Adsorption Process for Removal 2,4 Dichlorophenol from Wastewater by using Chitosan

F. Changani Khorasgani[1,3], M. Honarvar[2], M. Salari[3], M. Darvish[4] and S. Akbari[5]

[1,2,3,4,5]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
[2]Department of Food Science and Technology, College of Food Science and Technology, Tehran Science and Research Branch, Islamic Azad University, Tehran, Iran
[3]Civil Engineering Department Z.H. College Faculty of Engineering & Technology. A.M.U., Aligarh. India
E-mail: [1]changani_f@yahoo.com

Abstract

Background: *2,4 dichlorophenol (DCP), one of the most chlorophenol compounds family with highly toxic effect, exists in agricultural areas, chlorinated waters, discharging wastewater of pulp and paper industries. Chlorophenols can cause damages to the kidneys, liver, pancreas and weaken the central nervous system (CNS). In the current study we evaluate the adsorption of DCP by chitosan in aqueous environments.*

Materials and Methods: *In this study we evaluated the effect of operational parameters such as time (15-90min), pH values (3-9), initial concentration of DCP (15-100mg/l) and the dose of chitosan (0.1-0.9g) in a batch reactor. A spectrophotometer at wavelength of 280nm was used to measure the concentration of DCP. Freundlich and Langmuir isotherm model and Pseudo-first order kinetic models and Pesudo-second order kinetic was drawn by using of the results obtained in the adsorption process.*

Results: *Equilibrium time in the adsorption process was estimated to be 75 minutes (DCP concentration 15mg/chitosan Concentration 0.5g and pH 6.5) with 76% removal efficiency, pH 3 was calculated as the optimal pH in adsorption process (DCP concentration 15mg/l,Chitosan concentration 0.5g and time equilibrium 75min) with efficiency 79% and the value of efficiency decreased by increasing pH. In 15mg/l concentration of DCP maximum adsorption with an efficiency of 79% was observed. (Chitosan concentration 0.5g, time equilibrium 75 min. and pH 3) and the maximum 87% adsorption efficiency of DCP was observed. Adsorption process follows of Frundlich isotherm with correlation coefficient of 0.9599 and the pseudo second order kinetic model with correlation coefficient of 0.9649.*

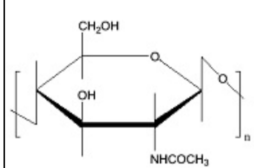
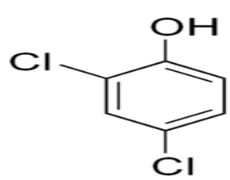
Conclusion: *According to results of the study, chitosan can be used to remove of DCP from industrial wastewater due to of its perfect characteristics such as biodegradability, resurgent ability, low cost and adsorption acceptable efficiency.*

Keywords*: 2,4 dichlorophenol, Chitosan, industrial wastewater, Adsorption process*

1. INTRODUCTION

Phenolic compounds are one of the most common pollutants which include a wide range of organic chemicals phenol and derivatives. phenolic compounds include phenol , chlorophenols , nitrophenol and can be amino-phenol. Chlorophenol is one of the compounds in this group with high toxicity and COD that has low biodegradability and has detrimental effects on living organisms and human health in the low concentrations[1]. The most common chlorophenols are 4-chlorophenol, 2, 4-dechlorophenol and 2, 4, 6 trichlorophenol. 2, 4-dechlorophenol (DCP) is one of the most toxic compounds of chlorophrnilics, which is solid in the open air as colorless crystals and has high solubility in alcohol. The most use of DCP is in manufacturing insecticides, pesticides and an important matter in seed antiseptics. Contaminants frequently resistant is seen mostly in agricultural areas, water disinfected by chlorine, pulp and paper mill waste industry output. Since chlorophenols cause damage to the kidneys, liver, pancreas, weakened the central nervous system and can cause denaturation of protein molecules, the Environmental Protection Agency (EPA) classified this compound as a hazardous air pollutants.United States of America Environmental Protection Agency (UEPA)has considered phenol and its derivatives as 11 combinations of 126 chemical composition in the class of pollutants with high risk level.EPA recommends DCP concentration in drinking water less than 0.03 mg / l. World Health Organization (WHO) recommended 1μg / l in drinking water and 1mg / l as the maximum allowable concentration in wastewater discharges to surface water sources. Removal methods such as biological processes, chemical oxidation, solvent extraction, burning, reverse osmosis, electrochemical methods and radiation were used to remove excess amounts of phenol and phenol compounds until now[5]. Most of these methods have disadvantages such as high cost, low efficiency, the need for pre-treatment before the main refining process and emissions are surplus. Adsorption process of refining the initial cost compared with other techniques, reuse of wastewater, simplicity and flexibility in design, easy operation and non- sensitive to pollutants and toxic substances, with excellence. Generating wastewater with high quality and lack of hazardous materials such as ozone and free radicals is another advantage of this method. The researchers followed the natural absorbents such as rice bran, coconut , ash, sawdust , clay and for the absorption process , which is economically viable and is attracting top performers. Chitosan is a natural cationic polyelectrolyte absorbent with high molecular weight which has a hydroxyl chemical groups , carboxyl , amine and amid. This absorbent is produced from the wastes of crabs and shrimps by D- acetylation of chitin[2]. In this study, we consider to use chitosan as a natural non-toxic and biodegradable absorbent through the mechanism of neutralization time, absorption and adsorption bridging between the particles, to absorb DCP in industrial wastewater.

Table 1: characteristics of chitosan and 2,4 dechlorophenol

Name	Chemical formula	Chemical structure	Molecula r Weight
Chitosan CAS Number: 9012-76-4	$(C_8H_{13}NO_5)_n$		110-150g/mol
2,4Dichlorophen ol CAS Number: 120-83-2	C6H4Cl2O		163g/mol

2. MATERIALS AND METHODS

This practical type of study was done at the Faculty of Health Tehran University in 2014 on wastewater samples prepared similar to industrial wastewater to assess the effectiveness of chitosan to study the absorption of DCP combination by chitosan. Consumed acid and ammonia with 99% purity DCP with purity of 98% were obtained from Merck Co. For the manufacture of various concentrations of pollutants in the stock solution, DCP 0.1% was used with a solution of 1 g/l of water twice distilled water.

3. PREPARATION OF CHITOSAN

After washing the shells of shrimp with enough water they were kept at room temperature in the presence of sunlight for a week, we had to dry and ground them to make them ready for chitin and chitosan. First, in order to de- mining, shrimp powder ratio (w / v) 1.14 was placed in 1 N choloriric acid for 36 hours. Then was washed twice with distilled water and kept at ambient temperature for 24 hours until it was completely dried. At the stage of protein creation we put the , obtained substance from the previous phase in ammonia with ratio of 1.12 (w / v) at 5% ammonia for 24 h at 90 ° C, to remove protein and produce chitin for producing chitosan, the dried chitin was added to ammonia of 70% in ratio of 1.14 (w / v) and set for 72 hours at ambient temperature. The resulted combination was washed with twice distilled water and what was produced finally was chitosan. Fig. 1 FT-IR Spectrometer was taken at the Faculty of Pharmacy, Tehran University of Medical Sciences of chitosan which to indicates the presence of amine functional groups (wavelength 1621.42 and 3289.91) and hydroxyl (wavelength 1401.28 and 3441.10) in chitosan.

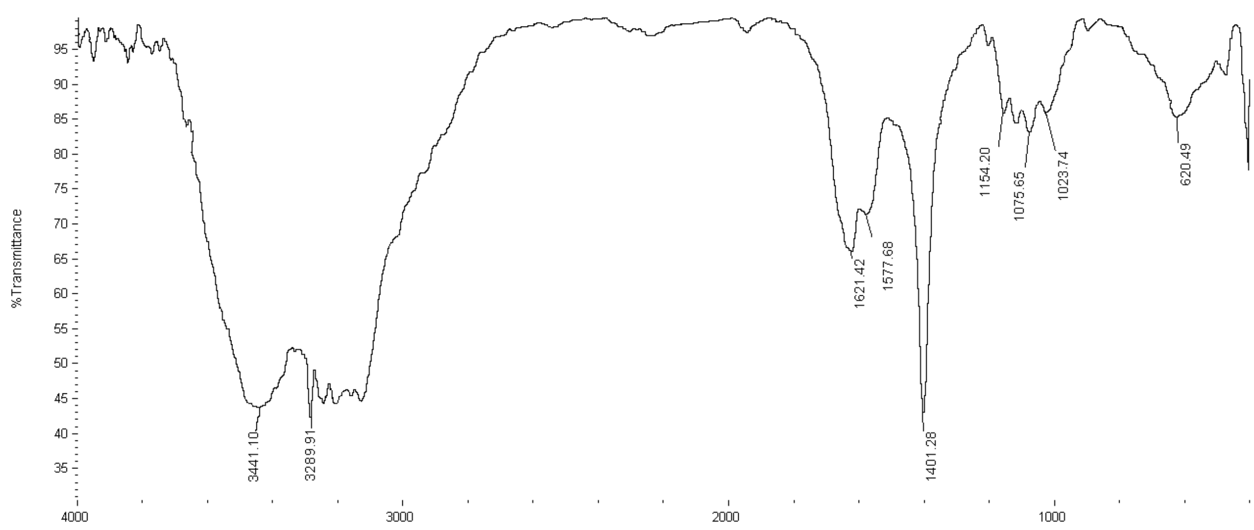


Fig. 1: FT-IR chitosan combination

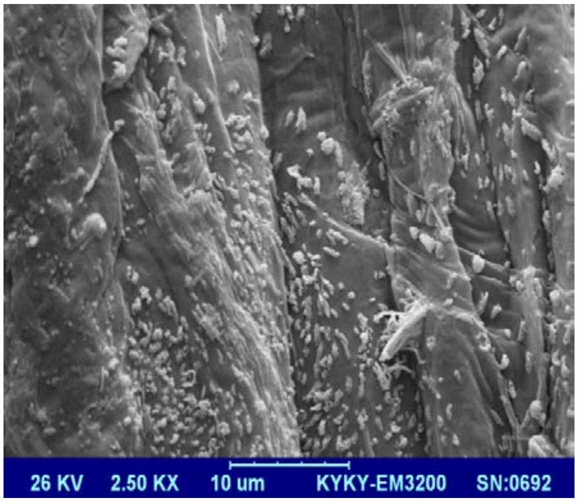


Fig. 2: SEM picture enlarged 10000 times

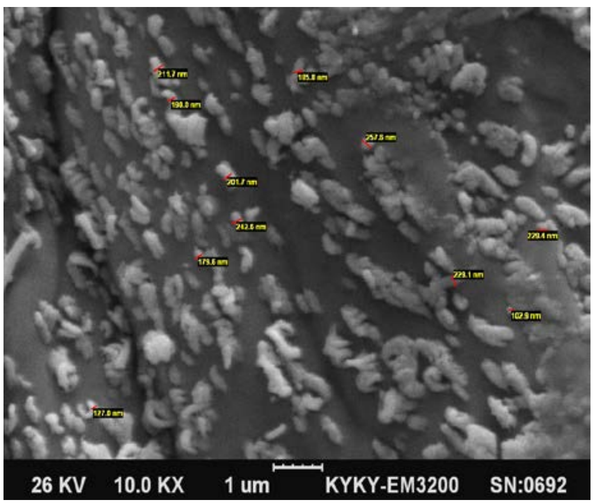


Fig. 3: SEM picture enlarged 2500 times

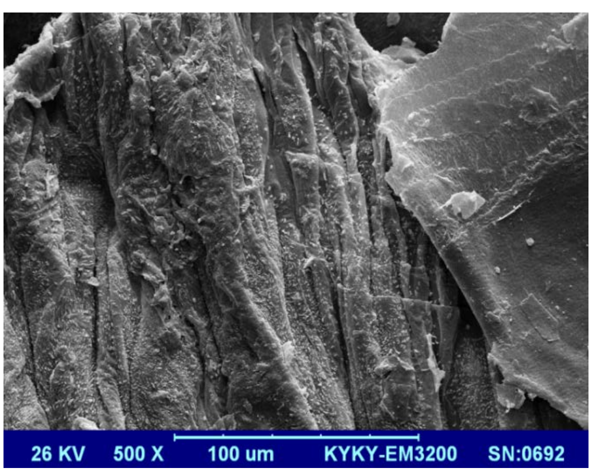


Fig. 4: SEM picture enlarged 10000 times

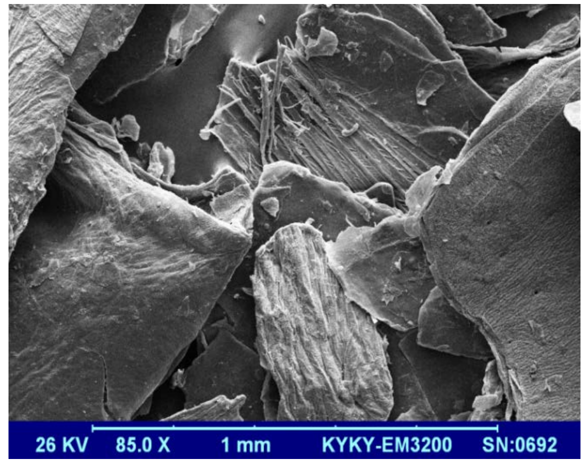


Fig. 5: SEM picture enlarged 2500 times

4. BATCH STUDIES

The batch examinations were done in the lab temperature (21±3 ºC). All of the solutions which were used in these examinations were made in 100 ml volume and the samples were put in the centrifuge machine after complete mixing in the shaker and pH determination. Then chitosan will be separated by 0.45 µ filter and the samples were put in the PerkinElmer machine with 280 nm wave length and the adsorption rate was calculated. All of the examinations will be done twice to decrease false answers.

5. CONTACT TIMES

The impact of the time variable on absorption capacity of DCP by chitosan were studied at 15, 30 , 45, 60 , 75 , 90 and 100 minutes, while other parameters (concentration of DCP, adsorbent dose and pH) were fixed .

6. PH EFFECTS

Effects of solution pH in the range of pH for the removal of DCP 3, 5 , 6.5 , 9 and 11 were tested . The normal pH of samples was 6.5 and 1.0 normal sodium hydroxide and hydrochloric acid were used for pH adjustment and the pH of produced wastewater were determined by Kent EIL7020 pH meter model. Other parameters (DCP, adsorbent dose and time) are fixed.

7. RESULTS AND DISCUSSION

In order to determine the concentration of DCP in spectrophotometer calibration curve in concentrations of 2, 5, 10, 25, 50, 80, 100 and 120 mg l was plotted with the correlation coefficient of 0.9995.

One of the crucial factors in the process of absorption, the absorption equilibrium time that should be investigated through absorption examinations and the dependence of the absorption process should be determined under different conditions. In Fig. 6 the effect of time on the uptake of DCP by chitosan was shown. The maximum DCP removal efficiency of 76% by chitosan was observed in 75 minutes and the remaining concentration of 3.6mg / l. When time passes more than 75 minutes, removal rate shows visible changes. The reason of absorption increase by passing time could be explained with accessing lots of surfaces and absorbing places at the beginning of the process of chitosan absorption[6].

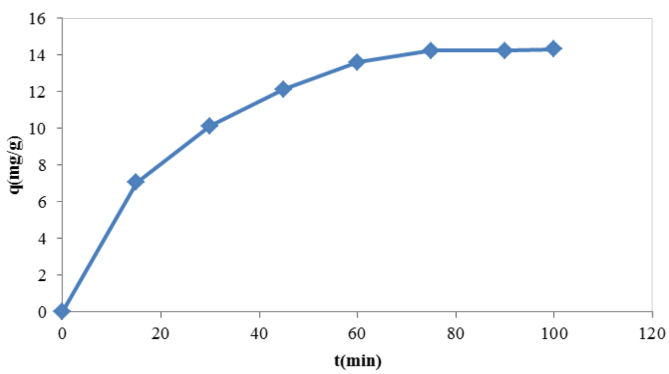


Fig. 6: Effect of time on absorption of 2,4 dechlorophenol (absorbent dosage=0.5 g, contact time=75 min, 2,4 dechlorophenol concentration=15 mg/l)

DCP ions are easily absorbed by the surfaces. By time passing and reduction in free spaces for absorption, the absorption rate will be reduced and eventually fixed. Senturk et al studied on phenol removal by modified bentonite as an absorbent from water 60 minutes was assigned as the balance time. Gholizadeh and colleagues obtained 60 and 120 minutes in absorption of 2- chlorophenol and 4- chlorophenol by activated charcoal and rice husk ash, respectively. Fig. 7 has shown the effect of pH on the removal of DCP in which the most removal efficiency of 79% at 3 = pH and residual concentration of 3.15 mg / l was obtained. As it is shown in the Fig. absorption will be decreased with increasing pH. At 3 = pH amine group will be protonated easily and cause the electrostatic attraction between DCP and chitosan. OH will be increased by increasing pH and composition of DCP will be presented as salt in the solution which causes a competition in the absorbent places and efficiency will be reduced.One of the affecting factors on absorption is Pka of the pollutant combination. PKa indicates pH that half of the compounds in the sample solution are charged and half are neutral. At higher pH, DCP will change to a more anionic form and at lower pH than PKa, DCP will change to a molecule form.The chlorophenol are Hydrophilic in the form of molecular and this characteristic will reduce when they turn to ionic compounds. The PKa combination in DCP is about 4.09, absorption process should be increased at lower pH due to the high repulsive force. Shokouhi and colleagues studied the performance of the biomass of Aspergillus niger in attracting penta chlorophenols in 2014 which showed increase of absorption while pH had decreased.

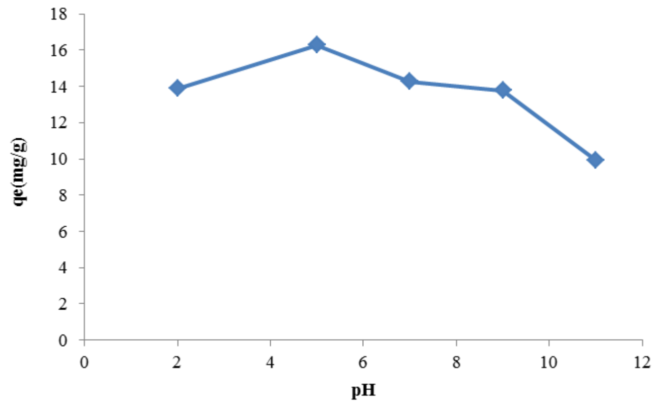


Fig. 7: Effect of pH on absorption of 2,4 dechlorophenol (absorbent dosage=0.5 g, pH=6.5, 2,4 dechlorophenol concentration=15 mg/l)

Removal efficiency of various concentrations of DCP was evaluated from 15 to 100 mg per liter, with a contact time of 75 minutes. According to Fig. 8, it can be concluded that the removal rate will be decreased by increasing the DCP concentration, in a way that increasing DCP concentration from 15 milligrams per liter to 100 milligrams per liter can cause the removal reduction of 79 % to 37.6 % and the most important reason of that can reduced levels of absorption by increasing the concentration of DCP[7].

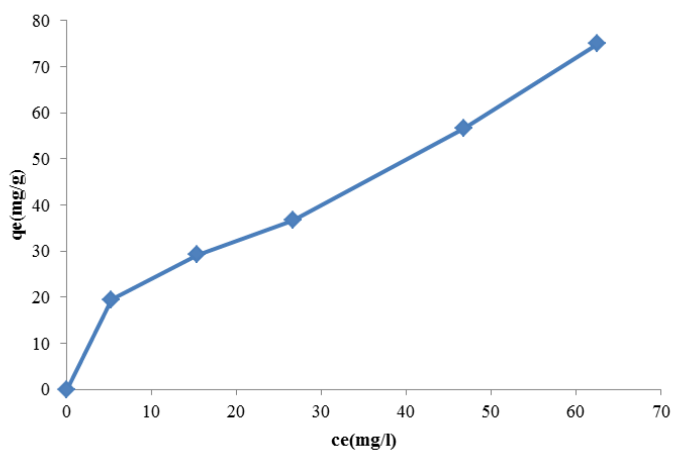


Fig. 8: Effect of 2,4 dechlorophenol concentration on absorption process (absorbent dosage=0.5 g, contact time=75 min, pH=3

However, at higher concentrations, the absorption capacity (qe) will be increased, so that the absorption rate of 11.85 mg/l will reach 37.6 mg/l, which can because of the increased possibility of contact between the DCP with chitosan as an absorbent[8]. In a related study of Wu and colleagues on removal of DCP in the aquatic environment by fungal biomass chrysosporium, they obtained absorption efficiency reduction and increase of absorption per unit mass of absorbent which had similarity to the results of their study.The changes in concentration of absorbent and its impact on DCP removal is shown in Fig. 9. As it can be seen in the figure, the specific absorption rate increased with increasing concentration so that in concentration of 0.8 gr of chitosan 87% will be absorbed and at in concentration of 2 g 52% will be absorbed. In high concentrations the absorption rate and efficiency will be increased because of the increased surface area available for absorption while at low concentrations absorbent surface available for absorption will be quickly saturated with ions of DCP and DCP drop-out rate will be reduced. On the other hand, by increasing the concentration of absorbent, the available absorbing surfaces will be increased more than the DCP amount and DCP absorption rate will be reduced compared to absorption per unit mass and qe amount will be decreased.

8. RESULTS

According to the results of the study on the removal of 2, 4 dechlorophenol by chitosan, and the need to reduce this pollutant in the exhaust sewage of the industries as standard, chitosan can be used as a biodegradable and cost-effective absorbent with a desirable efficiency in removal of 2, 4 dechlorophenol from industrial wastewater.

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