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Use of Biopolymer Adsorbent in the Removal of Phenol from Aqueous Solution

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Abstract In this work, chitosan was extracted from local shrimp shell waste as low cost raw materials by chemical methods. The chitosan was impregnated with granular activated carbon to be used as adsorbents for the removal of phenol from aqueous solution by adsorption technique. The adsorbents were characterized by (FTIR) and (BET). The optimum condition for batch adsorption of the phenol and the maximum adsorption efficiency were found to be 78.4% for Chitosan (CH), 90.49% for chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) $CHGAC_1$, 94.47% for chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) $CHGAC_2$ and 85.91% for Granular activated carbon (GAC) at 1.2 g, pH 7 and 6 hrs respectively. The equilibrium isotherm of (Chitosan CH, Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) $CHGAC_1$ and Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) $CHGAC_2$) for the phenol shows that the Langmuir isotherm fits the experimental data better than Freundlich and Temkin adsorption. The equilibrium isotherm of Granular Activated Carbon (GAC) for the phenol shows that the Freundlich isotherm fits the experimental data better than Langmuir and Temkin adsorption.

Keywords Adsorption, Phenol Removal, Chitosan, Biocomposite Adsorbents, Granular Activated Carbon

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1. Introduction

The presence of poly aromatic hydrocarbons, heavy metals and synthetic materials cause serious threat to human health, living resources, and ecological systems. For being non-biodegradable and tend to accumulate in living organisms. These pollutants accumulate in living organisms, which caused serious health problems such as cancer, brain damage [1].

Phenol is one of the most abundant organic pollutants in industrial wastewater and is considered as one of the priority pollutants by US Environmental Protection Agency [2]. Phenol is introduced in wastewater by many industries such as petroleum refining, coal tar, pharmaceuticals, resin, plastic, yarn, petrochemical, coal, ceramic, glue, leather, and food processing [3]. Environmental Protection Agency, EPA has set a limit of 0.1mg/lit of phenol in wastewater [4].

There are many methods for removal of the phenol from aqueous solution such as ion exchange, precipitation, coagulation, flocculation, chemical oxidation and adsorption [5-7]. Adsorption is considered as highly effective, inexpensive, easy to operate among the physic chemical treatment, and insensitivity to toxic pollutants [8].

Chitosan is the most abundant biopolymer in nature after cellulose, which is produced by a deacetylation procedure from chitin and is extracted from the shells of shrimp, prawns, crabs, insects and other crustaceans. Chitosan is useful in a wide application in various industries such as food biotechnology, biomidicine, cosmetics and pharmaceuticals. In addition the chitosan used in environment and agriculture, such as water treatment, seed treatment and other applications. Chitosan has many characterization such as biocompatibility, biodegradability, non-toxicity and adsorption properties [9]. Chitosan derivative has gained wide attention as effective biosorbent due to low cost and high contents of amino and hydroxyl functional groups which show significant adsorption potential for the removal of various aquatic pollutants [10].

The objective of this work is to extract chitosan from shrimp shells and impregnated it with granular activated carbon as biocomposite adsorbents for the removal of phenol from aqueous solution by adsorption. Using different adsorbents, the effects of adsorbent dosage, pH value and contact time on the adsorption process of the phenol for chitosan (CH), chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and granular activated carbon (GAC) were investigated. The equilibrium isotherms Langmuir, Freundlich and Temkin models were studied.

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2. Material and Methods

2.1. Materials

Preparation of Stock Solution of Phenol

Phenol was chosen as an adsorbate (MW=94.11g/mol). A stock solution of phenol was prepared by adding 1gm of phenol into 1L distilled water. The test solution of desired concentration was then prepared by diluting the stock solution. The equilibrium concentrations of phenol were measured using a UV spectrophotometer at a maximum wavelength of 263 nm. The pH of the solution was adjusted to the required value using 1 M HCl and 1 M NaOH solutions.

Granular Activated Carbon GAC

Granular activated carbon (GAC) was utilized in this work as an adsorbent. High purity 99.9% GAC supplied by Panreac, Barcelona, Espana. The typical properties of GAC are shown in the Table 1.

Table 1. Typical properties of GAC

Properties	Values
Chemical Formula	GAC
Particle size	1–5 mm
Mesh sizes	8 X 30
Bulk Density	Approximately 450 kg/m^3
Hardness (Abrasion No.)	95 – 99 (ASTM D3802)
Moisture	2 – 3% maximum, as packed
pH	7 (ASTM D3838)
Surface Area	500 – 1000 m^2 /g (BET N)

Extraction and Preparation of Chitosan

Fresh shrimp was collected from local market of Basrah. Shrimp head, tail and skin were separated from shrimp by using sharp knife. The collected shrimp wastes were washed with warm water several times to remove soluble organics, adhesion proteins and other impurities, and then crushed with mortar pestle. Crushed shrimp waste was kept in a polyethylene bags at the 25°C for 24 hours for partial autolysis to facilitate chemical extraction of chitosan and to enhance the quality of chitosan [11].

The chitosan was prepared by chemical methods, they are including Deproteinization, Demineralization and Deacetylation processes.

Deproteinization was carried out by soaking the shrimp shells (from pretreatment) in 1 M NaOH solution for 24 hours and 25°C in order to remove the protein. The solid to NaOH solution ratio is fixed at 1:10 (w/v) and slow mixing. The resulted material was washed with distilled water several times to remove the base. After rinsing the deproteinzed material was obtained by filtration under vacuum and then dried into oven at 70°C [12].

Demineralization of shrimp shell (obtained from deproteization process) was done by immersing into 0.25 M HCl solution in order to remove minerals (mainly calcium carbonate). The ratio of deproteinzed material to acid solution is maintained at 1:10 (w/v) for 15 minutes and 25°C. Then, the solid was washed with distilled water several times to remove excess acid and pH 7 was reached. After washing and filtration under vacuum, the material free of minerals was dried in an oven at 90°C for 1 hour to obtain Chitin [12].

Deacetylation is the process to convert chitin to Chitosan by removal of acetyl groups. It is generally achieved by treatment with concentrated sodium hydroxide solution 60% with shaker water bath at 80°C for 1hour and ratio of chitin to the solution (1:10), to remove the acetyl groups from the polymer and then dried into the oven at the 80°C for 2 hours. The solid was then crushed to obtain the Chitosan [13].

Preparation of Chitosan Treating with GAC

CHGAC was prepared as an effective adsorbent by treating the chitosan CH with the granular activated carbon GAC. The stock solution of the chitosan was prepared by adding 10 g/L into 1% (v/v) of the acetic acid solution. The GAC was soaked in the stock solution of chitosan with solid to solution ratio 10:50 (w/v) at the temperature 25°C for 24 hours. After that washing the CHGAC composite with distilled water several times and filtering under vacuum to remove of the excess chemicals and to obtain of the neutral pH. Then the adsorbent was soaked in 0.1 M of the NaOH solution for 3 hours so as to precipitate the adsorbed chitosan on the granular activated carbon. After that, the adsorbent was washed with distilled water for several times to remove the base, and then dried in an oven at the temperature 102°C for 2 hours and stored in a dryer for experimental use [14].

2.2. Batch Adsorption Experiments

Effect of Adsorbent Dosage

To determine the optimum weight of (CH, CHGAC$_1$, CHGAC$_2$) and GAC as an adsorbent of phenol solution. Different dosage (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, and 1.6 g) mg of Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) (CHGAC$_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) (CHGAC$_2$) and Granular activated carbon (GAC) were mixed with 50 mL of phenol solution. The solution was then shaken for about 5hrs in a water bath shaker at fixed speed 120 rpm and temperature of 25°C. After shaking the solutions were then separated by filtration using 0.45 µm filter paper. The remaining concentrations of phenol in the filtrate were measured by using the Ultraviolet–visible (UV-Vis) spectrophotometer. All experiments were performed at the pH 7 of the solution and 102.29 mg/L initial concentration of phenol solution. The desired pH was adjusted using 1 M HCl and 1 M NaOH.

Effect of pH

To obtain the optimum pH of the phenol solution adsorption onto Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) ($CHGAC_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) ($CHGAC_2$) and Granular activated carbon (GAC), a different pH (2, 3, 5, 7 and 9) were used with 50 mL of the phenol solution with an initial concentration of 102.29 mg/L. The pH of each samples was adjusted by 1M of concentrated HCl acid and 1M NaOH by pH meter. The phenol solution of different pH was added to the bottles containing the optimum weight of onto Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) ($CHGAC_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) ($CHGAC_2$) and Granular activated carbon (GAC). The bottles were then shaken in a water bath shaker for 5 hrs at 120 rpm and 25°C. The phenol solution was separated by filtration using 0.45 μm filter paper. The remaining concentration of phenol in the filtrate was measured by using the Ultraviolet–visible (UV-Vis) spectrophotometer. The best pH of each bioadsorbents Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) ($CHGAC_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) ($CHGAC_2$) and Granular activated carbon (GAC) for phenol was obtained at maximum adsorption efficiency.

Effect of Contact Time

In order to obtain the best contact time for adsorption of phenol adsorption onto bioadsorbents Chitosan (CH), Chitosan impregnated granular activated carbon with amounts of chitosan (10 wt.%) ($CHGAC_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) ($CHGAC_2$) and Granular activated carbon (GAC), a series of experiments were achieved at different contact time (2, 4, 6, 8 and 10 hrs) with best adsorbent dosages and the best pH of adsorbate solutions. The phenol solution was adjusted to the best of dosage and pH with the initial concentration 102.29 mg/L onto bioadsorbents Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) ($CHGAC_1$), Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) ($CHGAC_2$) and Granular activated carbon (GAC) respectively. A volume 50 ml of the phenol solution was placed in the bottles. The solution in the bottles was agitated for different times in a shaker with water bath at agitation speed of 120 rpm and the temperature was maintained at 25°C and then filtered. The equilibrium concentrations of phenol were determined by the Ultraviolet–visible (UV-Vis) spectrophotometer. The best time for phenol was then obtained at maximum adsorption efficiency.

2.3. Characterization of Adsorbents and Adsorbate

CH, CHGAC and GAC were characterized using the Fourier-Transformation Infrared Spectra (FT-IR) (Model IRTracer-100, Shimadzu Co., Japan). The specific surface area of Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC) were measured using the BET analyzers (Model 9600, USA). The Ultraviolet–visible (UV-Vis) spectrophotometer (Model UV - 160 A, Shimadzu Co, Japan) was used to measure the equilibrium concentrations of phenol.

2.4. Adsorption Isotherm

Equilibrium isotherm experiments were carried out using the optimum condition of adsorbent dosage, pH and contact time for adsorption of phenol onto each of bioadsorbents Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC). The phenol solution with different initial concentration (20, 40, 60, 80, 100, 150 and 200 mg/L) were adjusted to the best pH of phenol solution. A 50 ml of the phenol solution was placed in the bottles. Best dosage of each bioadsorbent Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC) were added to each bottle. The samples in bottles were agitated at a best adsorption period in a shaker with water bath at agitation speed 125 rpm and the temperature was maintained at 25°C. The samples were then filtered using 0.45 μm filter paper and the remaining concentration of phenol was measured by Ultraviolet–visible (UV-Vis) spectrophotometer.

The amount of adsorption at equilibrium, qe(mg/g), is given by Equation 1 [15].

$$q_e = \frac{C_o - C_e}{w} * V \qquad (1)$$

Where q_e is quantity of adsorbate (mg/g), V is the total volume of adsorbate solution (L). C_o and C_e are the initial and equilibrium concentration of adsorbate solution at equilibrium in (mg/L) respectively. W is the adsorbant weight (g).

The removal efficiency can be described by an adsorption isotherm according to the general Eq. (2) [16].

$$Removal\ \% = \frac{C_o - C_e}{C_o} * 100 \qquad (2)$$

Where

C_o = Initial concentration of adsorbate solutions (mg/L).

C_e = Concentration of adsorbate solution at equilibrium (mg/L).

Langmuir Isotherm Model

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption processes of monolayer adsorption. The Langmuir isotherm can be written as [17].

$$q_e = \frac{q_m b\, C_e}{1 + bC_e} \qquad (3)$$

The linearized form of the Langmuir equation:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{qm\ b} \quad (4)$$

Where:

q_e: is the equilibrium adsorbate concentration on the adsorbent (mg/g)

C_e: is the equilibrium concentration of the dye in solution (mg/l)

q_m: is the monolayer adsorption capacity (mg/g) and

b: is the constant related to the free energy of adsorption (L/g).

Freundlich Isotherm Model

The Freundlich isotherm is an empirical equation employed to describe heterogeneous surfaces with interaction occurring between the adsorbed molecules and is not restricted to the formation of a monolayer [18]. The Freundlich Equation is (5).

$$q_e = K_f\ Ce^{1/n} \quad (5)$$

The linear form of the Freundlich isotherm equation is expressed in (6):

$$\ln qe = [1/n] lnCe + lnKf \quad (6)$$

Where K_f is a constant describing the adsorption capacity (L/g) and n is an empirical parameter related to the adsorption intensity, the constants n and K_f were obtained from the slope and intercept respectively.

Temkin Isotherm Model

This isotherm contains at the factor that explicitly taking into the account of adsorbent and adsorbate interactions. As is clear from the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against ln C_e and the constants were determined from the slope and intercept [19]. The model is given by the following of the equation (7).

$$qe = \frac{RT}{b} \ln(A_T C_e) \quad (7)$$

$$qe = \frac{RT}{b_T \ln A_T} + \left[\frac{RT}{b}\right] \ln Ce \quad (8)$$

$$B = \frac{RT}{b_T} \quad (9)$$

$$q_e = Bln\, A_T + BlnC_e \quad (10)$$

Where:

B = [RT/b_T] in (J/mol): corresponding to the heat of adsorption

R: is the ideal gas constant (8.314J/mol/K)

T(K): is the Absolute Temperature at 298K

b_T: is the Temkins isotherm constant

A (L/g): is the equilibrium binding constant corresponding to the maximum binding energy.

3. Results and Discussion

3.1 Characterization of the Adsorbents

FTIR

The spectra of extracting chitosan from the local shrimp were obtained using an FTIR spectrophotometer (IRTracer-100, Shimadzu Co. Japan). FTIR was carried out in the various ranges from 4000-400 cm^{-1} to study the conformation of the extracted Chitosan with standard chitosan. FTIR spectra of extracting chitosan and standard Chitosan are presented in Figure 1 (a) and (b) respectively. The peaks at 3425.58 cm^{-1} due to the presence of the (O-H), and (-NH_2) groups of position of glucosamine, a major group present in chitosan. The vibrational band observed between 2924.09 -2885.51 cm^{-1} is due to the typical C-H stretch vibrations. These results are in agreement with the work of (Alhosseini S. et al, 2012) [20] and (Y. S. Puvvada et al, 2012) [21]. In the FTIR spectra, two characteristic bands for NH_2COCH_3 group were observed at 1654.92 and at 15558.48 cm^{-1}. The peak at 1654.92 cm^{-1} is known as Amide I band which is attributed to the occurrence of (C=O) in the NH_2COCH_3 group (Amide I band). The peak at 1558.48 cm^{-1} due to the secondary amine groups (Amide II). This band can be detected within the 1570-1530 cm^{-1} interval, depending` on the degree of intermolecular association between C=O and N-H groups. These results are in agreement with the work of (D. Zvezdova 2010) [22]. The peak at 1153.43 cm^{-1} due to (NH) free amino groups. The peaks at 1083.99, 1072.42, and 1033.85 cm^{-1} due to the presence of three distinct vibrational modes of C–C, C-O-C, and -CO is stretching vibrations. The peak at 894.97 cm^{-1} due to ring stretching. These results are in agreement with the work of (Y. S. Puvvada et al, 2012) [21], where the prepared Chitosan by processing shrimp waste (shell) and involved partial deacetylation of chitin.

FTIR analysis of granular activated carbon is presented in Figure 2. The surface functional groups present in the granular activated carbon were the band corresponding to O-H group at 3437.15-3008.95 cm^{-1}; a band at 2920.23-2846.93 cm^{-1} corresponded to aliphatic C-H stretching; a band at 1643.35- 1616.35 cm^{-1} known as Amide I band which is attributed to the occurrence of (C=O) groups; a band at 1546.91-1500.62 cm^{-1} corresponded to secondary amide and N-H bending with C-N vibrations; a band around 1465.90 cm^{-1} was ascribed to an aromatic ring of P-C stretching vibration; the peak around 1400.32-1334.74 cm^{-1} corresponded to phenolic OH and C-N groups; a band from 1180.44-1041.56 cm^{-1} ascribed to SO_2 symmetric stretching; an IR band around 840.96-756 cm^{-1} corresponding to NH_2 amines group and a band from 705.95-601.79 cm^{-1} attributed to C-H bending out of plane were observed. These results are in agreement with the work of (P. Sugumaran et al, 2012) [25].

Figure 3 shows the FTIR spectra of CHGAC adsorbent. The peak of the 3441.01 cm^{-1} is due to the O–H (H bonded) stretching. The peak of the 2920.23 cm^{-1} is due to the typical C-H stretch vibrations correspond to the asymmetric and symmetric stretching. The peaks in the range of 1643.35 cm^{-1}, 1562.34 cm^{-1}, 1627.92 cm^{-1}, 1516.05 cm^{-1}, 1462 cm^{-1}, 1381 cm^{-1}, 1145.72 cm^{-1}, 1095.57 cm^{-1}, 975.98 cm^{-1}, 875.68 cm^{-1} and 817.82cm^{-1} were assigned to N-H bending, C-N stretching, O-H in plane bending, C-C-C, -CO Skeletal in the backbone and CH3-C-OH stretching respectively. Bands around 698.23 cm^{-1} and 489 cm^{-1} indicate the presence of OH and C–C bending vibrations respectively. These results are in agreement with the work of (M. Soundarrajan et al, 2013) [26].

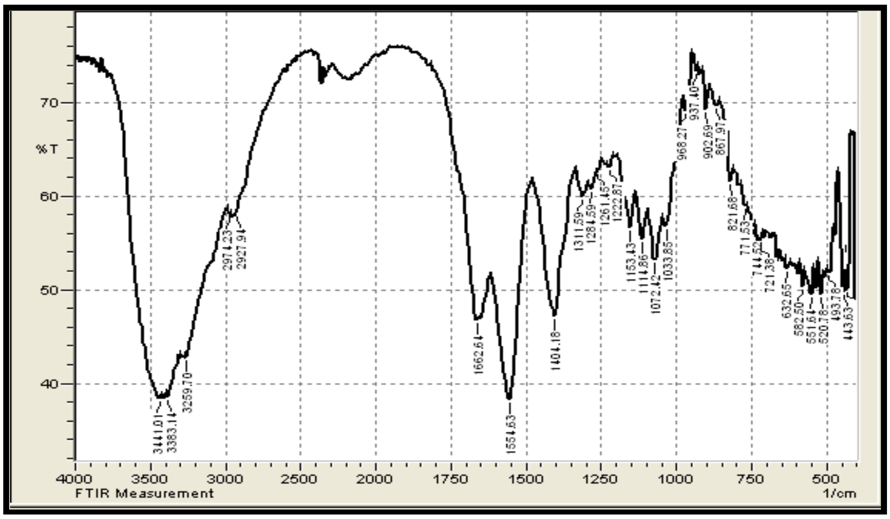

Figure 1(a). FTIR of chitosan extracted from shrimp shell

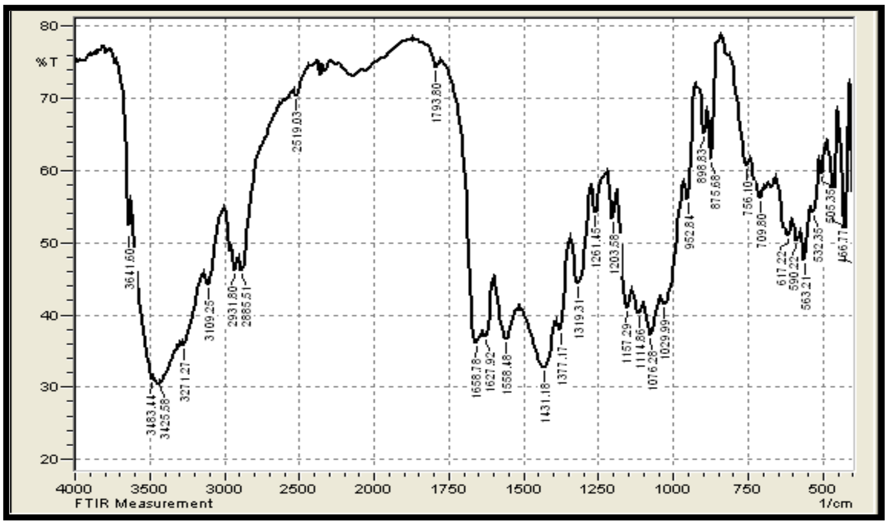

Figure 1(b). FTIR of standard chitosan

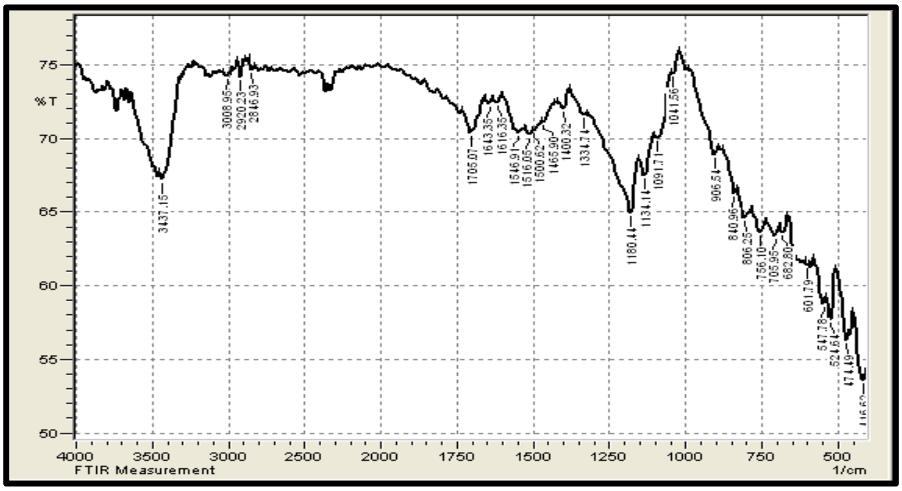

Figure 2. FTIR of Granular Activated Carbon

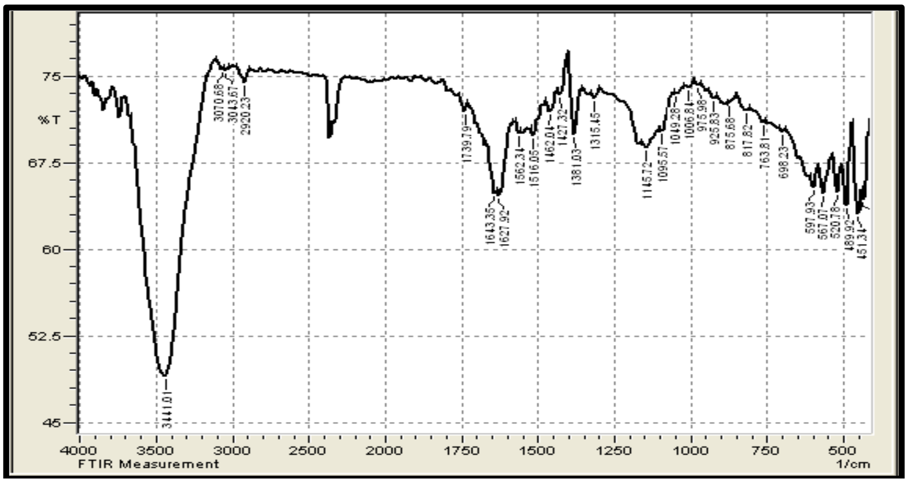

Figure 3. FTIR of CHGAC Composites

Specific Surface Area Analysis

The surface area characterization of chitosan, granular activated carbon, and chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) are listed in Table 2. The process of immobilizing chitosan onto granular activated carbon resulted in the homogeneous dispersion of the Chitosan polymer matrix onto the granular activated carbon surface. These results are in agreement with the work of (C. Futalana et al, 2011) [23]. The ($CHGAC_1$ & $CHGAC_2$) have the superior properties improved adsorption properties over chitosan and GAC alone in terms of high surface area These results are in agreement with the work of (M. Wan et al, 2010) [24].

Table 2. Surface area characterization of CH, $CHGAC_1$, $CHGAC_2$ and GAC Adsorbents by BET analysis

Adsorbents	BET Surface Area, m^2/g
Chitosan (CH)	7.45
Granular activated carbon (GAC)	723
$CHGAC_1$	750
$CHGAC_2$	795

3.2. Batch Adsorption Studies

Effect of Adsorbents Dosage

The effect of adsorbent dosage on the adsorption efficiency for phenol removal was performed at different dosages (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 and 1.6 gm), 25°C and 102.29 $mg.L^{-1}$ initial concentration as shown in Figure 4. It can be seen that the adsorption efficiency increased with increased of adsorbent dosage. Then the adsorption efficiency remained constant and increased slowly with increased in adsorbent dosage and reached to the equilibrium nearly at 1.2 g for each adsorbent Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC). This may be due to greater availability of the surface area of higher concentration of the adsorbent and the complete utilization for all active sites in the adsorbent dosage by phenol ions. These results are in agreement with the work of (P. Hariani et al, 2015) [27] and (S. Sugashini, K. Begum 2013) [28].

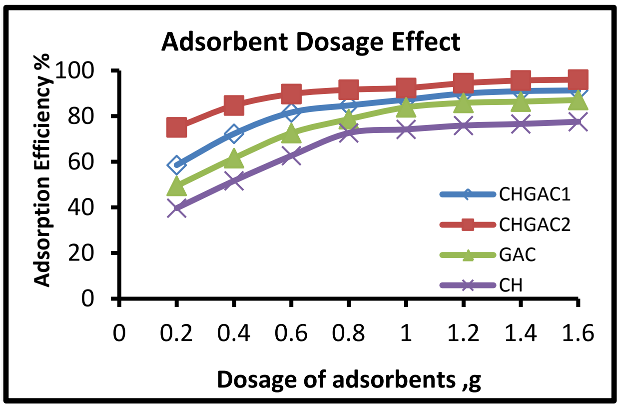

Figure 4. Effect of adsorbents dosage on the adsorption efficiency of phenol onto (CH, $CHGAC_1$, $CHGAC_2$ and GAC) adsorbents

Effect of pH Solution

Figure 5 shows the experiments results for the effect of pH on the adsorption efficiency of phenol onto CH, $CHGAC_1$, $CHGAC_2$ and GAC adsorbents. The experiments were performed at different pH (2, 3, 5, 7 and 9) of phenol solution. It was observed that the adsorption efficiency of phenol onto CH, $CHGAC_1$, $CHGAC_2$ and GAC increased from pH 2 to 7 and above pH < 7 the adsorption efficiency decreased slightly with increasing of pH. This behavior can be explained at the pH >7 that allows higher numbers of hydrogen (H^+) ions to favor the protonation of the active sites. The acidic condition, the amino groups of the chitosan reacts with H^+ for producing the ($-NH_3^+$). Then occurs the interaction between the ($-NH_3^+$) with the phenolate ($C_6H_5O^-$) of phenol due to the electrostatic repulsion. These results are in agreement with the work of (P. Hariani et al, 2015) [27] and (R. Dongre et al, 2012) [29]. The Adsorption efficiency increased at pH 7.0 onto all adsorbents due to electrostatic attraction between the active site and phenolate ($C_6H_5O^-$) of phenol. Then the Adsorption efficiency decreased at pH <7 due to breakup of OH^- with the active site of adsorbents carrying a net negative charged of the phenolate ion above this pH and repulsion between the surface layer and the anionic phenolate, so it will become more complex, results in reduced of the adsorption. These results are in agreement with the work of (M. Atieha 2014) [30].

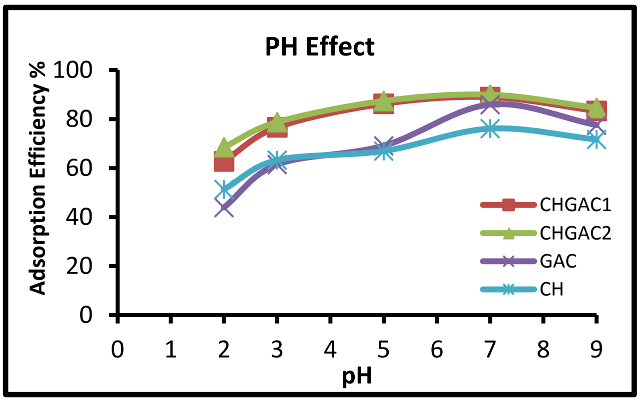

Figure 5. Effect of pH of adsorption of the phenol solution onto (CH, $CHGAC_1$, $CHGAC_2$ and GAC) adsorbents

Effect of Contact Time

The effect of contact time on the adsorption efficiency of phenol using CH, $CHGAC_1$, $CHGAC_2$ and GAC adsorbents was studied for 50 ml of 102.29 mg/L of initial phenol concentration at 1.2 g of adsorbent dosage at pH 7.0 and agitation speed of 120 rpm in order to determine the equilibrium time. The results are shown in Figure 6. It is observed that the adsorption efficiency initially increased and then gradually remained constant with increase in contact time and reached the equilibrium nearly at 6 hours. Hence the maximum adsorption was reached during this period. This may be due to the availability of a large number of active binding sites initially for adsorption. These results are in agreement with the work of (P. Hariani et al, 2015) [27], (S. Sugashini, K. Begum 2013) [28] and (B. Karabacakoğlu et al, 2008) [31].

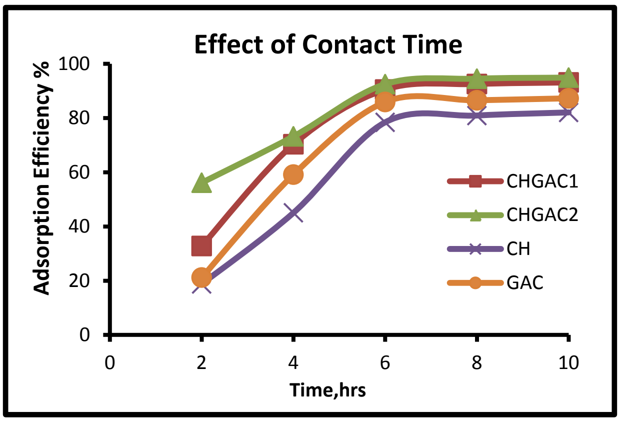

Figure 6. Effect of contact time for adsorption of phenol onto (CH, $CHGAC_1$, $CHGAC_2$ & GAC) adsorbents

3.3. Adsorption Isotherms

The adsorption isotherm curves of phenol onto each of CH, $CHGAC_1$, $CHGAC_2$ and GAC are shown in Figures 7, 8, 9 and 10 respectively. These Figures describe the experimental data and the theoretical data obtained from Langmiur, Freundlich and Temkin isotherm. All constants and correlation coefficients for Langmiur, Freundlich and Temkin isotherm theoretical model are listed in Table 3.

Figure 7 shows that the adsorption capacity of phenol onto CH increases with increasing the solution concentration. The initial adsorption rates were high, this may be due to the availability of a large number of vacant sites initially for adsorption and presence the functional groups of CH are (the amino and hydroxyl functional groups) to adsorbed phenolate ($C_6H_5O^-$) from aqueous solution. After that the adsorption sites were filled up and the phenol solution concentration decreased until equilibrium was reached. These results are in agreement with the work of (N. T. Abdel-Ghani et al, 2015) [32] and (I. Dakhil 2013) [33]. The results indicate that Langmuir isotherm gives a better the experimental data than Freundlich and Temkin adsorption isotherm for phenol removal onto chitosan (CH) depend on the values of the correlation coefficient R^2 from Table 3.

In the Figures 8 and 9 shows that the adsorption capacity of phenol onto $CHGAC_1$ and $CHGAC_2$ increases with increasing the solution concentration. The increase of the adsorption capacity of the $CHGAC_2$ compared with $CHGAC_1$, this can be explained because of the largeness of surface area of $CHGAC_1$ and $CHGAC_2$ about 750 and 795 m^2/g respectively, leads to contribute to the increased of the adsorption, As well as the functional groups of the $CHGAC_2$ increased more than that of $CHGAC_1$. Due to The functional groups of CH are (the amino and hydroxyl functional groups) and GAC is a very effective adsorbent to give additional functional groups to chitosan. Then the adsorption capacity with the $CHGAC_1$ and $CHGAC_2$ reached to equilibrium because of the chitosan content in the whole mass of the composite and chitosan is the main component due to the functional groups of chitosan. These results are in agreement with the work of (Sh. Maghsoodloo et al, 2011) [14], (M. Wan et al, 2010) [24], (N. T. Abdel-Ghani et al, 2015) [32] and (I. Dakhil 2013) [33]. The result indicates that Langmuir isotherm fits the experimental data better than Freundlich and Temkin adsorption isotherm for phenol removal onto $CHGAC_1$, $CHGAC_2$ depend on the value of the correlation coefficient R^2 from Table 3.

In the Figure 10 shows that the adsorption capacity of phenol onto GAC increases with increasing the solution concentration. The initial adsorption rates were high due to increased in surface area of GAC about 723 m^2/g and increases the number of active adsorption sites. Then phenol solution concentration decreased until equilibrium was reached. These results are in agreement with the work of (B. Karabacakoğlu et al, 2008) [31]. The result indicates that the Freundlich fits the experimental data better than the Langmuir and Temkin isotherm for phenol removal onto GAC depend on the value of the correlation coefficient R^2 from Table 3.

Table 3. Langmuir, Freundlich and Temkin isotherm constants for the phenol removal onto each of CH, $CHGAC_1$, $CHGAC_2$ and GAC at 25°C

Adsorbents	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm			
	q_m	b	R^2	1/n	K_f	R^2	A_T	b_T	B	R^2
CHGAC1	7.2	0.1	0.99	0.5	1.2	0.98	2.1	1873.9	1.3	0.96
CHGAC2	7.1	0.3	0.99	0.4	1.7	0.97	4.9	2069. 5	1.2	0.97
GAC	8.4	0.06	0.97	0.6	0.8	0.99	0.9	1637.6	1.5	0.9
CH	8.06	0.02	0.99	0.7	0.3	0.98	0.3	1604.7	1.5	0.96

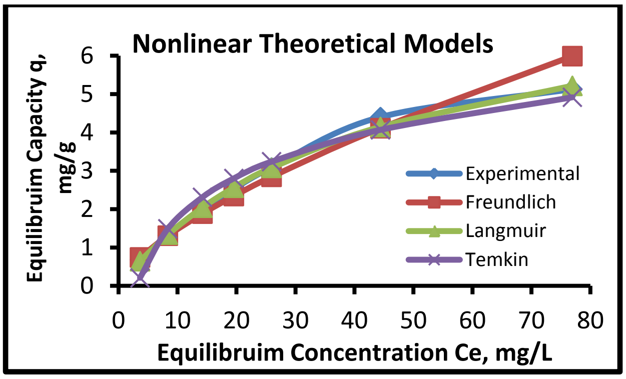

Figure 7. Adsorption isotherms of experimental and theoretical models of the phenol onto CH at (25°C, 1.2 gm, pH 7.0 & time 6 hours)

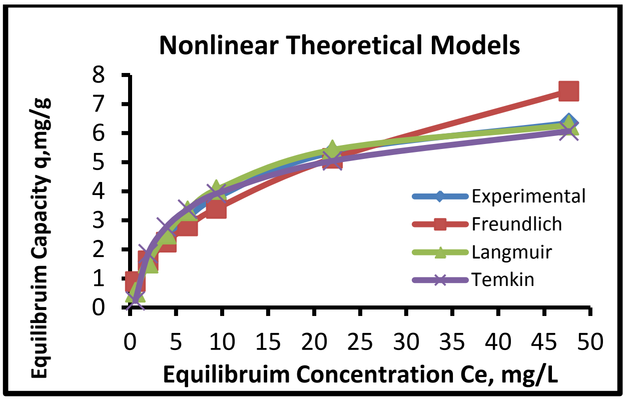

Figure 8. Adsorption isotherms of experimental and theoretical models of the phenol onto $CHGAC_1$ at (25°C, 1.2 gm, pH 7.0 & time 6 hours)

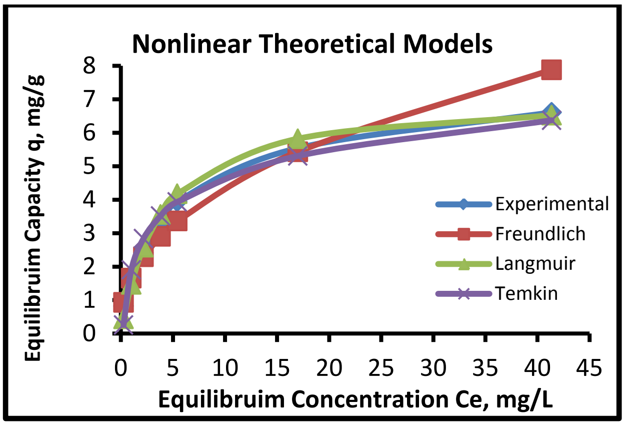

Figure 9. Adsorption isotherms of experimental and theoretical models of the phenol onto $CHGAC_2$ at (25°C, 1.2 gm, pH 7.0 & time 6 hours)

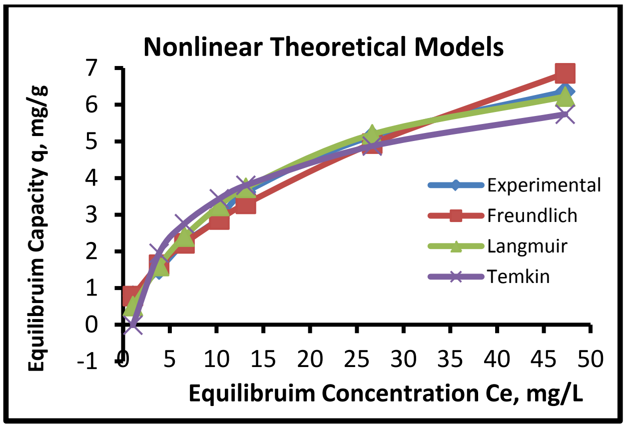

Figure 10. Adsorption isotherms of experimental and theoretical models of the phenol onto GAC at (25°C, 1.2 gm, pH 7.0 & time 6 hours)

4. Conclusions

In the present work, the bioadsorption of phenol from aqueous solution onto each of Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC) lead to the following conclusions:

1. Natural biopolymer “Chitosan” was synthesized using local low cost shrimp shells as raw materials by chemical methods involving deproteinization, demineralization, and deacetylation. Then Chitosan (CH) will be treated with Granular activated carbon GAC by impregnation to be used as adsorbents for the removal of phenol from aqueous solution.
2. For batch adsorption, the maximum adsorption efficiency of phenol onto each of Chitosan (CH), Chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.% and 20 wt.%) (CHGAC) and Granular activated carbon (GAC), were found to be 78.4% for Chitosan (CH), 90.49% for chitosan impregnated granular activated carbon with different amounts of chitosan (10 wt.%) $CHGAC_1$, 94.47% for chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) $CHGAC_2$ and 85.91% for Granular activated carbon (GAC) at

3. The equilibrium isotherm of phenol adsorption onto each of (Chitosan CH, Chitosan impregnated granular activated carbon with different amounts 1.2 g, pH 7 and 6 hrs, respectively and 25°C. of chitosan (10 wt.%) $CHGAC_1$ and Chitosan impregnated granular activated carbon with different amounts of chitosan (20 wt.%) $CHGAC_2$) shows that the Langmuir isotherm fits the experimental data better than Freundlich and Temkin adsorption isotherm. The equilibrium isotherm of phenol adsorption onto Granular activated carbon GAC shows that the Freundlich isotherm fits the experimental data better than Langmuir and Temkin adsorption isotherm.

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