Experimental Evaluation Use of Semifluidized Bed Adsorber for the Treatment of P-chlorophenol and O-cresol in Wastewater using Activated Carbon as Adsorbent

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ABSTRACT

In the present work the performance of semifluidized bed adsorber was evaluated for removal of phenolic compound from wastewater using commercial activated carbon as adsorbent. P-chlorophenol (4-Chlorophenol) and o-cresol (2-methylphenol) was selected as a phenolic compound for that purpose. The phenols percent removal, in term of breakthrough curves were studied as affected by hydrodynamics limitations which include minimum and maximum semifluidization velocities and packed bed formation in the column by varying various parameters such as inlet liquid superficial velocity (from U_{minsf} to $8U_{minsf}$ m/s), and retaining grid (sometimes referred to as adsorbent loading) to initial static bed height ratio (from 3-4.5). Inlet phenols concentration (50-400 mg/l) and initial pH of the liquid solutions feed (from 4 to 10) were also studied. The experimental semifluidized adsorber unit was designed and constructed in Chem. Eng. labs at Al-Nahrain University (consisted of a QVF glass tube 2.54 cm inside diameter, and 70cm length). The results showed that the initial percent removal of phenolic compounds (P-chlorophenol and o-cresol) decrease with increasing the superficial liquid velocity while the time required reaching equilibrium state decreased. Also it slightly affected with the increase in the retaining grid height and the time required to reach the equilibrium value decreased.

Keywords: wastewater; p-chlorophenol; o-cresol; Semi-fluidized bed; adsorption; activated carbon.

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تقييم استخدام العمود الماز شبه المميع مختبريا لمعالجة باراكلوروفينول و اورثوكريسول من المياه الملوثة بأستخدام الكاربون المنشط كمادة ممتزة

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الخلاصة

في هذا البحث تم تقييم استخدام العمود الماز شبه المميع مختبريا لازالة مركبات الفينول من المياه الملوثة باستخدام الكاربون المنشط التجاري كمادة ممتزة وقد اختير البار اكلوروفينول و اورثوكريسول كمواد فينولية ملوثة لهذا الغرض. تم دراسة نسبة الازالة مع الزمن وتأثرها بالحدود الهيدروديناميكية والتي تتضمن سرعة شبه التميع الدنيا والعظمى وتكون الطبقة الثابتة في العمود وذلك بتغيير عدة متغيرات وهي سرعة السائل الداخلة (من 1 الى 8 مرات من سرعة شبه التميع الدنيا) ونسبة ارتفاع الشبكة الحابسة الى ارتفاع العمود الساكن الابتدائي (من 3 الى 4.5). التركيز الابتدائي للفينولات المستخدمة (من 50 الى 400 ملغم / لتر) والدالة الحامضية للمحلول ابتداءا (من 4 الى 10) ايضا تم دراستها. وحدة العمود شبه المميع المختبرية تم تصميمها

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وبنائها في مختبرات قسم الهندسة الكيمياوية جامعة النهرين وتتألف من عمود زجاجي بقطر 2.54 سم وارتفاع 70 سم. بينت النتائج بأن نسبة الازالة الابتدائية تقل بزيادة سرعة السائل الداخلة بينما الزمن اللازم للوصول الى حالة التوازن يقل. وايضا تتأثر قليلا بزيادة نسبة ارتفاع الشبكة الحابسة الى ارتفاع العمود الساكن الابتدائي وكذلك الزمن اللازم للوصول الى حالة التوازن يقل.

الكلمات الرئيسية: المياه الملوثة, باراكلوروفينول, اورثوكريسول, الطبقة شبه المميعة, الامتزاز, الكاربون المنشط.

1. INTRODUCTION

Wastewater from chemical and petrochemical industries containing toxic pollutants such as phenolic compounds, dyes and heavy metals can have a several impacts on many organisms that live not only in aquatic ecosystem but also in the body of the human beings. The surface and ground waters are polluted by these compounds therefore the environmental concerns make it is necessary to remove these pollutants from the wastewater ,**Parida and Amaresh, 2010**.

Presence of phenol and its derivatives even at low concentration in the industrial wastewater adversely affects aquatic as well as human life directly or indirectly when disposed off to public sewage, river or surface water. The toxicity imparted by phenolic compounds is responsible for health hazards and dangerous to aquatic life ,**Meikap, 1997**.

Phenols are being discharged into the wastewater from various industrial processes such as oil refineries, petrochemical plants, ceramic plants, coal conversion processes and phenolic resin industries (such as phenol-formaldehyde and bisphenol-A plants) and other synthetic resin manufacturing units ,**Monteiro, 2000 and Vinod and Reddy, 2003**.

Removal of phenols from industrial effluents is required before sewage disposal. For that purpose, various methods have been suggested. According to, **Kulkarni and Kaware, 2013** review on the research for removal of phenolic compounds from wastewater several physicochemical and biological treatment methods such as polymerization, electro coagulation, solvent extraction, photodecomposition, ion exchange by resins, electro-fenton (EF-Fere) method, chemical oxidation by ozone, aerobic or anaerobic biodegradation and adsorption onto active solid materials has been used ,**Senturk et al., 2009.**

Activated carbon has been employed widely by numerous researchers as an adsorbent to remove phenol and its compounds from wastewater. Activated carbon is synthesized from various carbon containing raw materials such as coke, palm shell, rice hulls, and coconut shell by a process including dehydration of the raw material and carbonization and then activation **Singh and Srivastava, 2002.**

In the other words, various aspects of liquid-solid semifluidization which have been studied and reported earlier by different authors include packed bed formation, pressure drop, fluidized bed heights, and minimum and maximum semi-fluidization velocities are determined according to a number of variables such as the retaining grid height from inlet fluid distributer, inlet fluid velocity, density and viscosity of the liquid, static bed height, expansion ratio, and particle size.

When semi-fluidized bed is compared with both fluidized bed and fixed bed; there are some problems in fluidized and fixed beds such as back-mixing of solids particles, attrition and elutriation of particles, the necessity of considerable free board above the bed and erosion of surfaces in fluidized bed and high pressure drop, non-uniform bed temperatures, segregation of solids and channeling and blockage in fixed bed therefore the semi-fluidized bed merits when it compared to the fluidized bed and fixed bed **,Younk, et al., 1999**.

The main objective of this work is to study and evaluates the removal process of phenolic compounds P-chlorophenol and o-cresol from wastewater in semifluidized bed adsorber as a novel system. Single aqueous solutions of p-chlorophenol and o-cresol were passed through the column packed with activated carbon to get their breakthrough curves at different experimental conditions these conditions include inlet liquid superficial velocity, initial phenols concentration, and pH in addition to the hydrodynamic characteristics such as retaining grid height, static bed height and minimum and maximum semiflidization velocities.

2. EXPERIMENTAL
2.1 Materials
Commercial granular activated carbon supplied by Didactic company of purity 99.9% with surface area 1080 (m^2/g) and solid density 1.153 (g/ml) was tested as an adsorbent. The GAC solid was milled and screened to the range of 200-600 μm.

Analytical grade p-chlorophenol (powder state, $\geq$ 99.0 % purity, formula C_6H_5ClO, molecular weight 128.5) and o-cresol (solid powder state, $\geq$ 99.0 % purity, formula C_7H_8O, molecular weight 108.14) were provided from Sigma-Aldrich, Inc. and used without any further treatment. Firstly phenols (p-chlorophenol or o-cresol) solution was prepared by dissolving 1 gm of p-chlorophenol or o-cresol in 1 L of distilled water to obtain stock solution of concentration 1000 mg phenols/l. The stock solutions were diluted if necessary to get the required concentrations of 50, 100, 200, and 400 mg/l.

The pH of the solutions was adjusted by addition of 0.1M HCl or 0.1M NaOH solutions as needed at initial solution pH study.

2.2 Experimental Unit
The experimental unit used in this work consists of a semi-fluidized column equipped with a top retaining plate, and liquid distributor, liquid pump, two liquid rotameters and two tanks for feed and product. The semifluidized bed column used in this work is transparent QVF glass column of 2.54 cm. inside diameter and 70 cm. long with an expanding end of 10.16 cm diameter. A movable retaining grid made up of 100 mesh stainless steel screen is fixed on a Perspex perforated plate with outside diameter of which is very nearly the same as the inside diameter of the column. The retaining grid can be moved up and down to any position along the column by using a 4 mm diameter metal rod. **Fig.1** shows the schematic and photographic view of the experimental unit.

2.3 Procedure

As a preliminary study the hydrodynamic limits (such as minimum U_{minsf} and maximum U_{maxsf} semifluidization velocities and height of packed h_{pa} bed formation in the semi-fluidizer) were determined.

The minimum and maximum semiflidization velocities and packed bed formation h_{pa} were determined at each (h_r/h_s) ratio visually and compared with estimated value from equations given by **‚Jena et. Al, 2009**.

In the first set of experiments the retaining grid to static bed height ratio (h_r/h_s) and the initial static bed height (h_s) were fixed and selected as 3.5 and 5 cm respectively, therefore the height of grid $h_r = 17.5$ cm then the superficial liquid velocity was changed from one to eight times the value of minimum semiflidization velocity (i.e. $U_{minsf} - 8U_{minsf}$) to find its effect on the percent removal of p-chlorophenol. The determined value of minimum semiflidization velocity and the other experimental conditions were fixed as shown in **Table.1.** At this step the semifluidized bed was operated under continuous mode and the breakthrough curves of p-chlorophenol were generated. All experiments were performed at constant temperature of 30 ^{o}C.

After determining liquid superficial velocity that gives the best breakthrough curve of p-chlorophenol, the retaining grid to initial static bed height ratio (from 3 to 4.5) and by the way the initial static bed height (from 3 to 8 cm) were examined at particle size, initial p-chlorophenol concentration, and initial pH of (200-600) µm, 100 mg/l, and 6 respectively. The aim of this step is to determine the best value of the retaining grid to initial static bed height ratio. The best value of retaining grid to initial static bed height ratio which gives higher removal of p-chlorophenol will be selected for the next step.

In the next step the initial concentration of p-chlorophenol and o-cresol (50, 100, 200, and 400 mg/l) was tested at best values of liquid superficial velocity and retaining grid to initial static bed height ratio.

In the final step of the experimental procedure the initial pH (varied as 4, 6, 8 and 10) was studied on the removal of p-chlorophenol and o-cresol and new breakthrough curve will be generated.

Each sample of phenols was analyzed using UV-Vis. spectrophotometer at wavelengths of 279 for p-chlorophenol and 271 nm for o-cresol **(Thomas, 2007)**. The pH was measured using pH meter manufactured by HANNA Instruments Company (range 2 to 16 ± 0.01).

3. RESULTS AND DISCUSSION
3.1 Hydrodynamics

Fig.2 shows the experimental relationship between the retaining grid to initial static bed height ratio (h_r/h_s) and minimum U_{minsf} and maximum U_{maxsf} semifluidization velocities for the activated carbon of range of (200-600) µm particle diameter in water- solid carbon system. The benefit of this run was to know the limits of velocities at different (h_r/h_s) ratios in order to select the appropriate (h_r/h_s) ratio. It is seen from this figure that the minimum and maximum semifluidization velocities increase with the increasing of (h_r/h_s) ratio.

3.2 Effect of Liquid Superficial Velocity

Figs.3 and **4** show the effect of the superficial liquid velocity on the removal of p-chlorophenol. It is clear from this figure when C_o=100 mg/l, d_p=(200-600) µm, h_s=5 cm, h_r=17.5, U_{minsf} = 0.05 m/s, pH=6 and liquid superficial velocity was varied from U_{minsf} to $8U_{minsf}$ the initial percent removal decrease with increasing the superficial liquid velocity while the time required reaching equilibrium state decreased. The increase in superficial liquid velocity leads to decrease the contacting rate between the activated carbon adsorbent and phenols aqueous solution **,Younk G.P. et al., 1999**. The equilibrium time for adsorption of p-chlorophenol at superficial liquid velocity of U_{minsf}, $2U_{minsf}$, $4U_{minsf}$, $6U_{minsf}$ and $8U_{minsf}$ were 60, 75, 80, 90 and 100 min respectively.

3.3 Effect of Retaining Grid to Initial Static Bed Height Ratio (h_r/h_s)

To determine the effect of the retaining grid to initial static bed height ratio, the liquid superficial velocity was selected as (8 Uminsf) and the retaining grid to initial static bed height ratio was varied from 3 to 4.5 (initial static bed height varied from 3 to 8 cm), the other parameters were fixed as C_o=100 mg/l, d_p= (200-600) µm, and pH=6. **Table.2** shows the variation of hydrodynamic characteristics at this section.

Fig.5 shows the effect of retaining grid to initial static bed height (h_r/h_s) ratio on the breakthrough curve of p-chlorophenol. It can be seen from this figure that the initial removal of p-chlorophenol slightly affected with the increase in the retaining grid height also the time required to reach the equilibrium value decreased. For example when the initial static bed height was 5 cm and the height of retaining grid varied from 17.5 cm to 20 cm as shown in **Table.2** the percent removal increase from 0.71 to 0.8.

Increasing the retaining grid height leads to a slight increase in the value of minimum semifluidization velocity required therefore there is no big change in percent removal.

3.4 Effect of Initial Concentration of P-chlorophenol and O-cresol

Figs.6 and **7** show the effect of initial concentration of p-chlorophenol and o-cresol respectively on the breakthrough of these two compounds at retaining grid to initial static bed height ratio of 4, static bed height of 5 cm, superficial liquid velocity of 8 Uminsf, particle size of (200-600) µm, and pH= 6.

The initial percent removal decrease with increasing the initial concentration while the time required reaching equilibrium state decreased, this is due to increasing the amount of p-chlorophenol and o-cresol to be adsorbed onto activated carbon particles. This result is agree with numerous investigators such as **, Shabiimam and Dikshit , 2012),** Singh D. K. **(Singh D. K. and Bhavana Srivastava, 2002)** and Kulkarni S. J. **(Kulkarni and Kaware, 2013)** whose studied the removal of several phenolic compounds onto activated carbon using fixed and fluidized bed adsorber but not semifluidized bed.

3.5 Effect of Initial pH

Fig.8 shows the effect of initial pH of the solution in the bed on the percent removal of both p-chlorophenol and o-cresol after 40 min of operation at retaining grid to initial static bed height ratio of 4, static bed height of 5 cm, superficial liquid velocity of 8 Uminsf, particle size of (200-600) μm, and finally the initial concentration was selected for each component as 200 mg/l. It can be seen that the percent removal was highly dependent on the pH of the solution. The percent removal for both phenols increases with increasing pH of the solution up to about pH 7 then decreases with further increasing in pH. The maximum removal percent was at pH between 7 and 8. When increasing pH above 8 this is leads to affect the surface charge of the adsorbent and degree of ionization therefore the percent removal decrease. In other words, this effect can explain that because of the aqua-complex formation and it's following acid-base disintegration in the solid-liquid interface (**Singh and Srivastava, 2002, Amit and Minocha, 2006**).

4. CONCLUSIONS

Semifluidized bed adsorber was used and evaluated experimentally for removal of two phenolic compounds p-chlorophenol and o-cresol at different conditions. It is claimed that the use of semifluidized bed was very successful when use high to moderate superficial liquid velocity above minimum semifluidization velocity and initial pH between 7 and 8 and any retaining grid to initial static bed height ratio to enhance the percentage removal of these pollutants.

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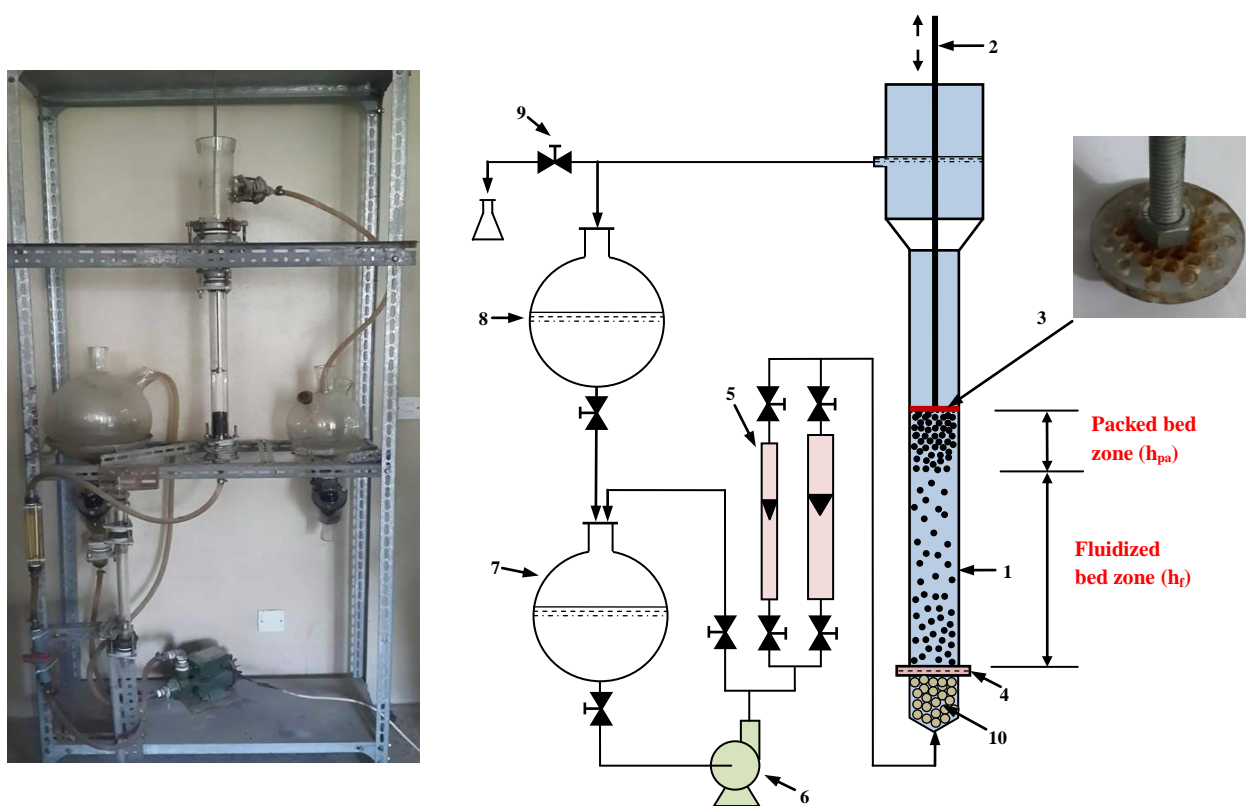
Figure 1. Schematic diagram and photographic view of the semi-fluidized bed unit. (1): Semi-fluidizer. (2): Movable retaining grid (3): Retaining grid (4): Liquid distributor (5): Rotameters (6): Pump (7): Feed tank (8): Liquid reservoir (9): Sampling valve (10) inert packing for distribution.

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Table1. Experimental conditions of the preliminary study.

| Parameter	Value
Phenolic compound	P-chlorophenol
Initial concentration (C_o), mg/l	100
Particle size (d_p), μm	200-600
Initial static bed height (h_s), cm	5
Retaining grid height (h_s), cm	17.5
(h_r/h_s)	3.5
Minimum semiflidization velocity (U_{minsf}), m/s	0.05
pH	6
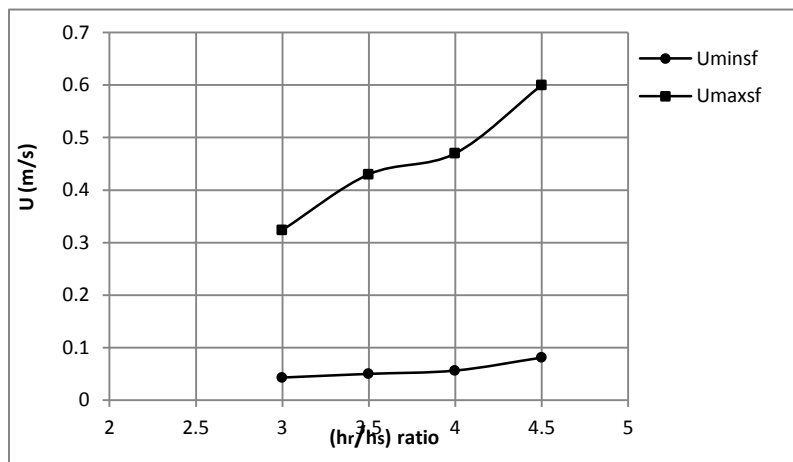
Figure2. The relation between (hr/hs) and minimum and maximum semifluidization velocities .
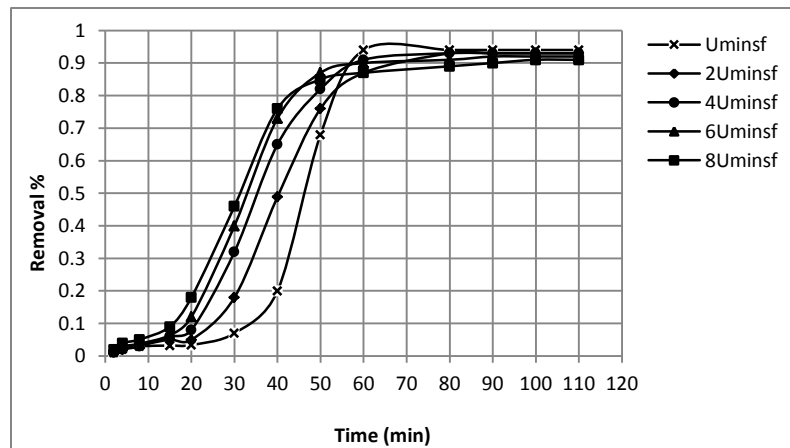
Figure3. Effect of liquid superficial velocity on the breakthrough curve of p-chlorophenol .
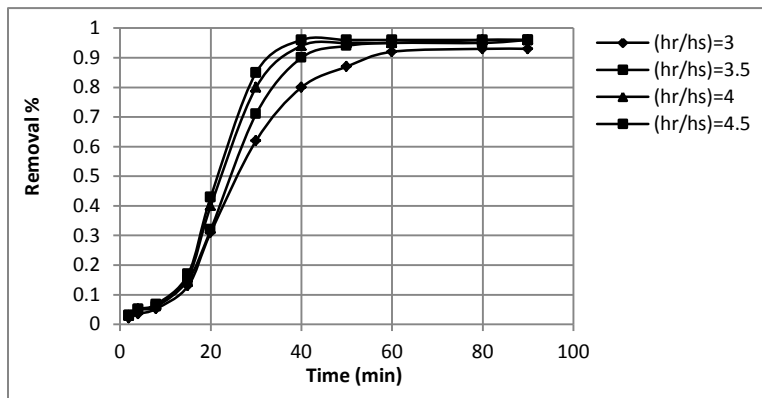
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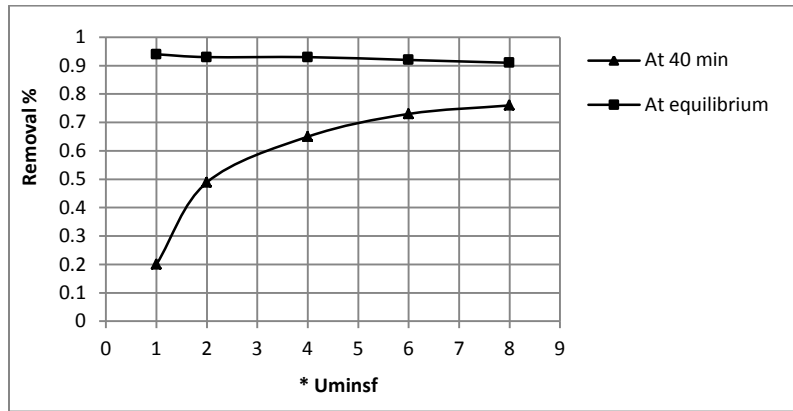
Figure4. Effect of superficial liquid velocity on the p-chlorophenol removal percent at 40 min and at equilibrium **.**

Table2. The hydrodynamic characteristics for determination (h_r/h_s) ratio.

Run #	(h_r/h_s)	h_s (cm)	h_r (cm)	U_{minsf} (m/s)	$U=8U_{minsf}$	h_{pa} (cm)
1	3	3	9	0.043452	0.347	2.5
2	3.5	5	17.5	0.049918	0.4	3
3	4	5	20	0.056293	0.45	2.5
4	4.5	8	36	0.062588	0.5	4.5

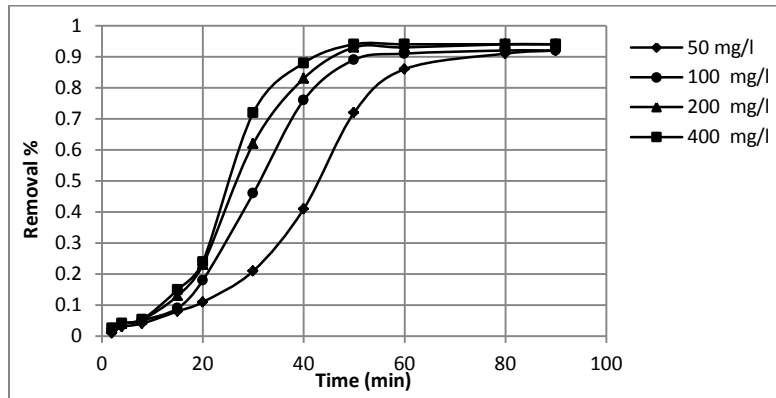**Figure5.** Effect of retaining grid to initial static bed height ratio **.**

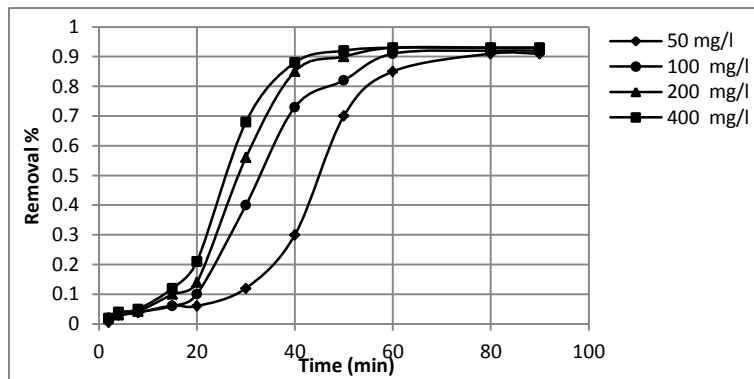**Figure6.** Effect of initial p-chlorophenol concentration on the percent removal.

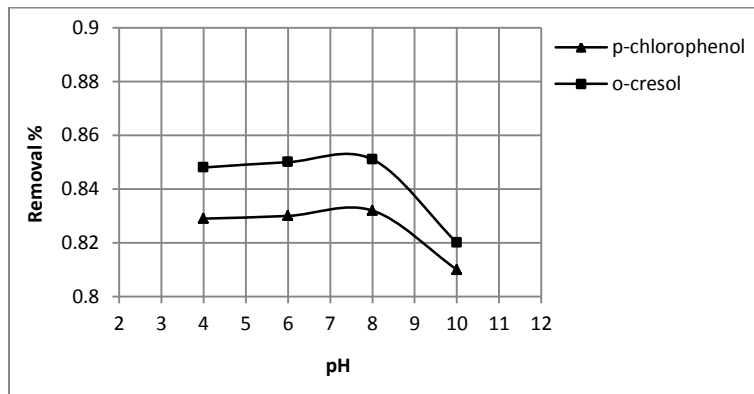**Figure7.** Effect of initial o-cresol concentration on the percent removal.

Figure8. Effect of initial pH on the percent removal of p-chlorophenol and o-cresol after 40 min.

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