

REMOVAL OF PHENOL AND CONVENTIONAL POLLUTANTS FROM AQUEOUS EFFLUENT BY CHITOSAN AND CHITIN

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The present study deals with phenol adsorption on chitin and chitosan and removal of contaminants from wastewater of a petroleum refinery. The adsorption kinetic data were best fitted to first- and second-order models for chitosan and chitin, respectively. The results of adsorption isotherms showed Langmuir model more appropriately described than a Freundlich model for both adsorbents. The adsorption capacity was 1.96 and 1.26 mg/g for chitin and chitosan, respectively. Maximum removal of phenol was about 70-80% (flow rate: 1.5 mL/min, bed height: 18.5 cm, and 30 mg/L of phenol). Wastewater treatment with chitin in a fixed-bed system showed reductions of about 52 and 92% for COD and oil and greases, and for chitosan 65 and 67%, respectively. The results show improvement of the effluent quality after treatment with chitin and chitosan.

Keywords: adsorption; chitosan; phenol.

INTRODUCTION

One of the major problems of the petrochemical industry is the great amount of wastewater produced and the high investment needed for the treatment of this effluent before it is released in the environment. In particular, phenol is present in significant concentrations, while it is highly toxic and accumulates in the environment.¹

Phenol can be removed from polluted water by chemical oxidation^{2,3} or solvent extraction,^{4,5} by using membranes^{6,7} and by biological treatments.⁸ However, these processes are not really efficient. An alternative is the use of adsorption methods and, in fact, this has been mostly applied for phenol removal and others organic compounds from polluted wastewaters.⁹⁻¹¹ A high efficiency is combined with recovery of solvents and removal of unwanted properties including color and odor. Activated carbon has been widely used for phenol removal,^{12,13} but other adsorbents have been applied as well including peat, bentonite,¹⁴ amberlite resin,^{15,16} biomass,⁸ silica gel and activated alumina,¹⁰ activated carbon zeolite,¹⁷ coir pith carbon,¹⁸ fly ash,¹⁹ chitin²⁰ and chitosan.²¹

Special attention has been paid to chitin, a natural polymer extracted from crab and shrimp shells, and chitosan, a derivative of chitin. These adsorbents have attracted much interest, because of their biodegradability, biocompatibility and hydrophilicity. Their use in the treatment of water and effluents has shown to be useful for removal of metals,²²⁻²⁴ phenols,²⁵ dyes,²⁶ quinones²⁷ and others.²⁸⁻³⁰

Chitin is obtained by treatment with dilute sodium hydroxide for deproteinization, followed by treatment with dilute hydrogen chloride for demineralization. Chitosan is produced by alkaline deacetylation

of chitin. Alternatively, enzymatic treatment³¹ has been developed to reduce the environmental impact and to reduce the cost of processing.

The present study focused on phenol adsorption by chitin and chitosan using batch and column systems for possible use in the treatment of wastewater from petrochemical industries. The improvement of the quality of the effluent was evaluated by removal of phenol and the changes of physicochemical parameters such as pH, conductivity, chemical oxygen demand (COD), total oil and greases (TOG) and dissolved solids (DS).

EXPERIMENTAL

Materials

The wastewater investigated was obtained from the petroleum refinery LUBNOR (Lubrificantes e Derivados de Petróleo do Nordeste, Fortaleza, CE, Brazil). Chitin (light white; ashes 0.30%; 60-200 mesh; molecular weight: 400,000 g/mol; pH 4.28) and chitosan (light yellow; 60-200 mesh; molecular weight: 174,205 g/mol, degree of deacetylation 90%, pH 7.93) were supplied by Delta - Natural and Dietary Products (Parnaíba, PI, Brazil). All reagents and solvents (Merck) were of analytical grade. A stock solution (1000 mg/L) of phenol was prepared and the standard solutions were obtained by diluting to the desired concentrations (10-50 mg/L). Chitosan and chitin were purified by soxhlet extraction and sonication as described by Rhee *et al.*³²

Methods

Batch adsorption studies

Water samples originating from a local petrochemical plant were

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spiked with known amounts of phenol ranging from 10 to 50 mg/L and adsorption studies were carried out batchwise in order to obtain kinetic rates and equilibrium data. Closed flasks containing a known amount of adsorbent were agitated by shaking (150 rpm) for a period of 24 h at a particular pH and all experiments were conducted at room temperature (28 ± 2 °C). pH changes during the course of the measurements were not observed.

The effects of the dosage of adsorbent (2.5×10^{-3} to 2.5×10^{-2} g/mL) and of pH (2 to 10) were studied. Kinetics and isotherms were determined using 0.2 g adsorbent and 20 mL phenol solution (10 to 50 mg/L) at equilibrium. After filtration (0.45 μ m membrane porosity), the residual phenol concentration was determined by HPLC. The adsorption capacity was obtained using Equation 1:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where: q_e is the adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively, of phenol in solution, V is the volume (L), and W is the weight (g) of the adsorbent.

Column adsorption studies

A glass column (30 cm x 11 mm i.d.) filled with known mass of adsorbent corresponding to bed heights of 3.5, 8.5 and 18.5 cm, respectively, was percolated with 30 mL phenol solution (30 mg/L, at pH 6) at flow rates of 1.5, 3.0 and 6.0 mL/min, respectively. The characteristics of the bed are given in Table 1.

Table 1. Properties of fixed-bed adsorbent

Property	Chitosan	Chitin
Granulometry (mesh)	60-250	60-250
Diameter (D) (cm)	1.10	1.10
Bed height (L) (cm)	18.5	18.5
Adsorbent mass (g)	1-3.90	1.2-3.36
Apparent density (ρ_a) (g/cm^3)	0.24	0.22
Packed density (ρ_p) (g/cm^3)	0.22	0.19
Particles volume (V_{ap}) (cm^3)	16.25	15.41
Porosity (ϵ)	0.08	0.12

Breakthrough curves of model and wastewater samples (spiked with 30 mg phenol/L) were determined in order to investigate the column capacity at complete exhaustion. The breakthrough curves were obtained by plotting C/C_0 versus eluent volume. Aliquots of 10 mL were collected at the exit of the column for measuring the phenol concentration.

Regeneration of the adsorbent was effected by using ethanol-water (1:1 v/v) as eluent (five times). For each cycle, 20 mL water was percolated first, followed by 10 mL effluent and 10 mL of eluent. The percentages of removal were calculated for each cycle.

All column experiments were performed in duplicate at room temperature (28 ± 2 °C) and pH 6.0.

Chromatographic analysis of phenol

The phenol concentrations were determined by high-performance liquid chromatography (HPLC) using a Shimadzu SPD-10 A chromatograph equipped with a LiChrospher 60 RP-select B column (12 cm, 5 mm i.d.) and an UV detector. The isocratic mobile phase was water-methanol 30:70 v/v, the flow-rate was 1 mL/min, and detection was done at 270 nm. Before analysis, supernatant samples were filtered (0.45 μ m membrane porosity).

Column adsorption in wastewater treatment

Treatment of the wastewater from a local petroleum refinery was carried out using a column filled with adsorbent (chitosan and chitin) for determination of various parameters including 'Chemical Oxygen Demand' (COD), 'Total Oils and Greases' (TOG), and 'Dissolved Solids' (DS) following procedures by 'Standard Methods for the Examination of Water and Wastewater'.

RESULTS AND DISCUSSION

Batch adsorption studies

Effect of adsorbent mass

The effect of the dosage of adsorbent (2.5×10^{-3} to 2.5×10^{-2} g/mL) on phenol removal is shown in Figure 1. It can be observed that phenol adsorption increases in the range (5×10^{-3} - 1×10^{-2} g/mL) for both chitin and chitosan. According to this result, the adsorbent dosage was fixed at 1×10^{-2} g/mL for all further experiments. Several factors influence the efficiency of phenol adsorption, such as changes pH and particle size (in this case: 60-200 mesh). Generally, smaller particles have greater capacity of analyte removal.

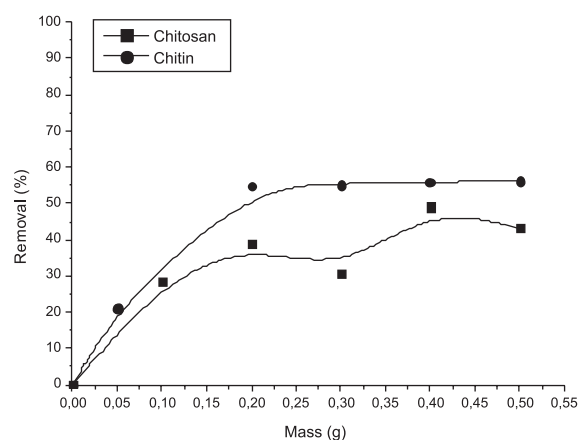


Figure 1. Effect of adsorbent dosage on removal of phenol by chitin and chitosan. Phenol concentration: 30 mg/L; pH 6; agitation time: 24 h; ambient temperature: 28 ± 2 °C

Effect of pH

The effect of pH on phenol adsorption by chitin and chitosan is represented in Figure 2. The data show that the phenol removal increased with decreasing initial pH for both adsorbents. Chitin and chitosan contain functional groups such as hydroxy, acetamido, and amino that are prone to adsorb molecules by hydrogen bonds, Van der Waals interactions, and ion exchanges. Depending on the pH, the amino groups are present in protonated or neutral forms. At low pH, the ammonium groups may exert electrostatic interaction with phenolates thereby increasing the adsorption efficiency. This behavior can be explained considering the fact that variations of pH affect the ionization of phenol (Equation 2a) and the surface properties of the adsorbent, denoted as Ads (Equations 2b, 2c).



As expected, adsorption decreases with increasing pH values (Fi-

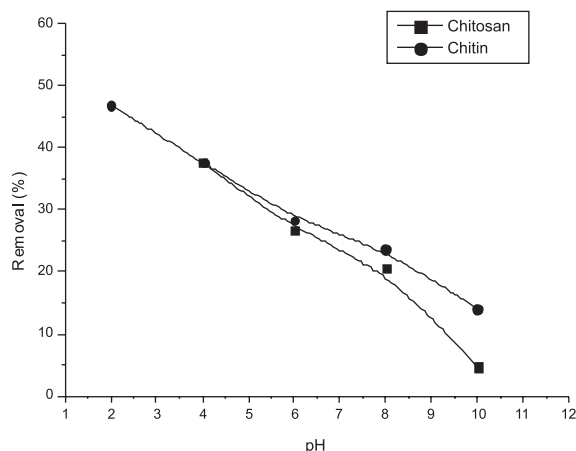


Figure 2. Effect of pH on phenol removal by chitin and chitosan. Adsorbent dosage: 1×10^{-2} g/mL; phenol concentration: 30 mg/L; agitation time: 24 h; ambient temperature: 28 ± 2 °C

Figure 2), which may be attributed to the above factors. The phenolate fraction can be calculated from Equation 3:

$$[C_6H_5OH] = \frac{C_0}{1 + 10^{(pH - pK_a)}} \quad (3)$$

where: C_0 is the initial phenol concentration, the pK_a of phenol is 9.9, and the pH is variable.

Phenol is adsorbed to a lesser extent at higher pH values due to repulsive forces. Similar behavior has been reported by Halhouli *et al.*³³ for phenol adsorption by activated carbon and by Banat *et al.*¹⁴ for phenol adsorption by bentonite. Similar results have also been obtained for phenol adsorption with chitosan,³⁴ chitin,³⁵ and bagasse fly ash.^{19,36} It should be taken into account that, in this work, all experiments were conducted at pH 6 due to the solubility of chitosan at low pH, furthermore because of the pH of the wastewater investigated.

Adsorption kinetics

In order to investigate the kinetics of phenol adsorption on chitin and chitosan, pseudo-first order, pseudo-second order, and intraparticle diffusion models were used. The adsorption kinetics were carried out for three initial phenol concentrations, 10, 30 and 50 mg/L, respectively, at adsorbent dosages of 1×10^{-2} g/mL. The results, presented in Figures 3a and 3b, show that equilibrium was reached within 3, 5 and 6 h for chitosan, and within 3, 4 and 5 h for chitin.

The experimental data were applied to the kinetic models for determination of the rate constants (K_1 and K_2) using the equations of pseudo-first order (Equation 4) and pseudo-second order (Equation 5), respectively:

$$\log(q_e - q) = \log q_e - \left(\frac{K_1}{2.303} \right) \times t \quad (4)$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where: q_e is the amount of phenol adsorbed at equilibrium, q is the adsorption capacity at time t , and K_1 and K_2 are rate constants of first order and second order, respectively.

The rate constants K_1 and K_2 were calculated from $\log(q_e - q)$ versus t and t/q versus t , respectively, for three initial concentrations. They are represented together with the correlation coefficients and adsorption capacities (Table 2). Based on results of experimental (q_e) and predicted (q_p) values, it can be noted that phenol adsorption on chitosan agrees well with first-order kinetics, indicating that the

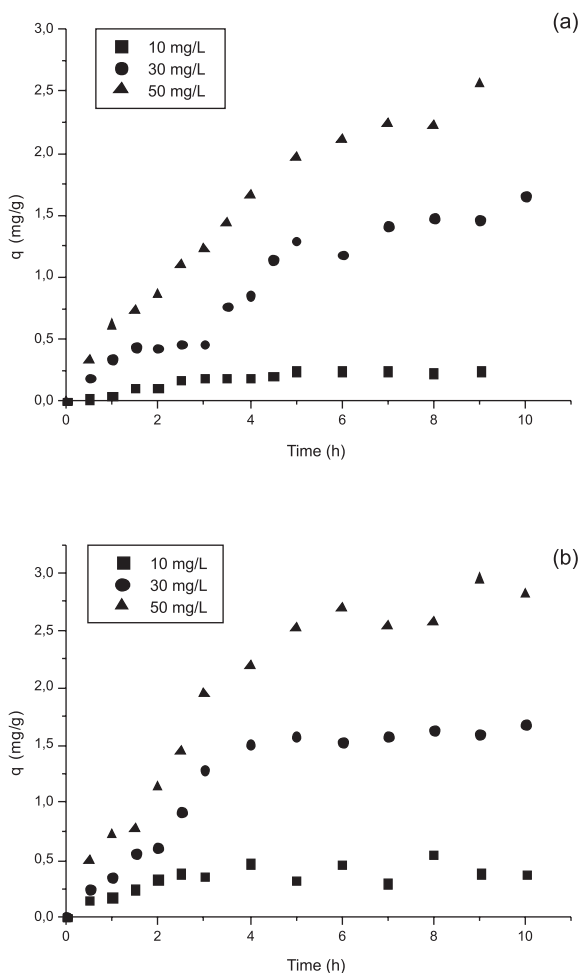


Figure 3. Effect of agitation time and phenol concentration on adsorption of (a) chitosan and (b) chitin. pH: 6.0; adsorbent dosage: 1×10^{-2} g/mL; ambient temperature: 28 ± 2 °C

limiting stage of the adsorption process is a weak interaction with reversible character. However, results for chitin (Table 2) show that a pseudo-second-order model describes satisfactorily the adsorption of phenol, suggesting that the limiting stage of adsorption is a chemical interaction between phenol and adsorbent. Dursun *et al.*³⁵ also observed that phenol adsorption onto chitin follows second-order kinetics.

As is known, two intraparticle diffusion mechanisms are involved in the adsorption rate: diffusion within the pore volume (pore diffusion), diffusion along the surface of the pores (surface diffusion). Pore diffusion and surface diffusion occur in parallel within the adsorbent particle.

Adsorption isotherms

The adsorption isotherms (relationship between adsorption capacities and phenol concentrations at equilibrium) are given in Figure 4. The equilibrium adsorption data of phenol are well described by Langmuir (Equation 6) and Freundlich (Equation 7) models:

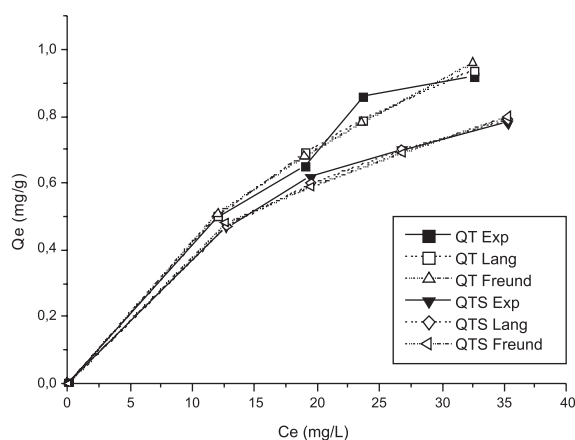
$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{K_L q_{\max} C_e} \quad (6)$$

$$\log q = \log K_F + (1/n) \log C_e \quad (7)$$

where: q is the amount adsorbed (mg/g), C_e is the equilibrium concentration of phenol (mg/L), q_{\max} and K_L are the Langmuir constants

Table 2. Kinetic parameters of phenol adsorption by chitin and chitosan

Adsorbent	Experimental		Pseudo -first-order kinetic model			Pseudo- second-order kinetic model			Diffusion model	
	C_0 (mg/L)	q_c (mg/g)	K_1 (h^{-1})	q_t (mg/g)	R^2	K_2 (g/mg.h)	q_t (mg/g)	R^2	K_i ($mg/g.h^{1/2}$)	R^2
Chitosan	10	0.24	0.45	0.27	0.98	1.46	0.31	0.96	0.15	0.97
	30	1.49	0.20	1.47	0.95	0.05	2.76	0.93	0.66	0.93
	50	2.33	0.38	2.71	0.96	0.03	4.46	0.96	1.04	0.98
Chitin	10	0.40	0.31	0.25	0.94	2.74	0.43	0.99	1.68	0.94
	30	1.58	0.66	2.27	0.91	0.69	1.83	0.99	1.08	0.93
	50	2.70	0.60	4.61	0.95	0.32	3.11	0.8	0.10	0.80

**Figure 4.** Adsorption isotherms of chitosan and chitin. pH: 6.0; adsorbent dosage: 1×10^{-2} g/mL; ambient temperature: 28 ± 2 °C

related to maximum adsorption capacity (mg/g) and energy of adsorption, respectively, and K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich constants calculated from the linear plots of $1/q_e$ versus $1/C_e$ and $\log q_e$ versus $\log C_e$ together with the correlation coefficients (r^2) are given in Table 3. The theoretical data using Langmuir and Freundlich parameters from Table 3 are shown in Figure 4 to assess the validation of the model from the experimental data indicating that the adsorption equilibrium data for phenol followed the Langmuir and Freundlich isotherms for the adsorbents.

However, a better criterion to test the correctness of the fits of the data is the normalized percent deviation,³⁷ which agrees with Equation 8:

$$P = \left(\frac{100}{N} \right) \sum \left(\frac{|q_{ex} - q_{pred}|}{q_{ex}} \right) \quad (8)$$

where: q_{ex} is the experimental adsorption capacity, q_{pred} is the predicted adsorption capacity, and N is the number of observations.

Table 3. Parameters for Langmuir and Freundlich models

Adsorbent	Langmuir				Freundlich			
	q_{max} (mg/g)	K_L	R^2	P	K_F	1/n	R^2	P
Chitosan	1.26	0.05	0.99	1.34	0.10	0.65	0.94	1.57
Chitin	1.96	0.03	0.96	4.52	0.14	0.49	0.98	4.96

The lower the value of the percent deviation P is, the better the fit is (for values less than 5). The calculated P values (Table 3) suggest that the adsorption process for both adsorbents follows a Langmuir model occurring in monolayer surface. Maximum adsorption capacity (mg/g) was found to be 1.96 and 1.26 mg/g for chitin and chitosan, respectively.

The favorable nature of adsorption can be expressed in terms of the separation factor R_L , which is defined in Equation 9:

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

where: K_L is the Langmuir constant and C_0 is the initial phenol concentration.

The parameter R_L can be used to predict the affinity between the adsorbent and the adsorbate according to the criteria: not-favorable for $R_L > 1$, linear for $R_L = 1$, favorable for $0 < R_L < 1$, and irreversible for $R_L = 0$. All values of R_L calculated for chitin and chitosan vary between 0 and 1 indicating that adsorption is favorable for both adsorbents.

Table 4 provides the values of the adsorption capacities (mg/g) of adsorbents reported in other papers. It can be seen that activated carbon, fly ash, and chitin are efficient for removal of phenols. Also, chitin and chitosan have efficiencies comparable to other low-cost adsorbents like rice husk, cooke breeze, and grain rusk. New technologies to increase the adsorption capacity of chitosan have been developed through chemical modification including substitution and cross-linking of chitosan chains. However, the cost of the material may be higher.

Column adsorption studies

Effect of flow rate

The results indicated that phenol removal decreased with increased flow rates for both adsorbents, which is due to an increase of the hydraulic load (1.58 - 6.32 mL/min cm^2) in the column by an increase of the flow rate (1.5 - 6.0 mL/min). A flow rate of 1.5 mL/min has been adopted for further work. Large-scale applications of fixed-bed systems using chitin may cause problems due to clogging during the continuous flow of wastewater. Hence, it is necessary to optimize the system by adjusting the operational parameters. Moreover, a change of downflow to upflow may minimize clogging.

Table 4. Comparison of the adsorption capacities of different adsorbents

Adsorbent	q (mg/g)	Particle size (mm)	Adsorbent dosage (g/mL)	pH	T (°C)	Contact Time	Reference
Chitin	1.96	0.074 - 0.246	1x10 ⁻²	6.0	28 ±2	24 h	This study
Chitosan	1.26	0.074 - 0.246	1x10 ⁻²	6.0	28 ±2	24 h	This study
Chitosan (Flake type)	0.14	-	1x10 ⁻³	Natural	5	4 days	34
Chitin	25.06	0.147-0.30	1x10 ⁻³	1.0	40	100 min	35
Rice husk	4.50	0.026 – 0.147	-	-	-	72 h	11
Coke breeze	0.18	0.016 – 0.141	-	-	-	72 h	11
Bentonite	1.71	-	5x10 ⁻²	5	20	48 h	14
Fly ash	23.83	0.045 - 1	-	6.5	30	24 h	36
Lignite	10.00	0.5	-	Natural	25	-	38
Activated carbon (comercial)	49.72	1.4	5x10 ⁻³	-	-	2h	13
Activated carbon (Derived from coconut shells)	49.88	0.074-0.589	1x10 ⁻³	4 ±0.2	25	30 h	39
Biomass	0.33	2.36-4.75	2.6x10 ⁻³	5.1	21 ±1	30 h	8

Effect of bed height

The effect of the bed height (mass of adsorbent) on phenol adsorption was done at a constant feed concentration of 30 mg/L and a flow rate of 1.5 mL/min. When the bed height increases from 3.5 to 18.5 cm, the percentage of phenol removal reaches 80% and this parameter was chosen for the studies on breakthrough curve.

Breakthrough curves

The breakthrough curves were obtained by plotting C/C_0 versus volume at 30 mg/L phenol concentration of phenol in order to determine the volume and capacity saturation. Figures 5a and 5b show the breakthrough curves for chitin and chitosan, respectively, for model and wastewater samples. It can be observed that the breakthrough volumes for chitin and chitosan are 30 and 20 mL, respectively. The volume of saturation (V_s), for the adsorbents were reached for a volume of 75 mL at 46.7 min (t_x).

The breakthrough capacities calculated from the curves (at $C/C_0 = 0.5$) are 0.10 mg/g for both adsorbents. The column capacities were lower than the Langmuir capacities (Table 3). This discrepancy may be due to incomplete saturation of the active sites due to the limited time of equilibration achieved under dynamic column conditions. The operational column parameters are helpful in designing a fixed adsorber for phenol removal from wastewaters. The length of 'Unused Bed' (LUB) was calculated using Equation 10:

$$LUB = L \times \left(1 - \frac{V_b}{V^*}\right) \quad (10)$$

where: L is the weight of the bed (cm), V_b is the breakthrough volume (mL), and V^* is the stochiometric volume (mL) that corresponds to half of the volume of saturation (V_s). The values of LUB for chitin and chitosan are 2.6 and 7.9 cm, respectively.

Adsorbent regeneration

Experiments were carried out using ethanol-water (1:1 v/v) at a flow rate of 1.5 mL/min, a bed height of 18.5 cm, and a phenol feed concentration of 30 mg/L. The adsorbents were regenerated using

ethanol-water (1:1 v/v) and could be reused after four cycles with a regeneration efficiency of 95%. The regeneration procedure leads to liquid containing ethanol-water and an organic residue. These can be easily separated by distillation.

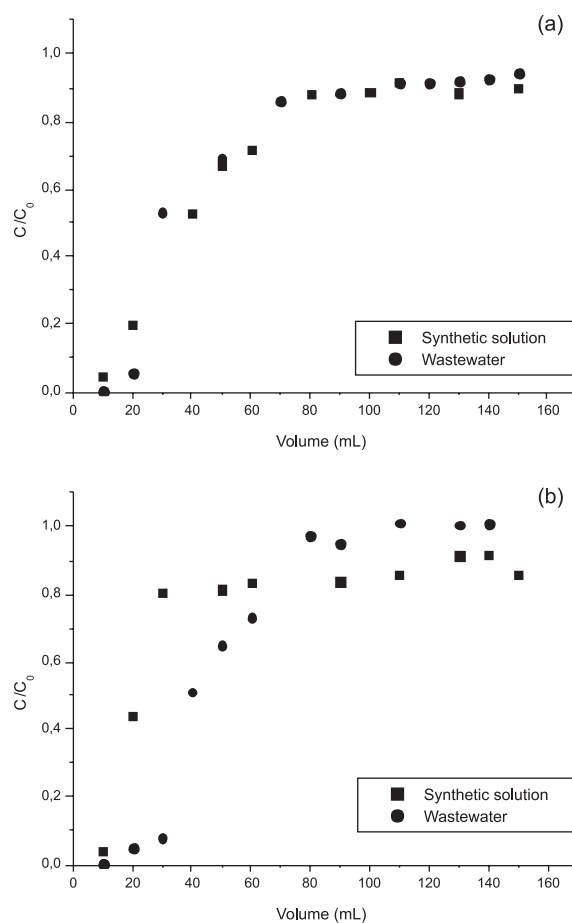


Figure 5. Breakthrough curves for (a) chitosan and (b) chitin. Phenol concentration: 30 mg/L; pH: 6; flow rate: 1.5 mL/min; bed height: 18.5 cm; ambient temperature: 28±2 °C

Wastewater treatment by adsorption in column

Experiments were carried out with a column filled with adsorbent (chitosan and chitin) for determination of following parameters: pH, conductivity, chemical oxygen demand (COD), total oil and greases (TOG), and dissolved solids (DS). The wastewater was taken from a local petroleum refinery local. The results are shown in Table 5. It can be observed that the wastewater contains high concentrations of COD (490 mg/L), TOG (653 mg/L) and DS (862 mg/L). The treatment with chitin and chitosan led to a significant reduction of the pollutants.

The wastewater after chitin treatment gave 52% COD removal and 92% TOG removal. After chitosan treatment, reduction of COD and TOG were around 65 and 67%, respectively. Conductivity, turbidity and DS were satisfactorily reduced from 1.4 to 0.80 mS/cm; from 27 to 6.0 UT, from 862 to 700 mg/L for chitin. For chitosan, reductions were as follows: from 1.4 to 0.80 mS/cm; 27 to 3.0 UT, 862 to 615 mg/L, as shown in Table 5. A drastic de coloration was observed after the treatments.

Table 5. Parameters of the wastewater quality

Parameter	Influent	Effluent	
		Chitin	Chitosan
pH	7.0	7.1	7.9
Conductivity (mS/cm)	1.4	0.8	0.8
Turbidity (UT)	27	6.0	3.0
Chemical Oxygen Demand (mg/L)	490	233	169
Total Oils and Greases (mg/L)	653	50	210
Dissolved Solids (mg/L)	862	700	615

CONCLUSIONS

Adsorption of phenol at chitin and chitosan was most efficient into the pH range of 2.0-5.0. The adsorption data followed pseudo-first order kinetics for chitosan and second-order kinetics for chitin. Complete removal of 30 mg/L phenol from industrial wastewater proved possible using 1×10^{-2} g/mL of adsorbent dosage. Four adsorption/desorption cycles were carried out with ethanol-water (1:1, v/v) as desorbing agent without appreciable reduction in adsorption capacity. The parameters from industrial wastewater as measured by pH, COD and TOG were drastically reduced after treatment with chitin and chitosan. Thus, the present study suggests that chitin and chitosan are attractive low-cost natural adsorbents for removal of phenol and other pollutants from industrial wastewaters.

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