

Use of Low-cost Adsorbents to Chlorophenols and Organic Matter Removal of Petrochemical Wastewater

Aretha Moreira de Oliveira^a, Maria Aparecida Liberato Milhome^b, Tecia Vieira Carvalho^c, Rivelino Martins Cavalcante^d and Ronaldo Ferreira do Nascimento^{a*}

^aUniversidade Federal do Ceará (UFC), Departamento de Química Analítica e Físico-Química, Bl 940. Av. Humberto Monte s/n- Campus do Pici, Fortaleza, CE, CEP 60451-970. Brazil.

^bFundação Núcleo de Tecnologia Industrial do Ceará - NUTEC, Rua Rômulo Proença s/n, CEP: 60451-970. Fortaleza - CE, Brazil.

^cParque de Desenvolvimento Tecnológico - PADETEC, Rua do Contorno, S/N Campus do Pici, Bloco 310. CEP: 60455-970. Fortaleza - CE, Brazil.

^dUniversidade Federal do Ceará (UFC), Instituto de Ciências do Mar-LABOMAR, Av. Abolição, 3207 - Meireles, CEP: 60165-081 - Fortaleza-CE, Brazil.

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Abstract: The removal of 2,4 diclorophenol (2,4-DCF) and 2,4,6 trichlorophenol (2,4,6 TCF) present in petrochemical wastewater was evaluated using low-cost adsorbents, such as chitin, chitosan and coconut shells. Batch studies showed that the absorption efficiency for 2,4 DCF and 2,4,6 TCF follow the order: chitosan > chitin > coconut shells. Langmuir and Freundlich models have been applied to experimental isotherms data, to better understand the adsorption mechanisms. Petrochemical wastewater treatment with fixed bed column system using chitinous adsorbents showed a removal of COD (75%), TOG (90%) and turbidity (74-89%).

Keywords: chlorophenols; low cost adsorbent; adsorption; chitosan; petrochemical wastewater

1. INTRODUCTION

It very well know that 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.

Chlorophenols are organic compounds considered priority pollutants by the American Environmental Protection Agency (USEPA) because of their toxicity and adverse effects that can cause to human health [1]. These compounds are generally present in effluents from pharmaceutical, plastics, pesticides, fertilizers and petroleum refineries [2]. In Brazil, legislations based on CONAMA 430/2011 and SEMACE 154/2002, consider the maximum limit of 0.5 mg.L⁻¹ total phenols in wastewater [3].

Despite the efforts that oil refineries have been demonstrating in recent decades for their effluents fit the standards set by legislation are still found significant levels of phenolic compounds in industrial

wastewater, which often are not removed by conventional treatment. Several techniques have been evaluated for phenolic compounds removal, such as ozonization [4], advanced oxidation processes [5], solvent extraction [6], membrane [7] and biological treatment [8-9]. However, these processes are not really efficient. An alternative for wastewater treatment is the use of adsorption process, which allows a high efficiency in the removal and recovery of persistent organic pollutants [10]. Activated carbon has been widely applied for phenolic removal, despite some disadvantages such as high costs and difficult regeneration, but the low-cost solid residues from agricultural activities have been applied such as wood and coir [11], sugarcane bagasse [12], chitin (QTI) and chitosan (QTS) [13].

In Brazil, huge amounts of waste are produced by large scale agriculture, mainly sugar cane bagasse and green coconut shell [14-15]. The use of these materials for removal of organic pollutants [16] and metals [17-18] from wastewater can be advantageous

*Corresponding author. E-mail: ronaldo@ufc.br

because reduce the environmental impact and to reduce the cost of processing. In addition, special attention has been paid to chitin, a natural polymer extracted from shells of crustaceans such as crab, shrimp and chitosan, a derivative obtained by alkaline deacetylation of chitin [19]. Due to its characteristics of biodegradability, biocompatibility and hydrophobicity of these materials have attracted great interest. Several authors have investigated the efficiency of chitinous materials as adsorbents for removal of organic compounds [20-22], metals [23, 24] and anions [25].

The purpose of this study was to investigate the adsorption features of adsorbents from chitinous and agricultural residues with respect to removal of chlorophenols, chemical oxygen demand (COD), Total oil and grease (TOG), nitrate, ammonia and turbidity from petrochemical wastewater. Results were compared with performances of some adsorbents used in practice.

2. MATERIAL AND METHODS

Reagents and solutions

Chromatographic grade solvents and 2,4-dichlorophenol (2,4 DCP) and 2,4,6-trichlorophenol (2,4,6 TCP) standards with purity > 99% were purchased from Sigma-Aldrich (Brazil). Stock solutions of 2,4-DCP and 2,4,6 TCP (1,000 mg.L⁻¹) were prepared in methanol. Calibration curves of chlorophenols were prepared by diluting the stock solution to concentrations of 5 to 400 mg.L⁻¹.

Effluent samples were obtained from LUBNOR - Lubricants and Petroleum products, located in Fortaleza-Ceará, Brazil. Samples were spiked with concentrations of 2,4 DCP and 2,4,6 TCP ranging from 10 to 300 mg.L⁻¹ for the batch study. The samples were filtered through a membrane (0.45 µm) before being injected into the GC

Adsorbents

Were used as adsorbents green coconut shells obtained from EMBRAPA (60-200 mesh), chitin (white powder, 80 mesh, molecular weight 400,000 g.mol⁻¹, pH 4.28) and chitosan (yellowish powder, 80% grade of deacetylation, 80 mesh particle, molecular weight 174,205 g.mol⁻¹, pH 7.93), obtained from company POLYMER SA (Fortaleza-Ceará, Brazil). Also were studied for a comparison, the

commercial adsorbents, activated carbon (100 mesh, Merck), silica (80 -200 Merck), Amberlite (80-100 mesh, Carlo Erba), bentonite (20 mesh, Merck).

Chromatographic analysis

The initial and final concentrations of 2,4-DCP and 2,4,6 TCP were determined by gas chromatography with flame ionization detector (GC-FID), Shimadzu 17A model, using a DB-5 capillary column (30 m x 0.25 mm x 0.32 µm). The chromatographic conditions were: detector and injector temperature 250 °C, temperature program 60 °C (10 °C.min⁻¹) → 190°C (3 min) → 225 °C (10 °C.min⁻¹) for 5 min. It was used a flow of carrier gas (H₂) of 1 mL.min⁻¹, at a injected volume of 1.0 µL and split ratio 1:30

Batch adsorption

In glass vials containing 0.2 g of dry adsorbent were added to 10 mL aliquot of effluent samples, filtered and spiked with known amounts (10-300 mg.L⁻¹) of 2,4 DCP and 2,4,6 TCP. The vials were sealed and placed on the shaker and kept under agitation (150 rpm) at room temperature (28 ± 2 °C) until it reaches equilibrium. After stirring the residual analyte concentrations were determined by GC-FID system. The adsorption capacity (Q_e) for each compound was calculated by equation 1:

$$Q_e = \frac{(C_o - C_e)V}{m} \quad \text{Equation 1}$$

Where C_o and C_e are the concentrations (mg.L⁻¹) of solute in the initial solution and equilibrium, V is the volume of solution (L) and m the mass of adsorbent (g).

Study of pH effect was performed with effluent solutions at pH 3.0, 6.5 and 9.0 using the adsorbents such as chitin, chitosan and coconut shell. The pH value was controlled using acetate buffer and ammonia buffer.

The adsorption isotherms were obtained by correlating the parameters of concentration versus equilibrium adsorption. Adsorption isotherms were studied using the Langmuir (Equation 2) and Freundlich models (Equation 3).

$$\text{Langmuir: } \frac{1}{Q} = \frac{1}{Q_{\max}} + \left(\frac{1}{Q_{\max} K_L} \right) \left(\frac{1}{C_e} \right) \quad \text{(Equation 2)}$$

$$\text{Freundlich: } \log Q = \log K_F + \frac{1}{n} \log C_e \quad \text{(Equation 3)}$$

Where Q is the amount of solute adsorbed ($\text{mg}\cdot\text{g}^{-1}$), Q_{max} is the maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), K_L is the equilibrium constant of Langmuir isotherm ($\text{L}\cdot\text{mg}^{-1}$), C_e is the equilibrium concentration of solute in solution ($\text{mg}\cdot\text{L}^{-1}$), $1/n$ is the Freundlich constant, K_F constant Freundlich adsorption. $1/n$ and K_F values represent the intensity of adsorption and adsorption capacity of adsorbent.

Different materials such as bentonite, activated carbon, silica and amberlit were evaluated through batch adsorption, for a comparison with the adsorbents studied in this work.

Wastewater treatment in fixed bed

50 mL of effluent contained chlorophenols at pH 7.5 and flow rate of 1.0 to 2.0 $\text{mL}\cdot\text{min}^{-1}$ were percolated through the column (20 cm x 4.0 mm ID), packed with 0.2 g of the adsorbent material in stages interspersed with cotton. The column adsorption capacity was determined by measuring the compound concentration in the solution by GC-FID system, before and after passing through the column.

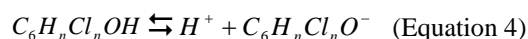
Wastewater samples collected for analysis of ammonia, nitrate, pH, turbidity, conductivity and chemical oxygen demand (COD) were performed at the Laboratory of Environmental Sanitation of the Federal University of Ceara (LABOSAN-UFC) as recommended by the procedures described in Standard Methods for the Examination of Waters and Wastewater (2005) [26]. The determination of oil and grease (TOG) in the wastewater effluent was carried out in the laboratory from company LUBNOR.

3. RESULTS AND DISCUSSION

Batch adsorption

pH effect

The pH effect on the compounds adsorption was studied at pH values of 3.0, 6.5 and 9.0 using the adsorbents chitin (QTI), chitosan (QTS) and coconut shell. The results showed that the pH influences on the adsorption of 2,4 DCP ($\text{pKa}=8.09$) and 2,4,6 TCP ($\text{pKa}=6.21$), this occur due to change in the ionization degree of these compounds. At $\text{pH} < \text{pKa}$, the molecular form predominates and at $\text{pH} > \text{pKa}$ the anionic form prevails in solution as shown by equation 4. This behavior is directly influenced by adsorbate and adsorbent characteristics.



Chitin and chitosan contain some functional groups such as acetamides, amines and hydroxyl which are capable of interacting with 2,4 DCP and 2,4,6 TCP through hydrogen bonding, Van der Waals interactions or ion exchange. In addition, changes at solution pH may induce a protonation or deprotonation process influencing in the adsorption capacity. For chitosan, in acid conditions, the amino groups are protonated, as showed by Equation 5.



The results obtained for chitosan indicated that the chlorophenols adsorption decreased at pH 3.0 to 9.0. In addition, was selected an intermediate value of pH 6.5. Zheng et al. [27] obtained similar results with the removal of chlorophenols from groundwater by chitosan. In contrast, for the chitin and coconut shells no significant changes on the adsorption of 2,4 DCP and 2,4,6 TCP was observed, probably due to the low influence of pH variation on the structure of these adsorbents.

Adsorption isotherm

The isotherms adsorption for chitin, chitosan and coconut shell were obtained by relating the amount of solute adsorbed (Q_e) with the solute concentration in the fluid phase at equilibrium ($\text{pH}=7.5$). The experimental data of adsorption isotherms were applied to the Langmuir and Freundlich models.

After fitting the equilibrium adsorption data, Freundlich and Langmuir parameters were obtained from straight regression lines. The values of adsorption capacity (Q_{max}) and the parameters K_L , K_F and $1/n$ are given in Table 1.

The results showed in Table 1 indicated that the adsorption efficiency of the solutes on the adsorbents follows 2,4 DCP < 2,4,6-TCP indicating that tends to increase with more chlorine in the molecule.

Satisfactory correlation coefficients were noted ($r > 0.90$). In order to more clearly define the model which represented the experimental data most correctly, the normalized percent deviation (P) [28] was applied, according to the following Eq. 6.

$$P = \left(\frac{100}{N} \right) \sum \left(\frac{|q_e - q_{\text{teor}}|}{q_e} \right) \quad (\text{Equation 6})$$

Where q_e is the experimental adsorption capacity, q_{teor} is the level theoretical adsorption capacity, N the number of trials.

For the lower P value, greater the correlation

between the experimental and theoretical, and therefore more favorable to the model. P values were calculated for the Langmuir and Freundlich isotherms for both adsorbents, as shown in Table 1, being considered acceptable P values <5 .

Table 1. Experimental parameters of 2,4 DCP < 2,4,6-TCP obtained from batch adsorption isotherms.

Compound	Langmuir				Freundlich			
	K_L (L.mg ⁻¹)	Q_{max} (mg.g ⁻¹)	R	P	1/n	K_F	r	P
2,4 DCP								
Chitosan	0.005	6.00	0.951	4.65	0.574	0.140	0.915	5.69
Chitin	0.014	4.58	0.979	11.57	0.455	0.313	0.903	5.08
Coconut	0.002	3.36	0.985	22.62	0.487	0.163	0.992	1.23
2,4,6 TCP								
Chitosan	0.002	27.55	0.995	3.61	0.808	0.106	0.990	4.71
Chitin	0.002	20.41	0.953	8.60	1.043	0.032	0.978	4.11
Coconut	0.003	4.73	0.952	15.29	0.599	0.264	0.966	2.04

Chitosan adsorption

Figures 1a and 1b show the experimental and theoretical isotherms for chitosan, which suggests that the adsorption of 2,4 DCP and 2,4,6 TCP on the chitosan follows the Langmuir model, which indicates a mono-layer adsorption.

The low P value observed for the Langmuir model (Table 1) confirms that the approach to the

model. The adsorption efficiency of the chlorophenols by the chitosan can be explained due to the high amount of free groups (amino and hydroxyl) present in its structure. The amino groups (R-NH₂), in the protonated form, adsorbs strongly ionic solutes such as chlorinated phenols (Eq. 7). The hydroxyl groups present in chlorophenols can also contribute to hydrogen bonds and provide a greater stability and adsorption of solutes on the surface of chitosan [27].

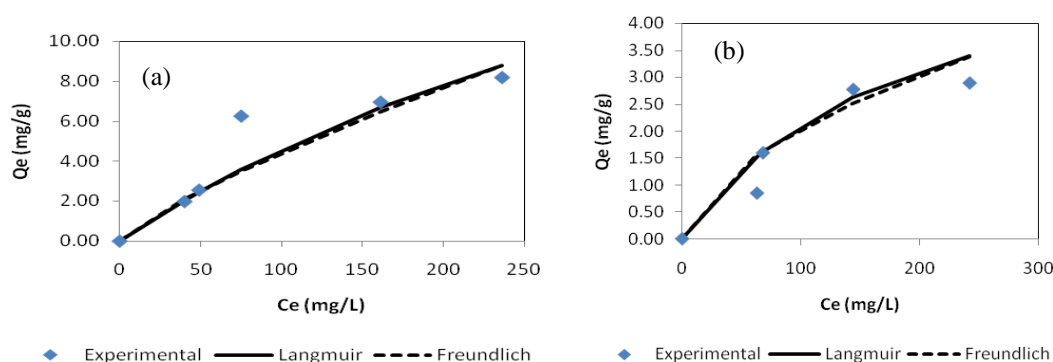
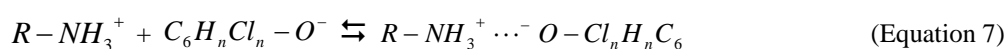


Figure 1. Adsorption isotherm of chitosan (a) 2,4 DCP, (b) 2,4,6 TCP.

Chitin adsorption

The results of adsorption isotherms with chitin are shown in Figures 2a and 2b, and it can be noted

that the experimental data, evidenced by the lower value of P , are well described by Freundlich model. Therefore, it is assumed a heterogeneous adsorption, where the energy distribution to the sites is essentially

exponential. Other authors [20, 27] also observed the similar process for phenol adsorption onto chitin. Chitin has a similar structure to cellulose, and its adsorptive properties are probably due to the groups



acetamide (-NHCOCH₃) and carbonyl of the glucose units. The phenol adsorption onto chitin could be described by equation 8.

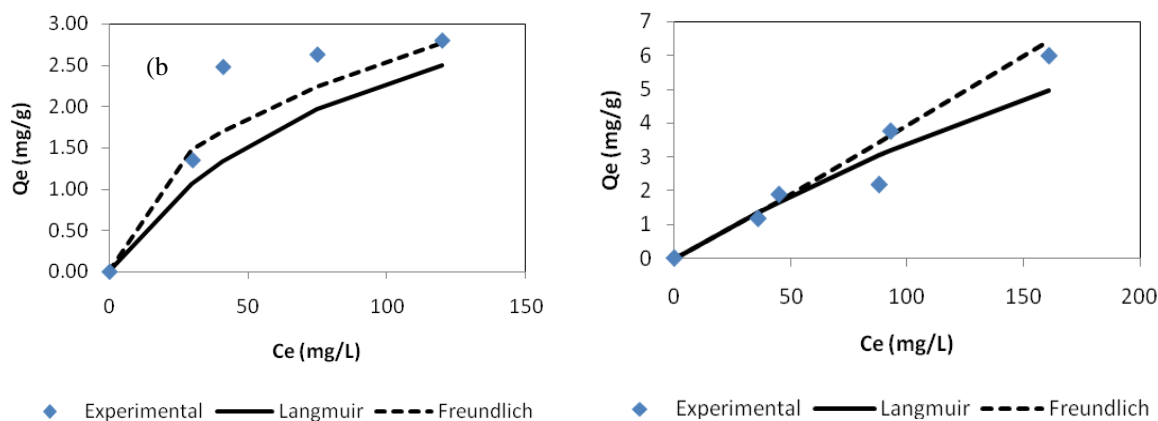


Figure 2. Adsorption Isotherm in Chitin (a) 2,4 DCP, (b) 2,4,6 TCP.

Coconut shell adsorption

The adsorption isotherms of 2,4 DCP and 2,4,6 TCP on the coconut bagasse are showed in Figures 3a and 3b. It can be observed that the experimental data are well described by the Freundlich model, which indicates a double-layer adsorption.

The composition of coconut shell contains largely cellulose, lignin and pentosanes [29]. These

constituents present in its structure some functional groups such as alcohols, aldehydes, carboxylics, ketones and phenolic hydroxides, which may engage in processes that combine forces of attraction and repulsion ionic, hydrogen bonding, dipole-dipole forces and Van der Waals forces in interactions with solutes. The chlorophenols adsorption onto coconut bagasse could be described by process in equation 9.

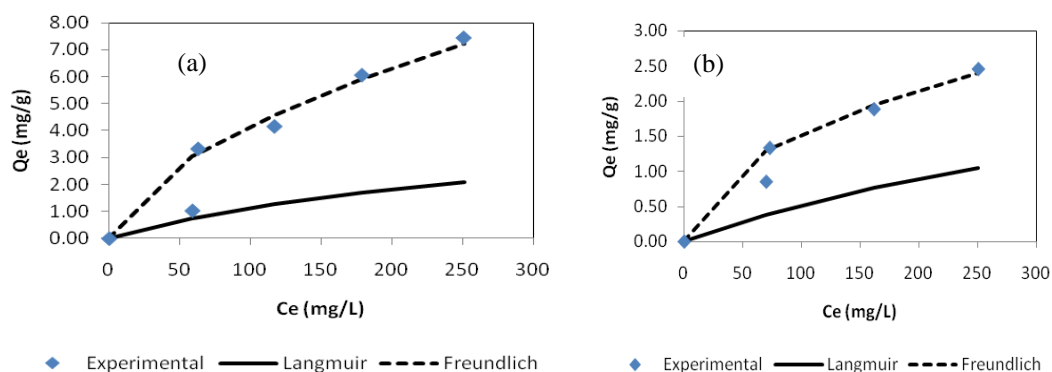
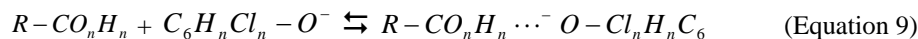


Figure 3. Adsorption isotherm in coconut bagasse (a) 2,4 DCP, (b) 2,4,6 TCP.

Comparison of adsorption capacity with other adsorbents

Adsorption capacity obtained for chitosan,

chitin and coconut shells has been compared for other commercial adsorbents such as activated carbon, amberlite, bentonite and silica, as shown in Figure 4. As noted the 2,4,6 TCP is more easily removed from

wastewater than 2,4 DCP by the chitinous materials. In contrast, coconut shell and other commercial adsorbents exhibit a removal efficiency for 2,4-DCP (Figure 4).

Table 2 shows the adsorption capacity values for some materials studied reported in literature [8, 20, 27, 29-32]. The high adsorption capacity of 2,4,6 TCP by chitin (27.55 mg.g⁻¹) and chitosan (20.41

mg.g⁻¹) for our study, is approaches to the fly ash (23.83 mg.g⁻¹) [29, 30]. Chitinous materials have different adsorption capacities depending on the experimental condition, such as pH, contact time and particle size. In addition, the performance of coconut shell can be efficiently improved by chemical or physical activation [29]. Removal of 2,4 DCP and 2,4,6 TCP about 55% and 95%; 50% and 99% were obtained using chitosan and chitin, respectively.

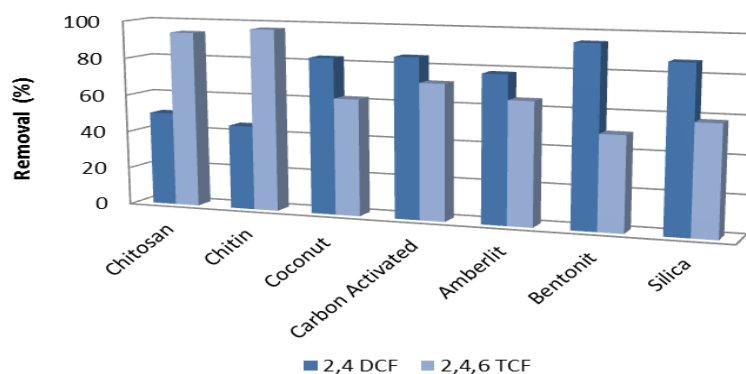


Figure 4. Removal (%) of 2,4 DCP and 2,4,6 TCP in commercial adsorbents.

Table 2. Comparison of adsorption capacity on various adsorbents.

Adsorbent	Compound	q (mg/g)	Particle size (mm)	pH	T (°C)	Contact time (h)	References
Chitin	2,4 DCP	6.00	0.18	7.5	28±2	4	This paper
Chitosan	2,4 DCP	4.58	0.18	7.5	28±2	4	This paper
Coconut	2,4 DCP	3.36	0.18	7.5	28±2	4	This paper
Chitin	2,4,6 TCP	27.55	0.18	7.5	28±2	4	This paper
Chitosan	2,4,6 TCP	20.41	0.18	7.5	28±2	4	This paper
Coconut	2,4,6 TCP	4.73	0.18	7.5	28±2	4	This paper
Chitin	Phenol	25.06	0.15 - 0.30	1.0	40	1.6	[20]
Chitosan (Flake)	2,4,6 TCP	0.14	2.0 x 3.0 x 0.03	natural	5	96	[27]
Fly Ash	Phenol	23.83	0.04 - 1	6.5	30	24	[30]
Activated Carbon (Derived from coconut bagasse)	2,4 DCP	50.53	0.07- 0.58	4 ± 0.2	25	30	[29]
Biomass	Phenol	0.33	2.36 -4.75	5.1	21±1	30	[8]
Rice Rusk	p-chlorophenol	14.36	0.03 - 0.15	-	-	72	[31]
Petroleum coke	p-Chlorophenol	9.33	0.03 - 0.15	-	-	72	[31]
Lignite	Phenol	10.00	0.5	Natural	25	-	[32]

Wastewater treatment in fixed bed

For evaluate the efficiency of the adsorbents in the wastewater petrochemical treatment was employed a system of fixed bed, through which the effluent was percolated and the physicochemical parameters of the solutions were analyzed before and after leaving the fixed bed.

The effluent sample from process of oil refinery company (LUBNOR) presented an alkalinity median, high load of organic matter (COD), high oil and grease (TOG) and turbidity.

The results show that after effluent treatment with chitin, the reduction of COD reached approximately 75.0% (reduction 320.4 to 79.9 mg.L⁻¹), and therefore higher than the reduction observed for the treatment used by the company (LUBNOR), which was around 45% (from 320.4 to 184.2 mg.L⁻¹). These results are satisfactory, considering that the maximum limit (ML) established by environmental law (SEMACE 154/2002) is 200.0 mg.L⁻¹. In contrast, chitosan shows a low efficacy for COD removal.

The performance of chitin and chitosan for

removal of oil and grease (TOG) reached about 90%. These results also are significant since the SEMACE determines that the maximum TOG for the release of effluent is 20 mg.L⁻¹.

Wastewater treatment with chitin and chitosan, showed no significant changes in pH and conductivity. The reduction in the concentration of ammonia and nitrate after sample treatment with chitin was satisfactory. In contrast, the performance of

the chitosan was not satisfactory. The turbidity removal from wastewater sample by the chitin and chitosan achieved 89% and 74% respectively.

The all the results obtained with coconut shell (not showed) were not satisfactory, probably due to the large increase in organic matter caused by the dissolution of the polysaccharides present in the its structure.

Table 3. Results of the physical-chemical parameters of wastewater before and after treatment.

Parameters	E _{Raw}	E _{Comp}	E _{QTI}	E _{QTS}	ML
					Semace 154/2002
COD (mg.L ⁻¹)	320.4	184.2	79.9	332.5	200
TOG (mg.L ⁻¹)	81.6	-	8.4	8.4	20
pH	7.66	7.79	7.85	7.90	5-9
Conductivity (μs.cm ⁻¹)	2.42	2.30	2.63	2.67	-
Nitrate (mg.L ⁻¹)	32.3	29.7	18.6	53.5	-
Ammonia (mg.L ⁻¹)	5.05	4.40	3.39	7.92	5.0
Turbidity (NTU)	23.2	4.41	2.40	6.01	-

E_{Raw} = raw wastewater

E_{Comp} = effluent treated by the company,

E_{QTI} = effluent treated with chitin adsorbent

E_{QTS} = = effluent treated with chitosan

4. CONCLUSION

Based on the results can be concluded that chitosan, chitin and coconut bagasse have a performance considerable on the adsorption of 2,4 dichlorophenol and 2,4,6 trichlorophenol. The order of adsorption capacity was as follow: chitosan> chitin> coconut shell. The wastewater treatment employed chitin showed high removal efficiency for COD and TOG with performance around 90%. In contrast, coconut shell showed low performance. The adsorption capacity of chitin was comparable to those of conventional adsorbents. The results indicated that a fixed bed column using chitinous materials can be very practical for organic compounds removal from petrochemical wastewater..

5. ACKNOWLEDGMENTS

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