PHENOL REMOVAL FROM WASTEWATER USING RICE HUSK

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ABSTRACT

This investigation is related to study the potential of Iraqi Rice Husk (IRH) (which is considered as a type of agricultural waste that is difficult to discard in a conventional methods) on thephenolpollutant removal from wastewaterusing different design parameters by adsorption process.The design parameters studied to adsorb phenol using IRH as an adsorbent material were initial concentration of phenol, adsorbance material packingheight which was IRH, pH of phenol feed inlet,treatment time,feed flow rate and feed temperature, these parameters were varied from (1-100) mg/l, (10-100) cm, (1-8), (1-60) min, (5-100) ml/min and (20–55°C) respectively. Results show that the higher removal efficiency was89.73% for phenolfrom aquatic solution and this efficiency was decreased with increasing of initial concentration,flow rate andpH while the removal efficiency increased with increasingabsorbance material bed height and feeding temperature. Statistical model is achieved to find an expression combined all operating parameters with the removal efficiency for phenolused in this paper in a general equation.By this way we can possess different benefits which are: removal of the toxic phenol contaminated water, and get rid of agricultural waste IRH.At in the same time, we can discard more toxic waste in an eco-friendly way.

Key Words: rice husk, phenol, aqueous solutions, adsorption, wastewater

INTRODUCTION

The chemical pollutant removal from wastewater isessential to reduce the harmful effect on the environmentand human health [1].The pollution of the surface water with phenol is a highly important environmentalproblem, first of allbecause of the propagation of the pollution, and second because ofits unfavourable consequences on the aquatic life, on the organoleptic properties anduses of water[2]. Phenol has already been listed as oneof the top priority contaminants and also the most importantsubstructure of potentially carcinogenic pollutantsdischarged from fine chemical plants [3,4]. Their presence in water supplies is noticed by its bad taste and odour [5].The problem of the cleaning/recovery of the phenolic wastewater were andstill are a matter of concern for the researchers and the designers, and they are eithersearching for new methods, or trying to improve the existing ones.The permissible concentration of phenolic contents inpotable water is 1 μg L^{-1} according to the recommendationof the World Health Organization [6]. There is growing concern about wide spread contamination of surface and ground water by various organic compounds due to the rapid development of chemical and petrolchemical industries over the past several decades. Therefore, many industrial wastes contain organics, which are difficult, or impossible to remove by conventional biological treatment processes [7].In the past several decades, extensive researches have been conducted to develop innovative and promising adsorbent material for dealing with the treatment problem of contaminate industrial effluents. The ultimate goal of this endeavour is to identify an effective and expensive adsorbent for the Volatile Organic Compound (VOC) removal from aqueous solution [8].There are many methods such as oxidation, precipitation, ion change, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution [9,10].Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon [11,12].In the search for new and low cost agricultural wastes as source material for widely uses. Rice husk are an agricultural waste produced as by-product of the rice milling industry to be about more than 100 million tonnes,96% of which is generated in developing countries. The utilization of this source of biomass would solve both a disposal problem and also access to cheaper material for adsorption in water pollutants control system [13].Since, the main components of rice husk are carbon and silica (15-22% SiO_2 in hydrated amorphous form like silica gel), it has the potential to be used as an adsorbent [14,15].The aim of this search was to study the possibility of using rice husk for removing phenol from aqueous solution in eco-friendly method.

EXPRIMENTAL WORK

Materials

Iraqi Rice husk (sorptionmedia)

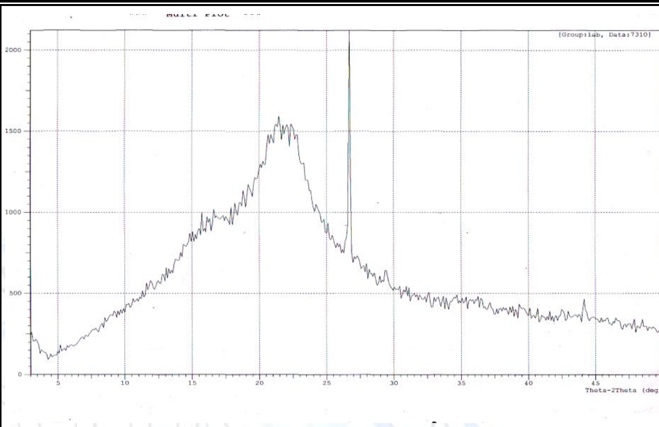
Iraqi Rice husk was collected from Al-Shanafia fields for rice in the Southern of Iraq. The rice husk was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk bringing from the field, boiled to remove colour and other fine impurities may be found in the rice husk, and then dried at 105°C for 24 hours and the adsorbent thus processed was used in its original piece size. The surface area of IRH was measured by BET (Brunauer – Emmett – Teller nitrogen adsorption technique). Characteristics of IRH were presented in **Table 1**. When the IRH was heated at 105°C in an oven, most of the water had been removed from the rice husk while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

Table1: Characterization properties of Iraqi rice husk

Chemical Composition

Compound	Composition wt %
SiO_2	90.70
Al_2O_3	0.13
Fe_2O_3	0.06
TiO_2	0.015
CaO	0.61
MgO	0.25
Na_2O	0.09
K_2O	2.64
P_2O_5	0.73
LOI	4.71
S.A (m^2/g)	17.5

XRD of Iraqi Rice Husk



Stock solutions

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different phenol concentrations. 1000 mg/l stock solution of phenolwas prepared by dissolving known weight of phenolinoneliterofdoubledistilledwater, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The phenol concentrations were measured using spectrophotometer thermo – genesys 10 UV, USA.

Adsorption unit

Fixed bed column of continuous mode experiments were conducted in order to test phenol removal by treated SSAS of above phenoleach one alone at desired concentration with the various bed heights of the adsorbent media IRH using different flow rates of SSAS of phenol at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in **Figure1** where the flow direction is downward by gravity. The sorption unit consists of two glass container of SSAS of phenolone for inlet and another for outlet each of (1 liter) capacity. Glass column has 2.54 cm

ID and 150 cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder has (0.5 cm ID, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column. The IRH is packed in the column to the desired depth, and fed to it as slurry by mixing the media IRH with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the phenol SSAS of required concentration and pH down flow through the sorption column from inlet container by gravity at a precise flow rate in experiment which is adjusted by the valve as shown in **Figure 1**. To determine the best operational conditions, the experiments were carried out at a temperature between (20–55°C), various pH values which are (1–8) and initial feed concentrations of SSAS of different phenolwhich are between (1–100) mg/l each one alone and at different flow rates which are between (5–100) ml/min for phenol initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unadsorbed concentration of phenol ion in SSAS was analyzed by spectrophotometer.

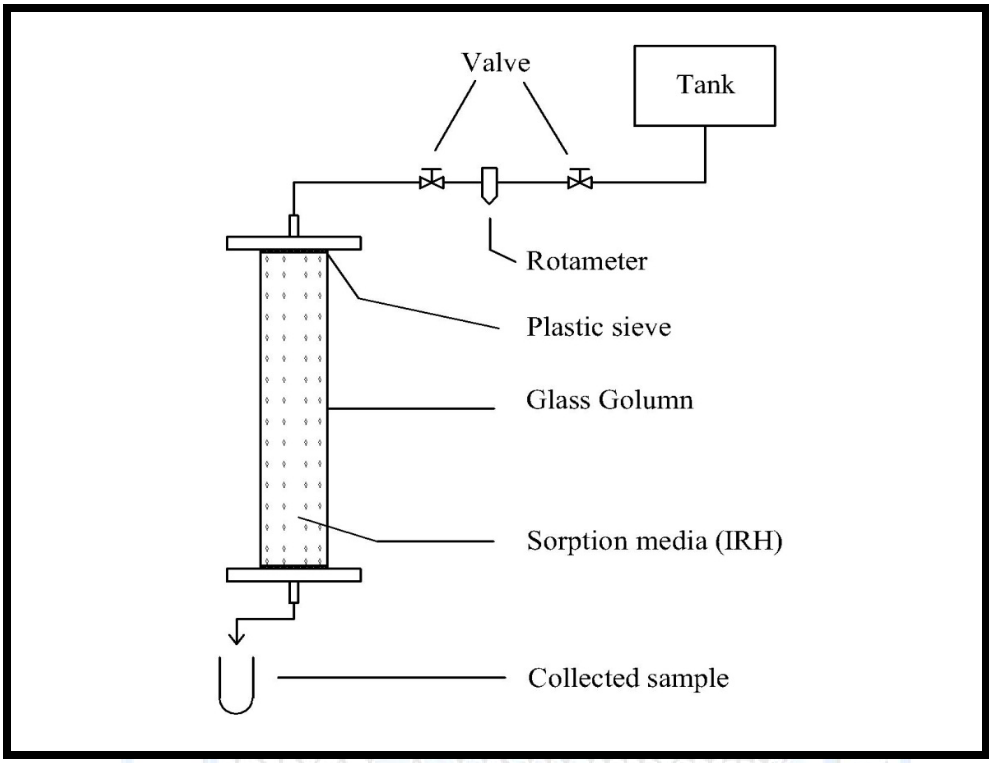


Figure1: The experimental setup of adsorption unit

Reusability of Iraqi rice husk

In order to check the reusability of sorbent media treated IRH with different phenol concentrationswere firstly dried and tested again in sorption unit at the conditions of experiment gives the best percent removal of phenol from SSAS aforementioned. The capacity of the sorbent was found to be decreased until be constant at destined percent removal after different times repeated use. The destined percent removal and number of repeated uses were dependent on phenol concentrations; thus ten times ofsorbent use was seen to be feasible.

RESULTS AND DISCUSSION

The ability of IRH to remove phenol from SSASin fixed bed column of continuous mode at various parameters which are pH's of SSAS of a phenol (pH), height bed of adsorbent media IRH (h), flow rates of SSAS (F), SSAS temperature (T_{feed}) and time of treatment (t) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (C_o) of SSAS of phenol. Thus, the results obtained are explained below.

Effect of Initial Concentration

The results showed that using adsorbent material, the percent removal of phenol was decreased when the initial concentration (C_o) of SSAS of phenol was increased at constant other variables as shown in **Figure 2**. This can be explained by the fact that the initial concentration of phenol had a restricted effect on phenol removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This functional was lead to the increase in the number of phenolmolecules competing for the available function groups on the surface of adsorbent material. Since the solution with low concentration has a small amount of phenolthan the solution of higher concentration the percent removal was decreased with increasing initial concentration of phenol. For adsorbent media, higher percent removal were 89.73% for phenol at initial phenolconcentration of 1 mg/l, so adsorbent material was found to be efficient to phenolremoval from SSAS and wastewater.

Effect of pH

The results showed that using adsorbent material, the percent removal of phenol was increased when the pH of SSASof phenolwas decreased at constant other variablesas shown in **Figure 3**. This decrease can be explained as follows: The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate species. This can be attributed to the depending of phenol ionization on the pH value. Phenol, which is a weak acid $(pK_a = 10)$, will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH value. In addition, in the higher pH range phenol forms salts, which readily ionize leaving negative charge on the phenolic group. At the same time, the presence of OH^- ions on the adsorbent prevents the uptake of phenolate ions. pHvaluealso affects the surface properties of the sorbent, i.e., surface charge of the cells used as sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with binding site of the sorbent by greater attractive forces, hence its uptake on polar adsorbent is reduced (16).

Effect of Adsorbent MediaBed Height

The results elucidated that when the adsorbent media bed height was increased, the percent removal of phenol was increased too at constant other variables as shown in **Figure 4**. The increased of bed height (h) meaning increased in the amount of adsorbent mediaIRH, thus increasing the surface area of adsorbent material, hence increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase phenolremoval capacity on IRH. This lead to increase in the ability of adsorbent media to adsorb greater amount of phenolfrom SSAS at different initial concentrations and ultimately the percent removal of phenol increased.

Effect of Flow Rate

The results illustrated that when the flow rate of SSAS of phenolwas increased, the percent removal of phenolwas decreased at constant other variables as shown in **Figure 5**. This may be due to the fact that when the flow of SSAS of phenol increase, the velocity of solution in the column packed with the adsorbent media IRH was increasing too, so the solution spend shorter time than that spend in the column while at low flow rate, the SSAS of phenol resides in the column for a longer time, and therefore undergoes more interaction with the adsorbent media, thus the adsorbent media uptake low amount of phenol from SSAS of phenol for high flow rate, therefore the percent removal of phenolwas decreased when the flow rate was increased.

Effect of Feed Temperature

The results demonstrated that when the temperature of feed which was SSAS of phenol was increased, the percent removal of phenolwas increased too at constant other variables as shown in **Figure 6**.The effect of temperature is fairly common and increase the mobility of the acidic ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling phenolions to penetrate further. It was indicated that phenol adsorption capacity increased with increasing feed temperature from 5 to 55°C. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

Effect of Treatment Time

The results demonstrated that when the treatment time of SSAS of phenol increased the percent removal of phenolincreased at constant other variables as shown in **Figure 7**. This may be due to the fact that when the time of treatment of SSAS of phenol increasing and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of phenol from SSAS, therefore the percent removal of phenol from SSAS was increased.

STATISTICAL MODEL

A statistical model was carried out on the experimental results obtained from this study. Regression Analysis and **π** Theorem was adopted to maintain a relation between the percent removal of phenol and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of phenol, adsorbent media IRH bed height, treatment time and column diameter. These relations are shown in **equation 1** below, which has a correlation coefficient (R^2)0.992.

$$\%R = 3.855 \times 10^{6} \left(\frac{T_f \, . P \, . h_h \, . C_{P_{sol}} \, . t}{F \, . d \, . C_o \, . g} \right)^{0.251} \left(\frac{1}{pH}\right)^{0.247} \ldots (1)$$

where:	$\%R$	Percent Removal of Phenolfrom SSAS
	T_f	Feed Temperature, (K)
	P	Pressure, (Pa)
	h_b	Adsorbent Material Bed Height, (m)
	$C_{P_{sol}}$	Heat Capacity of Aqueous Solution, (J/g. K)
	F	Aqueous Solution Flow Rate, (m^3/s)
	d	Internal Diameter of Sorption Column, (m)
	C_o	Initial Concentration of Phenol, $(g/m^3)_p$
	t	Treatment Time, (s)
	g	Acceleration of Gravity, (m/s^2)

CONCLUSIONS

The following conclusions can be drawn:

1. IRH showed a good ability to remove phenol from SSAS using fixed bed adsorption unit. So, it could be recommended for removal of phenol from wastewater in Iraq instead of other material because it is valid, cheap, economic, easy and simple for using, and has a high ability to adsorb phenol, can be used several times by cost regeneration method and can be used finally in another benefit uses.
2. Maximum removal of phenol was 89.73% at initial phenol concentration of 1 mg/l.
3. The percentage removal of phenol was increased with decreeing flow rate of SSAS, pH and initial concentration of phenol while the percentage removal was increasing with increasing of treatment time and the height of adsorbent material IRH.

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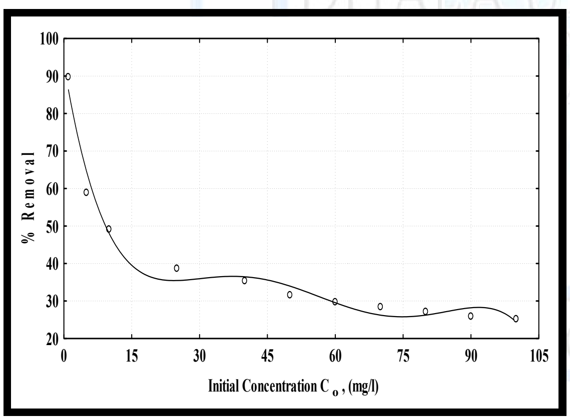

Figure 2: Effect of initial concentration (C_o) on the percent removal of phenol @ T_f =55°C, h_b = 1 m, pH=1, t=60 min. and F=5 ml/min.

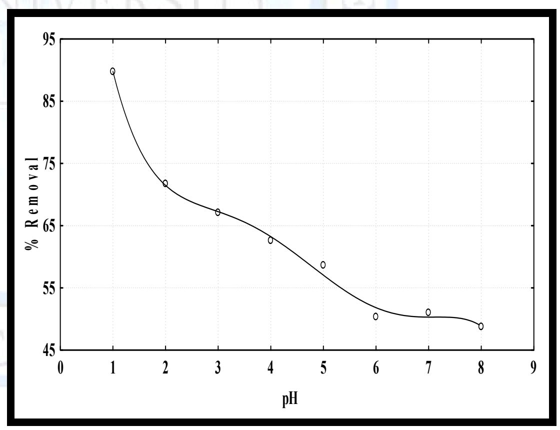

Figure 3: Effect of pH on the percent removal of phenol @ C_o= 1 mg/l, T_f =55°C, h_b = 1 m, t=60 min. and F=5 ml/min.

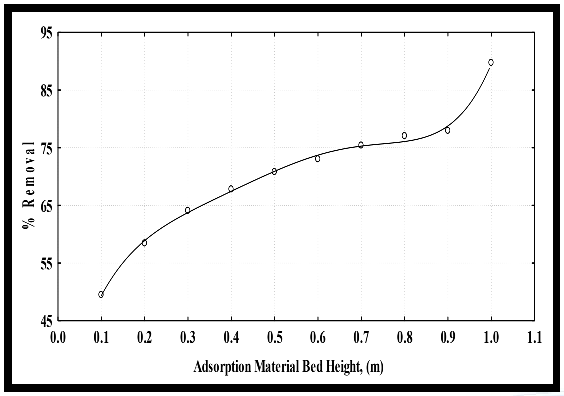

Figure 4: Effect of adsorbent media bed height (h_b) on the percent removal phenol @ $C_{\circ}$= 1 mg/l, pH=1,T_f =55°C, t=60 min. and F=5 ml/min.

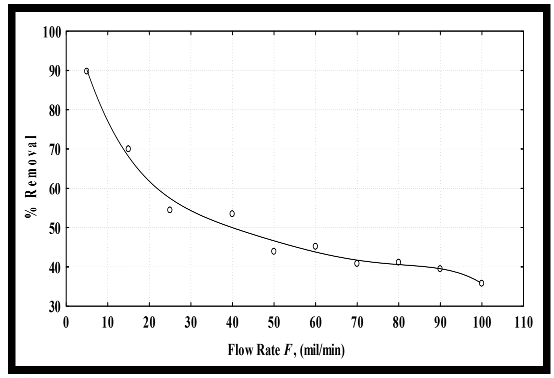

Figure 5: Effect of aqueous solution flow rate (F) on the percent removal of phenol @ $C_{\circ}$= 1 mg/l, pH=1, T_f =55°C, h_b = 1 m and t=60 min.

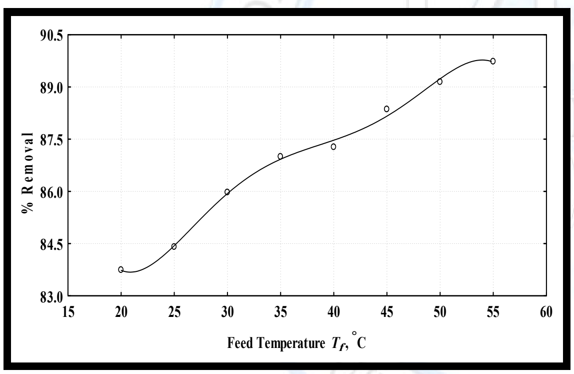

Figure 6: Effect of feed temperature (T_f) on the percent removal of phenol @ $C_{\circ}$= 1 mg/l, pH=1,h_b = 1 m, t=60 min. and F=5 ml/min.

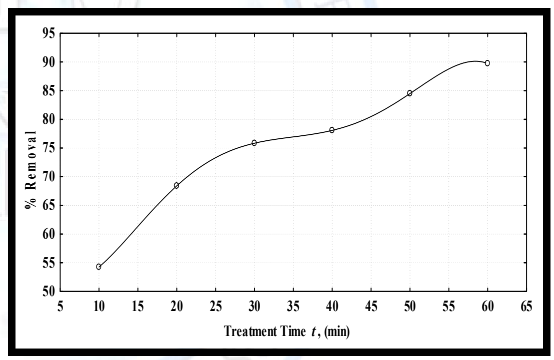

Figure 7: Effect of treatment time (t) on the percent removal of phenol @ $C_{\circ}$= 1 mg/l, T_f =55°C, pH=1, h_b = 1 m, and F=5 ml/min.

إزالة الفينول من مياه المخلفات بإستخدام قشور الرز

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الخلاصة

يتناول هذا البحث دراسة قابلية قشور الرز العراقي (التي تعتبر واحدة من أنواع المخلفات الزراعية التي يصعب التخلص منها بالطرق التقليدية) لإزالة الفينول من مياه المخلفات بإستخدام عدة عوامل تصميمية مختلفة بطريقة الإمتزاز. العوامل التصميمية التي درست في إزالة الفينول من مياه المخلفات بإستخدام قشور الرز العراقي كانت التركيز الإبتدائي للفينول، طول العمود المحشو للمادة الممتزة والتي هي قشور الرز العراقي، الدالة الحامضية للفينول الممتز، زمن المعالجة معدل الجريان للقيم الداخل إلى المنظومة، ودرجة الحرارة للقيم الداخل، هذه القيم كانت قد تغيرت من (1-100) ملغم/ لتر، (10-100) سم، (1-8) ، (1-60) دقيقة ، (5-100) مل / دقيقة ، و(20-55)°م على التوالي . أظهرت النتائج أن أعلى نسبة إزالة هي 89.73% للفينول من المحلول المائي وأن نسبة الإزالة كانت تقل بزيادة التركيز الإبتدائي ومعدل الجريان للقيم الداخل والدالة الحامضية وتزداد بزيادة طول العمود المحشو للمادة المازة ودرجة الحرارة. تم إيجاد موديل رياضي يربط كافة المتغيرات المستخدمة في هذه الدراسة بمعادلة واحدة. وبهذه الطريقة تم التخلص من أكثر من ملوث بطريقة واحدة إقتصادية وصديقة للبيئة.

الكلمات المفتاحية: قشر الأرز ,الفينول , المحاليل المائية, الامتزاز , مياه الصرف الصحي .