Removal of Toxic Dichlorophenol from Water by Sorption with Chemically Activated Carbon of Almond Shells – A Green Approach

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Summary: Chlorophenols (CP) represents a group of organic compounds having substituted chlorines attached to phenol ring. These trace organic pollutants represent a major environmental concern, because of toxicity, non-biodegradability, carcinogenic and stubborn properties. The adsorption of 2, 4-dichlorophenol (DCP) by chemically activated carbon of almond shells (CAC-AS) has been studied in the batch setup. Operational parameters like adsorbent dose, pH, and shaking speed were investigated. Langmuir and Freundlich isotherms were employed to calculate adsorption capacity and other sorption features of CAC-AS. The maximum amount of DCP adsorbed was 24.3 mg per gram of activated carbon derived from almond shells. Optimum conditions for DCP uptake were 2.5g adsorbent dose, pH 5 and agitation speed of 200 rpm whereas the concentration of DCP solution was 25 mg/L (50 mL). Results corroborated that almond shells pretreated chemically, can be an excellent low cost adsorbents for removal of DCP from contaminated water.

Introduction

Chlorophenols (CP) represents a group of 19 organic compounds having substituted chlorines attached to phenol ring. These trace organic pollutants represent a major environmental concern, because of toxicity, non-biodegradability, carcinogenic and recalcitrant properties [1, 2]. They are being used in different applications like wood preservatives, insecticides, flame retardants and industrial solvents [1-3]. 2, 4-Dichlorophenol (DCP) is a crystalline colorless solid and is one of the seven CPs (mono-CP; 2,4-DCP; 2,4,6-TCP; 2,4,5-TCP; 2,3,4,5-TetraCP; 2,3,4,6-TetraCP; PCP) with industrial production [1]. It is used in making of pesticides, antiseptic and wood preservatives. This hazardous chemical poses much health and environmental problems. It can penetrate through the human or animal skin and absorbed readily by gastro-intestinal tract [4]. It imparts a medicinal taste and smell to fish, making it unfit to human consumption [5]. DCP like other chlorophenols is a suspected carcinogen for humans but more efforts are required to confirm this information [6]. United States Environmental Protection Agency (US-EPA) has set 3.09 µg/mL as the maximum tolerable limit of DCP for drinking water.

Removal of contaminants from water by adsorption on activated carbon [7-9] is one of the most efficient processes [10]. In adsorption, species are transferred from the liquid phase to the surface of the solid particles suspended in a vessel or packed in a column. Nature and concentration of adsorbent and adsorbate, pH, and time of contact are the factors that influence adsorption significantly [11]. During the last two decades, agricultural wastes have proven to be useful and cost effective adsorbents for water treatment in comparison to ground activated carbon (GAC) that is pricey. Examples of some adsorbents employed for water treatment are pine wood [12], pine bark [13], bagass [14], rice husk [15], tea waste [16], apricot stone [17] and Tamarindus indica seeds [18].

In the present work, chemically activated carbon of almond shells (CAC-AS) was tested to remove DCP from water. This work was intended as a feasibility study to evaluate the capacity of almond shells to remove DCP from water.

Results and Discussion

The release of toxic chemicals in water has catastrophic effects on the aqueous ecosystem. Although, various physical and chemical methodologies are being utilized for removal of toxic substances from aqueous systems but these methods are either costly or have operational shortcomings. Adsorption is an efficient alternative of these techniques. Almond shells are very good adsorbents and in the present work, activated carbon originated from almond shells has been tested to remove DCP from water.

Characterization by FTIR

The first step was the preliminary characterization of almond shell based activated carbon in order to understand the way that they

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interact with DCP in water. FTIR spectrum was obtained with nujol mull that is expressed in terms of transmittance (4000-650 cm^{-1}) More important values that point to the presence of related functional groups were: O–H (3400–3700 cm^{-1}), C–H (2850–2950 cm^{-1}), C=O (1750–1650 cm^{-1}) and C=C (1600–1500 cm^{-1}). Spectrum indicated the presence of hemicelluloses and cellulose as the possible DCP uptake sites. The composition of almond shells, (% mass weight) as mentioned in literature is: hemicelluloses 28.9%, cellulose 50.7% and lignin 20.4% [19]. Chemical pretreatment was carried out to enhance the up taking potential of almond shells towards DCP. Experiments have confirmed that basic (alkaline) pretreatment of almond shells increase the adsorption capacity to a significant extent. The same effect of pretreatment was reported by different researchers [20, 21]. Huang has reported that alkaline pretreatment removes surface impurities and can rupture the cell membrane as well. That can expose some active centers for adsorption [22]. Other researchers have reported structural changes associated with chemical pretreatment of adsorbent that increased the adsorption capacity of adsorbent considerably [23].

Effect of Adsorbent Dose

The effect of sorbent dose on DCP (25 µg/mL, 50 mL) removal was investigated at pH 6 and shaking speed 100 rpm. It was found that percentage adsorption by CAC-AS was increased by increasing sorbent dose. (Fig. 1) Initially, the change was significant but after 2.5 g, (optimum dose level) there was no significant increase in adsorption, even by increasing adsorbent dose up to 5 g. Increase in percentage adsorption by increasing the adsorbent dose means availability of greater surface area or otherwise, more active centers [24]. Beyond 2.5 g, there was a little decrease in adsorption with an increase in the adsorbent dose. This can be attributed to the fact that at the higher adsorbent doses, the interaction between adsorbent particles increases in comparison to interaction between adsorbent and adsorbate particles [25]. The effect was reported by Quek and coworkers as well [26]. Interaction between particles of adsorbent leads to the assemblage of adsorbent and that accumulation can reduce the total available surface area resulting in decreased adsorption [27].

Effect of pH

The effect of pH on the adsorption of 2-4 dichlorophenol by chemically activated carbon of almond shells was studied by varying pH from 3 to 10. The results are given in Fig. 2. Effect of pH is quite significant and maximum adsorption has occurred at pH 5. While increasing the pH further, adsorption has decreased. Influence of pH on adsorption is related to nature of adsorbate and functional groups of adsorbent. Change in pH largely affects the dissociation of different functional groups from adsorbents surface [24]. At low and high pH values, the surface of the adsorbent would be surrounded mainly by hydrogen and hydroxyl ions. These positively and negatively charged ions may compete with the adsorbate molecules resulting in decreased percentage adsorption [28]. In this study, slightly acidic pH increases the interaction of DCP (protonated) with the hydroxyl groups of the cellulose and hemicellulose of almond shells by possibly making hydrogen bonds.

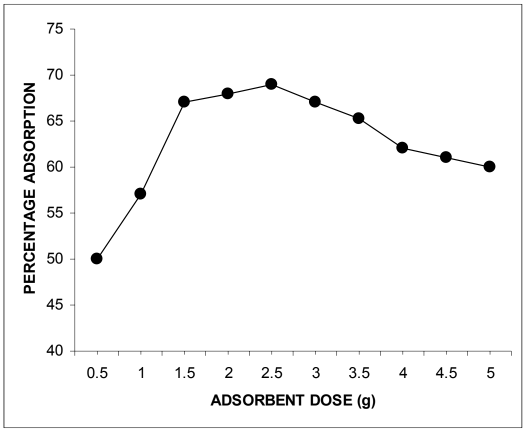

Fig. 1: Effect of adsorbent dose (0.5-5 g) on percentage adsorption of DCP (25 µg/mL); pH, 6; Agitation speed, 100 rpm; Volume, 50 mL.

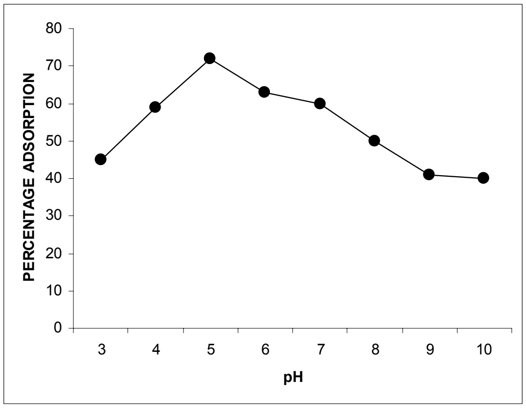

Fig. 2: Effect of pH (3-10) on percentage adsorption of DCP (25 µg/mL); Adsorbent dose, 2.5 g; Agitation speed, 100 rpm; Volume, 50 mL.

Effect of Agitation Speed

Effect of agitation speed on the adsorption of 2, 4 DCP was studied. (Fig. 3) Initially, with increasing shaking speed, percentage adsorption increases but away from optimum speed of 200 rpm, percentage adsorption decreases. When shaking speed was slow, adsorbent assembled at bottom and various active centers buried under the above layers of adsorbent [11]. Adsorption is the surface phenomenon, the absence of under buried layers for adsorption resulted in less DCP removal. At very high speed, the kinetic energy of adsorbate molecules as well as of the adsorbent particles increased enough that they collide with each other hastily resulting in detachment of loosely bounded DCP molecules. Same observation was reported in another work as well [29].

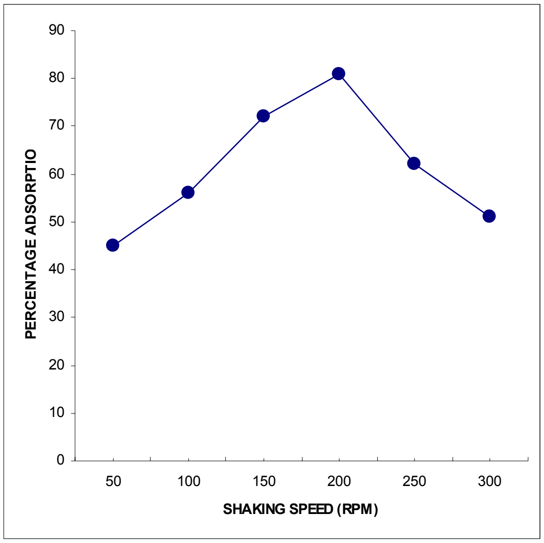

Fig. 3: Effect of shaking speed (rpm) on percentage adsorption of DCP (25 μg/mL); Adsorbent dose, 2.5 g; pH, 5; Volume, 50 mL.

Adsorption Isotherms

Langmuir (Fig. 4) and Freundlich (Fig. 5) models were used to describe the sorption process. Corresponding parameters of isotherms and thermodynamic measurements are given in Table-1. Maximum adsorption capacity, Q, corresponding to complete monolayer coverage of adsorbent is 24.3 mg of DCP per gram of CAC-AS. b (0.124 dm^3/g), the adsorption coefficient, is related to apparent energy of sorption. R^2 (correlation coefficient) values indicate that Freundlich model provides a good linear model for adsorption of DCP in comparison to Langmuir isotherm. Less suitability of Langmuir isotherm for adsorption of chlorophenols by almond shells was observed in another study as well because monolayer coverage is not valid for such experiments [1]. Value of K (sorption capacity) as evaluated by Freundlich isotherm is 2.624 mg/g, less in comparison to adsorption of DCP by granulated activated carbon (GAC-R1, 6.934 mg/g) but greater than another type of adsorbent, CG (1.750 mg/g) used in that study [30]. Thermodynamic parameters ΔH (enthalpy change), ΔS (entropy change) and ΔG (Gibbs free energy) provide useful information about the nature of sorption. Positive value of ΔH indicates that adsorption has endothermic nature, where the positive value of ΔS shows that the bonding forces between DCP and CAC-AS impart randomness to the system. Negative value of ΔG suggests the spontaneity and naturalness of the phenomenon.

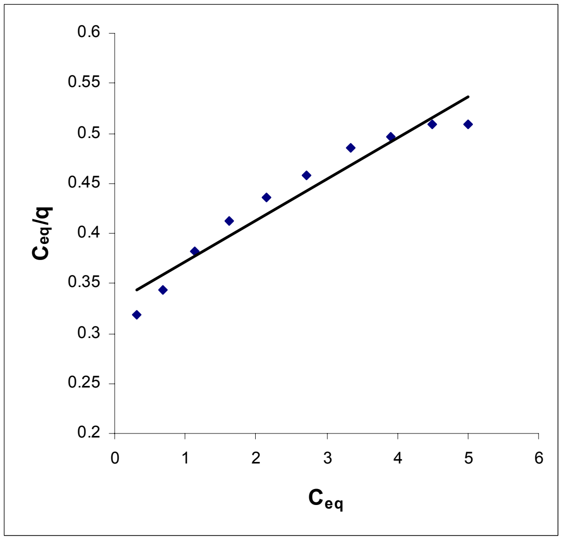

Fig.4: Langmuir adsorption isotherm, Adsorbent dose, 2.5 g; pH, 5; DCP concentration, 1-10 μg/L; Volume, 50 mL; Agitation speed, 200 rpm; Temperature, 30°C.

Table-1: Langmuir, Freundlich and thermodynamic parameters.

Langmuir isotherm parameters		
Q (mgg^{-1})	**b (Lmg^{-1})**	**R^2**
24.3	**0.124**	**0.9347**
Freundlich isotherm parameters		
K (mgg^{-1})	**n**	**R^2**
2.624	**1.228**	**0.9993**
Thermodynamic parameters (30°C)		
ΔG ($kJmol^{-1}$)	**ΔH ($kJmol^{-1}$)**	**ΔS ($kJmol^{-1} K^{-1}$)**
-7.51	**6.0922**	**0.045**

Experimental

Preparation of Adsorbent

Almonds (local name "*American badams*") were obtained from the local market of Lahore, Pakistan and shells were separated. These shells were washed with distilled water to remove dust and dirt and dried in the open air for 72 h. The dried biomass was powdered in a food processor (Moulinex, France) and sieved to get particle size range 70-80 mesh (ASTM).

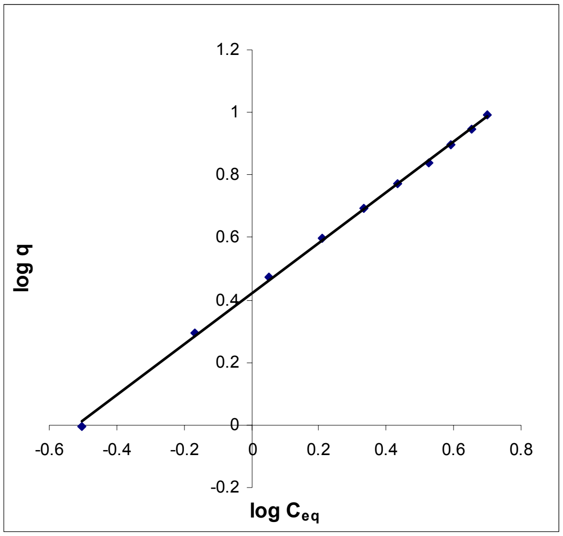

Fig.5: Freundlich adsorption isotherm, Adsorbent dose, 2.5 g; pH, 5; DCP concentration, 1-10 µg/L; Volume, 50 mL; Agitation speed, 200 rpm; Temperature, 30°C.

Chemical activation of powdered almond shells was carried out with NaOH. 100 g of fine-grained almond shells were soaked in excess of aqueous solution of NaOH (0.1 mol/L) for 1 h at room temperature. Afterward, the supernatant was filtered off and adsorbent was extensively washed with deionized water. The resulted adsorbent was air dried. Chemically activated almond shells were placed in a furnace at 800°C, for 2 h to get the almond shell based activated carbon.

Characterization of Adsorbent

The surface chemical characterization of chemically activated almond shell was performed by Fourier Transform Infrared Spectroscopy (FTIR) in Perkin Elmer, Spectrum R XI.

Stock Solutions and Standards

Stock solution of 1000 mg/L was prepared by dissolving appropriate weighed quantity of 2, 4-dichlorophenol (Merck, Purity 98%) in distilled water. Standard solutions of the desired concentrations were prepared by adequate dilution of the stock solution.

Reagents and Chemicals

Analytical grade chemicals, purchased from Merck and Sigma-Aldrich were used without further refinement. Aminoantipyrine solution (2%) and potassium ferricyanide solution (8%) were prepared by dissolving 2 g and 8 g of respective chemical in 100 ml of distilled water. Buffer (pH 10) was prepared by dissolving 17 g NH_4Cl in 143 ml concentrated NH_4OH and diluted to 250 ml with distilled water.

DCP Analysis

DCP was analyzed spectrophotometrically. To 100mL of DCP solution, 2 mL of buffer (pH 10) was added to sustain pH. After that, 2 mL of 4-aminoantipyrine (2%) was added followed by the addition of 2mL of potassium ferricyanide (8%). After 15 minutes, reddish brown coloration appeared whose absorbance was measured at 510 nm on double beam UV-Vis spectrophotometer (UVD-3500, Labomed, Inc.) bearing distilled water in reference cell.

Batch Sorption Studies

A series of experiments was carried out to study the effects of parameters like adsorbent dose, pH and agitation speed on adsorption of DCP by CAC-AS. To study the effect of a certain parameter, all other parameters were kept constant and only that parameter has been varied, which was under investigation. All the glassware used, was washed with distilled water thoroughly and dried in an oven at 105 °C for 1 h. After adsorption under specific conditions, contents of the flasks were filtered and filtrates were subjected to analysis of DCP.

The effect of the adsorbent dose on adsorption of DCP (25 mg/L) was studied by varying the dose from 0.50 to 5.0 g for 50 mL solution. The effect of the pH was studied by varying the pH from 3 to 10 and the effect of agitation speed was studied in the range 50 to 300 rpm.

Study of Adsorption Isotherms

Solutions (1-10 mg/L) of DCP were tested to find out up taking capacity of CAC-AS at optimum conditions determined by early experiments. Langmuir, (Equation 1) and Freundlich, (Equation 2) isotherms were plotted by using standard straight line equations and corresponding parameters were calculated from the respective graphs.

$$\frac{Ce}{q} = \frac{1}{Q.b} + \frac{Ce}{Q} \qquad (1)$$

$$\log q = \frac{1}{n}\log Ce + \log K \qquad (2)$$

q (mg/g of adsorbent) is the amount of DCP adsorbed whereas Ce (mg/L) is concentration at equilibrium. Q (mg/g) and b (dm^3/g) are Langmuir isotherm parameters. K (mg/g, sorption capacity) and n (energy distribution of sorption sites) are Freundlich isotherm parameters. For thermodynamic calculations, equation 3 is used.

$$\ln Q = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (3)$$

Slope and intercept of plot between lnQ and 1/T can be useful to calculate parameters like ΔS and ΔH. T is operating temperature, R is gas constant and Q is Langmuir parameter. The data can be helpful to calculate Gibbs free energy using equation 4.

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

Safety Measures

DCP is a hazardous chemical and must be handled with caution, assuring the necessary ventilation (has strong phenolic odor) and body protection (skin immediately absorbs DCP and that can cause death). [MSDS-000715, Product code-20636] Special gloves and lab coats were used to avoid skin contact with DCP. The residuals (contaminated almond shells) were placed in a container marked as 'hazardous chemical' and sent to external treatment.

Conclusion

Detailed isotherm and thermodynamic analysis of experimental data was carried out to explain the adsorption of DCP on powder of activated carbon derived from almond shells. Optimum conditions for DCP ingestion were 2.5g adsorbent dose, pH 5 and agitation speed of 200 rpm whereas the concentration of DCP solution was 25 mg/L (50 mL). Freundlich isotherm was more suitable in comparison to Langmuir to explain the sorption process. The conclusion of the present work is that chemically activated carbon derived from almond shells can be a good sorbent for DCP.

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