g and was measured with Micromeritics Flowsorb II-2300. The grounded particles was used for taking the advantage of micropores.

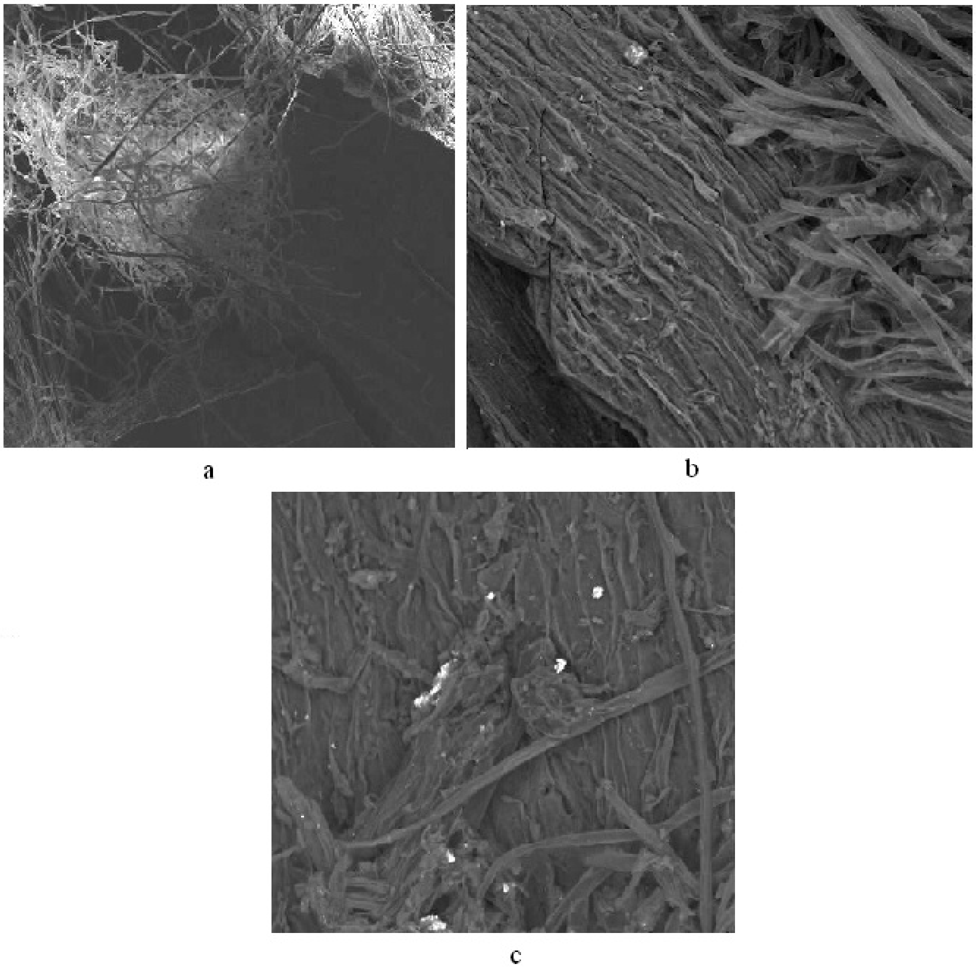

Fig. 2. SEM graphics of chest nut shell a) At the beginning b) After carbonization treatment c) After experiment in 2,4-D solution) (a, 500 µm, b and c 50 µm were drown)

2.3 Adsorption Studies

A stock solution was prepared by dissolving 0.22 g 2,4-D in a liter of demineralized water as 10^{-3} g/l solution. The experimental solutions were prepared by dilution of this stock solution with deionized water to obtain concentrations of $1x10^{-4}$, $2x10^{-4}$, $4x10^{-4}$, $6x10^{-4}$ $8x10^{-4}$. The adsorbance-calibration data were derived from these solutions.

In the batch method, a fixed amount of adsorbent (0.1 g activated chest nut shell) was added to 100 ml solutions of 10^{-3} at 25 and 35ºC. The solution was stirred with a magnet for 30 minutes following which the concentration of pesticides after equilibrium adsorption was determined spectrophotometrically at λ_{max}=280 nm on a double beam 150-02 Shimadzu.

3. RESULTS AND DISCUSSION

3.1 Contact Time and Initial Adsorbate Concentration

The effect of initial 2,4-D concentration on adsorption on CCS was studied. Fig. 3 shows the contact time of 2,4-D for $4x10^{-4}$ and 10^{-3} M initial concentrations at 25ºC. The adsorption becomes almost constant after 250 minutes.

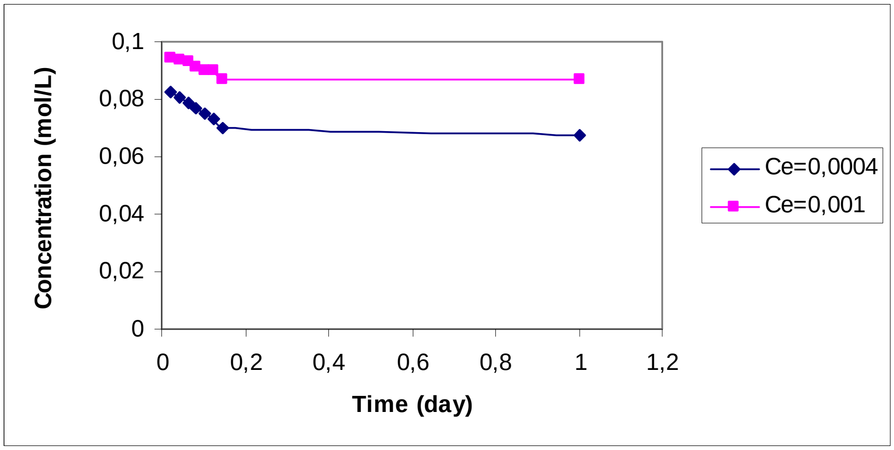

Fig. 3. Equilibrium concentrations versus time at 25 ºC temperature, adsorbent dose 0.1 g(100 ml) (C_0=10^{-3} M and $4x10^{-4}$ M concentrations)

3.2 Temperature Effect

The effect of temperature on adsorption on CCS was studied. Fig. 4 shows the temperature effect of 2,4-D for 10^{-3} M initial concentration at 25 and 35ºC. The system reached the equilibrium almost after 250 minutes.

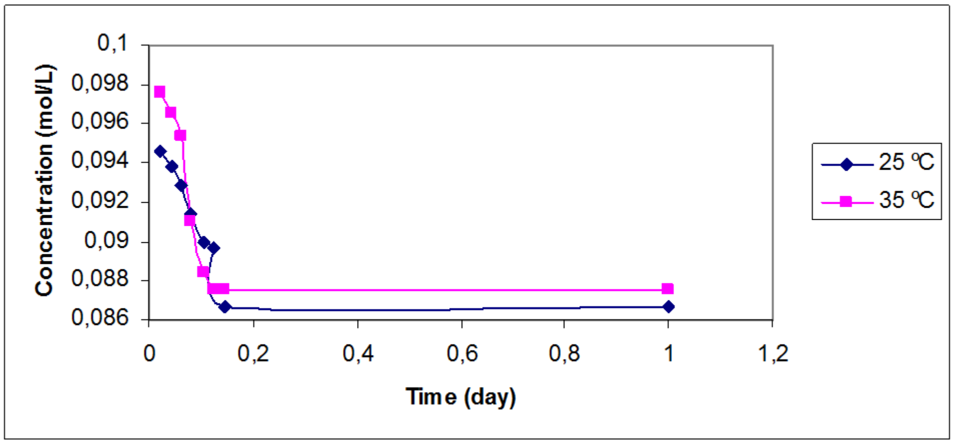

Fig. 4. Equilibrium concentration versus time at 25 and 35ºC temperatures, adsorbent dose=0.1 g(100 ml) (C0=10^{-3} M)

3.3 Adsoption Isotherms

The equilibrium data for 2,4-D adsorption on CCS were compared by using Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm model gives the uniform energies of adsorbent surfaces.

Langmuir isotherm is represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b} + \frac{C_e}{Q_0} \tag{1}$$

where C_e is the concentration of pesticide mg/l at equilibrium, q_e is the amount of adsorbate on per unit mass of adsorbent at equilibrium in mg/g, Q_0 is the maximum adsorption at monolayer coverage in mg/g, b is the adsorption equilibrium constant related to the energy of adsorption in L/mg. The plot of C_e/q_e versus C_e is linear and is presented in Fig. 5. Q_0 and b constants were found from the slope and the intercept in Fig. 5.

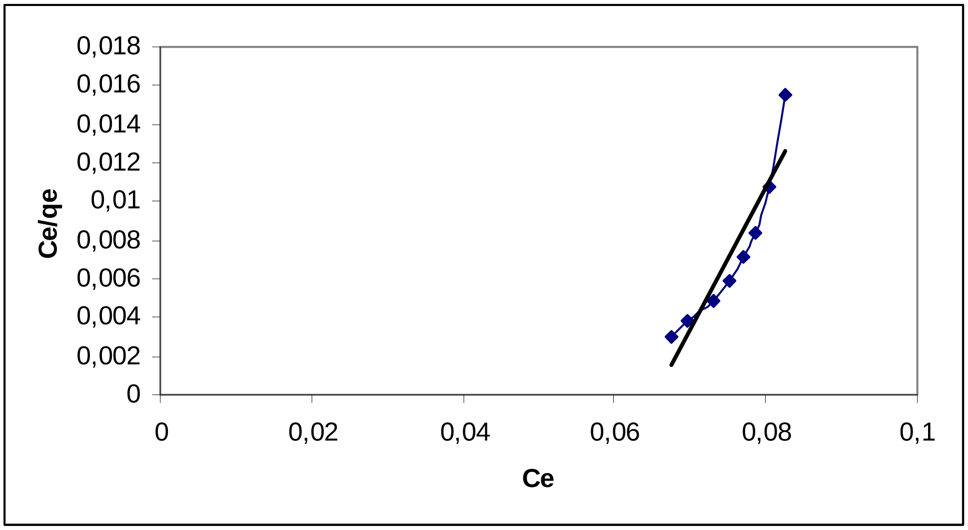

Fig. 5. Langmuir sotherm model of 4x10^{-4} M pesticide solution at 25ºC

The Freundlich isotherm equation which corresponds to heterogeneous adsorbent surfaces is given as

$$qe = K_f . C_e^{1/n} \tag{2}$$

and the logaritmic form is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate mg/l) and K_f and n are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. The values of K_f and n can be calculated from the intercept and slope in Fig. 6. The Langmuir and Freundlich constants are given in Table 1.

The Freundlich isotherm gives a better correlation than Langmuir isotherm as is evident from the correlation factors.

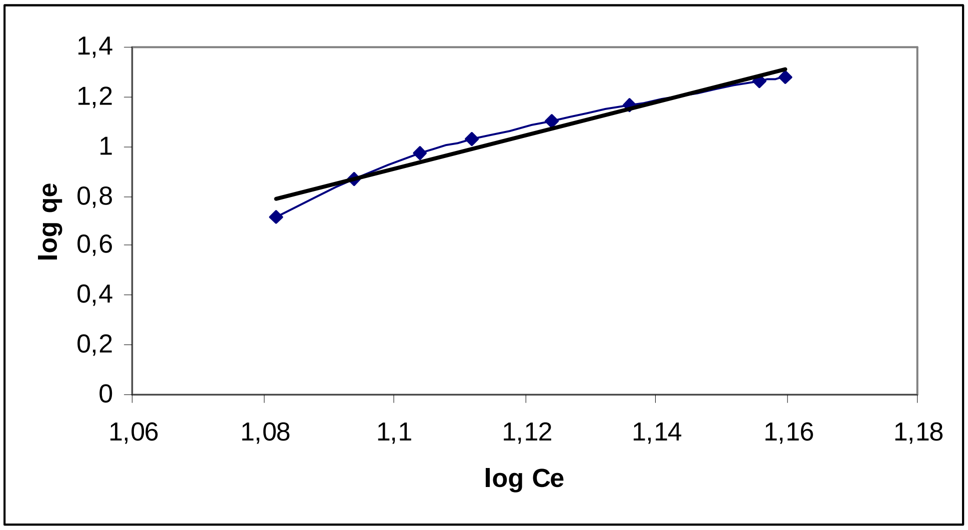

Fig. 6. Freundlich isotherm model of $4x10^{-4}$ M pesticide solution at 25 ºC

Table 1. The Langmuir and Freundlich constants

Langmuir constants			**Freundlich constants**		
Q_0	b	R^2	n	K_f	R^2
0.73	-0.049	0.86	0.15	6.46	0.96

3.4 Effect of pH

The pH value of the initial experimental solution was 6. The experiments were performed at different pH values such as 3, 5, 7, 9 and 11. The pH value of the stock solution was monitored using either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solution. The measurements were performed using WTW series inolab meter.

A known weight of adsorbent (0.1 g) was added to each solution. After equilibrium, the adsorbance equilibrium values were measured by UV spectrometer. The experiments were performed at temperature of 25 ºC. The effect of pH is shown in Fig. 7 in terms of uptake % -pH.

$$Uptake\% = \frac{C_0 - C_e}{C_0} x100 \tag{4}$$

C_0 = Initial concentration (mg/ml)
C_e = Equilibrium concentration (mg/ml)

Based on experimental values obtained, the adsorption capacity is quite high in acidic medium (pH=3) at 25ºC as seen from Fig. 7. This is due to the acidic character of the pesticide. The lower adsorption at basic pH is believed to be due to repulsion between the adsorbent surface and pesticide.

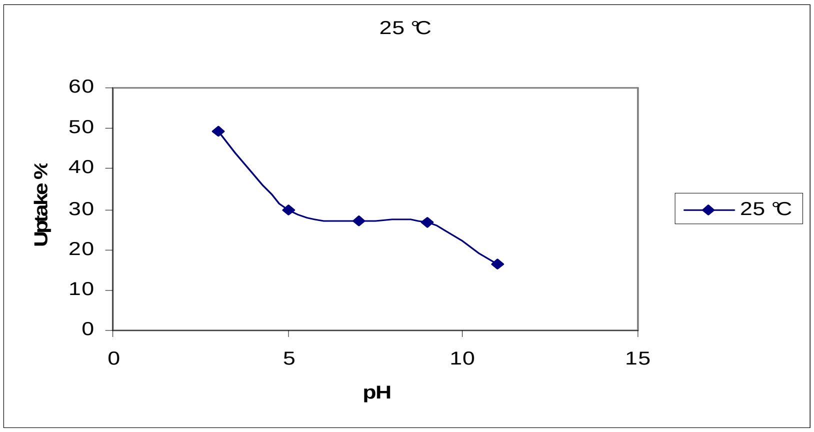

Fig. 7. Uptake percent versus pH graphic of 4x10^{-4} M pesticide solution at 25 ºC

3.5 Effect of Pesticide Concentration

Different pesticide concentrations were used to determine the effect of pesticide concentration (4x10^{-4}, 6x10^{-4}, 8x10^{-4} and 10^{-3} M). This effect was studied at pH 3. The increase in pesticide concentration over 6x10^{-4} g/l did not affect the adsorption capacity significantly (Fig. 8).

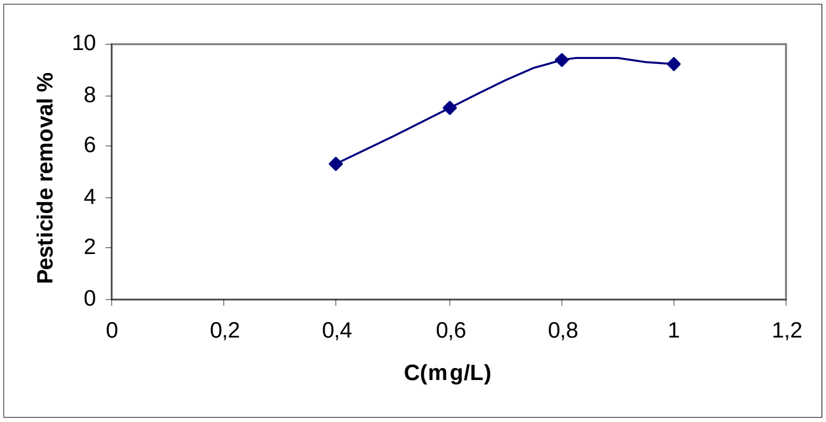

Fig. 8. Effect of pesticide concentration on the removal of 2,4-D by CCS (Contact time 250 ninutes, adsorbent dose 0.1 g, pH:3 and 25 ºC)

4. CONCLUSION

The removal of 2,4-D from aqueous solutions by carbonized chest nut shell has been investigated under different experimental conditions in batch adsorption model. The equilibrium time of adsorption was 250 minutes for $4x10^{-4}$ and 10^{-3} mol/l of 2,4-D at room temperature. The batch model adsorption studies were followed with Langmuir and Freundlich adsorption isotherm models. The pH effect was investigated from the point of adsorption yield and the increase of pesticide amount at this pH was also investigared from the point of pesticide removal.
The carbonized chest nut shell was a good and cheap adsorbent which can be utilized in the place of active carbon.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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