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Removal of phenol and chlorophenols from water with reusable dye-affinity hollow fibers

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Abstract

Reactive Green HE 4BD carrying polyamide hollow fibers were investigated as dye-affinity adsorbents for removal of chlorophenols (i.e., phenol, *o*-chlorophenol, *p*-chlorophenol and 2,4,6-trichlorophenol). Adsorption rates of chlorophenols were very high. Equilibrium was achieved in about 30 min. The applicability of two kinetic models including pseudo-first order and pseudo-second order model was estimated on the basis of comparative analysis of the corresponding rate parameters, equilibrium capacity and correlation coefficients. Results suggest that chemisorption process could be the rate-limiting step in the adsorption process. The maximum adsorption values of chlorophenols onto the Reactive Green HE 4BD carrying hollow fibers were 145.9 μmol/g for phenol, 179.2 μmol/g for 2,4,6-trichlorophenol, 194.5 μmol/g for *p*-chlorophenol and 202.8 μmol/g for *o*-chlorophenol. The affinity order was as follows: *o*-chlorophenol > *p*-chlorophenol > 2,4,6-trichlorophenol > phenol. The adsorption capacity of chlorophenols decreased with increasing pH. Desorption of chlorophenols was achieved using methanol solution (30%, v/v). The Reactive Green HE 4BD-carrying hollow fibers are suitable for repeated use for more than 10 cycles without noticeable loss of adsorption capacity.

Keywords: Reactive Green HE 4BD; Polyamide; Hollow fibers; Phenol; Chlorophenol removal

1. Introduction

Wastewaters containing phenolic compounds present a serious environmental problem. Phenol containing wastewater may not flow into open water without treatment because of the toxicity of phenol. The toxic and hazardous nature of phenols and substituted compounds, and their increasing amounts in industrial wastewaters have been well documented [1–4]. They are known or suspected human carcinogens [5]. Loss of appetite, marasmus, headache, rapid fatigue and severe chronic insomnia are given as symptoms of chronic phenol intoxication in humans after long-term intake of excessive phenol concentrations [6]. Phenolic compounds are present in the wastewater generated from paint, solvent, petroleum (petrochemical), coal-conversion, pharmaceutical, wood preserving chemicals, plastic, rubber-proofing, pesticide, iron-steel, phenol-production, paper and pulp industries. Large scale coal gasification and carbonization plants generate wastewater containing large quantities of high strength phenolic compounds. The United States Environmental Protection Agency (EPA) regulates lowering phenol content in the wastewater to less than 1 mg/L from the several thousand mg/L.

Current methods for removing phenols and their derivatives from wastewater include microbial degradation, adsorption on activated carbon, biosorption, chemical oxidation (using agents such as ozone, hydrogen peroxide, chlorine dioxide), deep-well injection, incineration, solvent extraction and irradiation [7–11]. The high cost of activated carbon, solvent extraction and oxidation treatments has stimulated interest to use cheaper raw materials. Deep-well injection may lead to contamination of ground water. The biological treatment of phenolics is limited by the intrinsic properties of these compounds owing to their toxicity; they are slow to biodegrade, and the degrading microorganism must be exposed to only low concentrations of the substrates [12]. Therefore, alternative technologies have to be explored.

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In recent years, reusable polymeric adsorbents have been increasingly considered as an alternative to activated carbon and other available adsorbents for efficient removal of phenols from wastewater for its good properties and mechanical stability [13–18]. The increasing attention has been paid for polymer's unique adsorption properties resulting from its high surface area, high volume of micropores and broad range of surface functional groups introduced in their structures. Among them dye carrying polymeric adsorbents was reported to be an ideal one for removing phenols from aqueous solutions [16,17]. Commercially available reactive dye-ligands are able to bind most of pollutants [19–21]. They are inexpensive, and can easily be attached especially polymeric matrices having hydroxyl groups.

The purpose of this investigation was to examine the extent of adsorption and removal of model chlorophenol pollutants. In this study, Reactive Green HE 4BD carrying polyamide hollow fibers were prepared and adsorption/removal of phenol, *o*-chlorophenol, *p*-chlorophenol and 2,4,6-trichlorophenol were investigated. Because, they are some of the most challenging species of priority pollutants to be removed from waste streams and ground water. The porous nature of polyamide hollow fiber and its high internal surface area are favorable properties for adsorption.

2. Experimental

Polyamide hollow fibres (PA386C) were a gift from Akzo (Wuppertal, Germany). Reactive Green HE 4BD was obtained from Polyscience (Warrington, USA) and used without further purification. Phenol and chlorinated phenols were obtained from Sigma (St. Louis, USA) and used without further purification. Other chemicals were of analytical reagent grade and supplied from Merck (Darmstadt, Germany). All water used in the experiments was purified using a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed bed system.

2.1. Reactive Green HE 4BD-attached hollow fibers

Polyamide hollow fibres were used as received and cut to small segments (1 cm in length). Physical properties of polyamide hollow fibres are listed in Table 1 as obtained from the manufacturer. The cut fibres (250 mg) were magnetically stirred (at 400 rpm) in a sealed reactor in 100 mL aqueous solution containing Reactive Green HE 4BD for 30 min at 60 °C. This was followed by the addition of 7.0 g NaCl in order to stimulate the deposition of the dye on the surface of the hollow fibre. After 30 min, 1.0 g sodium carbonate (Na_2CO_3) was added to accelerate the reaction between dye and hollow fibre. Dyeing reaction was performed at 80 °C for 4 h. In order to change the amount of Reactive Green HE 4BD loading, the initial concentration of dye was varied between 0.1 and 0.6 mg/mL. After completion of reaction, the Reactive Green HE 4BD-derived polyamide hollow fibres were washed with distilled water and methanol several times until all the physically attached Reactive Green HE 4BD molecules were removed. The modified hollow fibres were then stored at 4 °C with 0.02% sodium azide to prevent microbial contamination.

Table 1
Physical properties of the PA 386C polyamide hollow fiber

Inner diameter	300 μm
Wall thickness	110 μm
Normal pore size	200 nm
Maximum pore size	430 nm
BET surface area	16.0 m^2/g
Flux	13 mL/min bar cm^2 (water, 25 °C)
Length per area	1.1 km/m^2 (inside); 0.6 km/m^2 (outside)

In other dyeing preparations, in order to optimize the amount of dye incorporated into the polyamide hollow fibres, these materials were exposured to partial hydrolysis under condition of not destroying mechanical integrity as follows: the hollow fibres were magnetically stirred at 100 rpm with 3 M HCl at a constant temperature of 30 °C for 20 min. The acid hydrolysis was then arrested by washing with cold water (4 °C). After hydrolysis the polyamide hollow fibres were dyed with Reactive Green HE 4BD applying the optimal parameters determined from the previous preparations using the same method mentioned above.

2.2. Characterisation of hollow fibers

2.2.1. Elemental analysis

The amount of Reactive Green HE 4BD attached on the hollow fibre was evaluated by using an elemental analysis instrument (Leco, CHNS-932 USA) by considering the sulfur stoichiometry.

2.2.2. SEM studies

In order to observe surface structure of the polyamide hollow fibres, scanning electron micrographs of coated samples were taken with a SEM (Model: Raster Electronen Microscopy, Leitz-AMR-1000, Germany).

2.2.3. Surface area measurements

Average pore diameter greater than 20 Å were determined by mercury porosimeter up to 2000 kg/cm^2 using a Carlo Erba model 2000 (Milano, Italy). The surface area of the hollow fiber sample was measured with a surface area apparatus (Brunner–Emmet–Teller method).

2.3. Chlorophenols adsorption/desorption

Adsorption of chlorophenols (i.e., phenol, *o*-chlorophenol, *p*-chlorophenol and 2,4,6-trichlorophenol) from the single species aqueous solutions was investigated in batch adsorption-equilibrium experiments. Effects of the initial concentration of chlorophenols and pH of the medium on the adsorption rate and capacity were studied. A 20 mL of aqueous chlorophenol solutions with different concentrations (in the range of 25–1000 mg/L) were treated with the unmodified and/or Reactive Green HE 4BD-carrying hollow fibers (100 mg hollow fibers per batch) at different pHs (in the range of 2.0–8.0, adjusted with HCl–NaOH) at room temperature, in the flasks agitated magnetically at 600 rpm. Stock solutions of chlorophenols were 1000 mg/L and all were prepared daily. The adsorption time was selected as 60 min in the preliminary experiments, which was assumed as the equilibrium adsorption time, because there was no significant change in the amount of adsorption after 60 min. The hollow fibers were centrifuged from the adsorption medium at the end of each experiment, and the concentration of the chlorophenols in the aqueous phase was measured by high performance liquid chromatography. The experiments were performed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 96% were calculated for each set of samples in order to determine the margin of error. The LC equipment consisted of a Shimadzu liquid chromatograph pump and Hewlett Packard HP 3395 integrator. Shimadzu UV variable wavelength monitor was used as detector. In the chromatographic determination, Spherisorb ODS1 column (length: 25 cm; inside diameter: 4.6 mm) containing 5 μm particles was used. Samples were injected through a Rheodyne injector with a 20 μL loop. For the detection of the chlorophenols the wavelength was set at high absorption wavelength. The mobile phase was prepared by addition of phosphoric acid to deionized water until a pH of 2.35 was obtained. The aqueous phosphoric acid was modified with 38% methanol. Tetrabutylamonium bromide was used as ion-pair reagent with the concentration of 1.4×10^{-4} M. The mobile phase was degassed in an ultrasonic water bath immediately before use. Prior to use, the mobile phase was also filtered through a 0.45 μm filter. A flow rate of 1.2 mL/min was used in all experiments. The amount of adsorbed chlorophenols was obtained using mass balance.

In order to determine the reusability of the Reactive Green HE 4BD-carrying hollow fibers, consecutive adsorption–desorption cycles were repeated 10 times using the same sorbent. Desorption of chlorophenol was achieved using methanol solution (30%, v/v). The Reactive Green HE 4BD-carrying hollow fibers loaded 145.9 μmol phenol/g, 179.2 μmol 2,4,6-trichlorophenol/g, 194.5 μmol *p*-chlorophenol/g and 202.8 μmol *o*-chlorophenol/g were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final chlorophenol concentration in the aqueous phase was determined using a HPLC. The desorption ratio was calculated from the amount of chlorophenol initially loaded on the hollow fibers and the final chlorophenol concentration in the desorption medium.

3. Results and discussion

3.1. Characteristics of polyamide hollow fibers

The water uptake ratio of polyamide hollow fibers is 36% (w/w). It should be mentioned that the water uptake properties of the hollow fibers did not change after Reactive Green HE-4BD attachment. The scanning electron microscope (SEM) micrographs given in Fig. 1 shows the surface morphology of the hollow fibers. They have large pores and narrow pore size distribution. The hollow fiber surface seems very rough and heterogeneous. According to the mercury porosimetry data, the pore radii of the polyamide hollow fibers changed between 200 and 450 nm. This indicated that the hollow fibers contained mainly macropores. This pore diameter range is possibly available for diffusion of the phenol and chlorophenol species. Specific surface area of the hollow fiber is found to be 16.0 m^2/g by BET method after Reactive Green HE-4BD attachment. Therefore these macropores were not blocked by the attached dye molecules.

Polyamide hollow fibers have a disadvantage. They have a low concentration of primary amino groups leading to low ligand density. This problem can be solved by hydrating the fibers to increase the number of amino groups on the fiber, binding with polyhydroxyl containing materials such as polyglucose, dextran, starch and cellulose to increase reactive sites.

Reactive Green HE-4BD is a dichlorotriazine dye (Fig. 2), and it contains six sulfonic acid groups, five basic primary and secondary amino groups. Reactive Green HE-4BD is covalently attached on polyamide hollow fibers, via the reaction between the chloride groups of the reactive dye molecules and the primary amino groups of the polyamide. Coupling of Reactive Green HE-4BD to hollow fibers was studied under different conditions. The dye loadings reached on hollow fibers are listed in Table 2. The maximum dye loading obtained

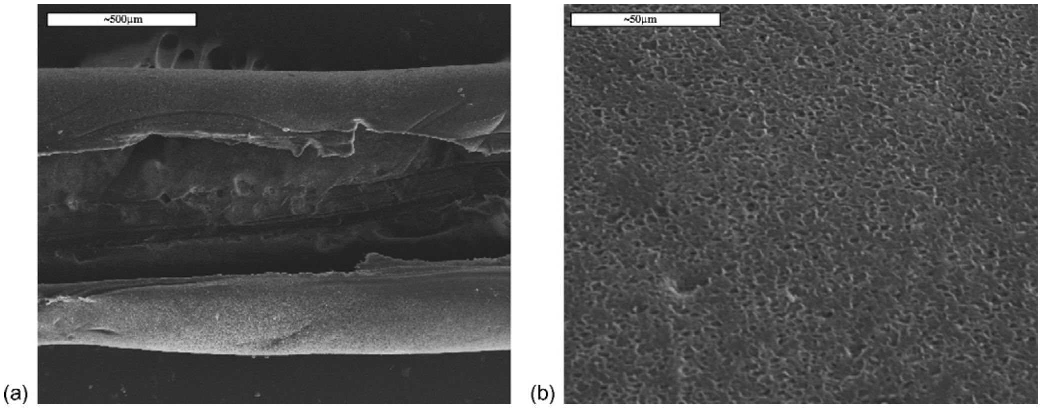

Fig. 1. Representative SEM micrographs of polyamide hollow fibers: (a) inner surface; (b) outer surface.

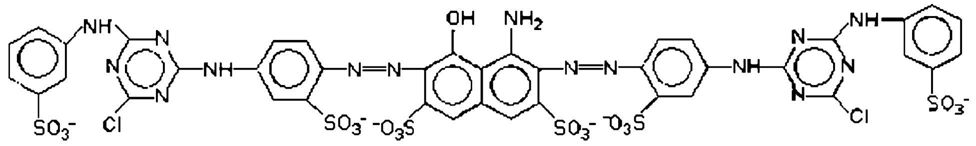

Fig. 2. Chemical structure of Reactive Green HE-4BD.

Table 2
Influence of Reactive Green HE-4BD concentration, and HCl treatment on the dye loading

Reactive green HE-4BD, concentration (mg/mL)	Reactive green HE-4BD[a], loading (μmol/g)
0.1	11.7 ± 0.59
0.2	13.4 ± 0.46
0.3	17.5 ± 0.41
0.4	21.2 ± 0.61
0.6	26.3 ± 0.45
0.6 (HCl treatment)	48.7 ± 0.59

[a] Each data are average of three parallel studies.

without hydrating of hollow fibers was 26.3 μmol Reactive Green HE-4BD/g polymer. When hollow fibers hydrating with HCl the amount of Reactive Green HE-4BD was much higher (48.7 μmol Reactive Green HE-4BD/g). The higher dye–ligand loadings are due to the larger number of primary amino groups produced as a result of the acid hydration.

The visual observations (the colour of the hollow fibers) ensured attachment of dye molecules. The Reactive Green HE-4BD-attached hollow fibers were extensively washed with methanol until to ensure that there is no dye leakage from any of the dye-attached hollow fibers and in any media used at adsorption–desorption steps. The release of dye-molecules was also measured in three different kinds of media. There was no measurable release of dye into the acidic medium (pH 2.0). Dye was released in the neutral medium while some was released in the alkaline medium too. The release in the strongly alkaline medium indicates the existance of strong ionic interactions. The release in neutral medium might just be the physically occluded dye along with any weakly/physically bonded dye. It can be said that there was not a significant increase in the amount of dye released (more than 12 weeks).

4. Chlorophenol adsorption

4.1. Adsorption time

The effect of adsorption time of chlorophenols (i.e., phenol, *o*-chlorophenol, *p*-chlorophenol and 2,4,6-trichlorophenol) on the Reactive Green HE 4BD-carrying polyamide hollow fibers was shown in Fig. 3. Note that these batch experiments were performed by using single (not together) solutions of the concerned chlorophenol. The initial concentration of the chlorophenol within the aqueous phase was kept constant at 500 mg/L. These kinetic studies point out that the phenol adsorption is carried out by means of a rapid rate at the first 20 min. Then the adsorption is slower, possibly due to the less active adsorption sites being available and/or the difficulty of the edge molecules in diffusing the adsorbent small pores. Saturation levels are gradually reached within 30 min for all chlorophenols. Notice that o-chlorophenol was adsorbed faster than other chlorophenols due to much higher affinity of the ligand (i.e., Reactive Green HE 4BD) molecules. The adsorption rate order is as follows: *o*-chlorophenol > *p*-chlorophenol > 2,4,6-trichlorophenol > phenol.

Adsorption of phenolic species was quite fast especially when the solution concentration was high. Data on the adsorption kinetics of phenolic compounds by various sorbents have shown a wide range of adsorption rates. For example, Streat and Sweetland have studied phenol and chlorophenol adsorption on a new series of hypercross-linked porous polymeric ion-exchange sorbents (Hypersol-Macronet$^{\text{TM}}$) and reported a 20 days equilibrium adsorption time [13]. Yenkie and Natarajan have considered 4 h as a equilibrium time in their phenol adsorption kinetic studies, in which they used granular activated carbon as sorbent [22]. Ravi et al. investigated phenol and cresol isomers adsorption on activated carbon and reported 20 h equilibrium adsorption time [23]. Furuya et al. investigated the adsorption of chloro-and nitrophenols on granular activated carbon and reported that equilibrium adsorption time is 2 weeks [24]. Shu et al. considered 48 h as a short equilibrium time in their chlorophenol adsorption kinetic studies, in which they used aluminosilicate-based microporous materials as sorbent [25]. Gupta et al investigated phenol and *p*-nitrophenol adsorption on a low cost adsorbent, i.e., bagasse fly ash and they reported that the equilibrium adsorption time was 24 h [26]. The stirring rate in the aqueous phase, structural properties of adsorbent (e.g. porosity,

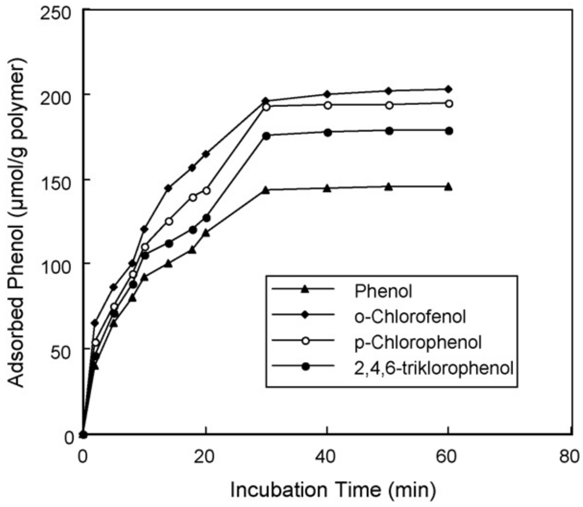

Fig. 3. Adsorption rates of chlorophenols on the Reactive Green HE 4BD-carrying polyamide hollow fibers—dye loading: 48.7 μmol/g; concentration of chlorophenols: 500 mg/L; *T*: 20 °C; pH 6.0.

Table 3
The first- and second-order kinetic constants

	Exp	First-order kinetic			Second-order kinetic		
	q_{eq} (μmol/g)	k_1 (min^{-1})	q_{eq} (μmol/g)	R^2	k_2 (g/μmol min)	q_{eq} (μmol/g)	R^2
o-Chlorophenol	202	0.145	228	0.990	8.1	238	0.996
p-Chlorophenol	194	0.138	278	0.939	4.9	232	0.989
2,4,6-Trichlorophenol	179	0.125	270	0.961	4.4	217	0.988
Phenol	145	0.110	167	0.966	4.2	166	0.995

surface area), amount of adsorbent, adsorbate properties (e.g. molecular dimensions and solubility), initial concentration of phenolic species determine the adsorption rate. Existence of other species which may compete with the phenolic species of interest for the active adsorption sites is also an important parameter for the adsorption rate. The extent of adsorption is also influnced by the surface chemistry of the adsorbent. The adsorption rates obtained with the Reactive Green HE 4BD-carrying hollow fibers seem to be very promising.

4.2. Kinetics of the adsorption process

The kinetics of adsorption is important from the point of view that it controls the process efficiency. In order to analyze the adsorption kinetics of phenolic compounds the pseudo-first-order and the pseudo-second-order kinetics models were applied to the experimental data [27–29]. The first-order equation of Lagergren is one of the most widely used for the adsorption of solute from a liquid solution. It may be represented as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_{eq} - q_t) \tag{1}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_{eq} and q_t (μmol/g) denote the amounts of adsorbed phenol at equilibrium and at time t (min), respectively. After integration by applying boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives

$$\log\left[\frac{q_{eq}}{q_{eq} - q_t}\right] = \frac{k_1 t}{2.303} \tag{2}$$

Eq. (2) can be rearranged to obtain a linear form

$$\log(q_{eq} - q_t) = \frac{\log(q_{eq}) - (k_1 t)}{2.303} \tag{3}$$

A plot of $\log(q_{eq} - q_t)$ versus t should give a straight line to confirm the applicability of the kinetic model. In a true first-order process $\log q_{eq}$ should be equal to the interception point of plot of $\log(q_{eq} - q_t)$ versus t.

In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the following form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_{eq} - q_t)^2 \tag{4}$$

where k_2 (g/μmol min) is the rate constant of pseudo-second-order adsorption process. Integrating Eq. (4) by applying boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, leads to

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + k_2 t \tag{5}$$

or equivalently for linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \left(\frac{1}{q_{eq}}\right) t \tag{6}$$

A plot of t/q_t versus t should give a linear relationship for the applicability of the second-order kinetics. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively.

According to the values in Table 3, the optimum results are for both the second and first order models. These results suggest that the both the pseudo-first and pseudo-second order mechanisms are predominant. A higher rate constant for *o*-chlorophenol indicates that the dye-attached polyamide hollow fibers has a higher affinity for phenol. This is consistent with a higher adsorption value observed for this phenol as compared other. As a matter of fact, the rate constants for *o*-chlorophenols are in an order parallel to their adsorption values.

4.3. Effects of chlorophenols concentration

The chlorophenol adsorption capacities of the Reactive Green HE 4BD-carrying hollow fibers are given as a function of concentration of chlorophenol within the aqueous phase in Fig. 4. It was observed that the amount of adsorption was significantly increased with the chlorophenol concentration. The increase of adsorption capacity of the dye-attached hollow fibers with the increase of pollutant concentration may be due to higher probability of collision between pollutant and adsorbent. We assume that the different adsorption behaviors of different chloro phenolic species on Reactive greed HE 4BD-attached polyamide hollow fibers mainly includes: (i) hydrophobic interaction; (ii) van der Waals force. It mainly includes dispersion interaction, dipole–dipole and dipole–induced dipole interactions; (iii) hydrogen bonding interaction. The maximum adsorption capacities of the Reactive Green HE 4BD-carrying hollow fibers are 145.9 μmol/g for phenol, 179.2 μmol/g for 2,4,6-trichlorophenol, 194.5 μmol/g for *p*-chlorophenol and 202.8 μmol/g for *o*-chlorophenol at pH 2.0, which are corresponding an initial concentration of 500 mg/L. Maximum adsorption capacity of chlorophenols occured in the order *o*-chlorophenol > *p*-chlorophenol > 2,4,6-trichlorophenol > phenol. The difference in adsorption capacity

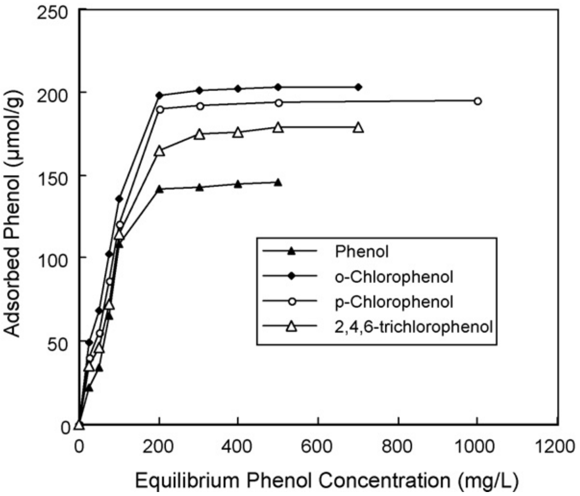

Fig. 4. Chlorophenols adsorption capacity of the Reactive Green HE 4BD-carrying hollow fibers—dye loading: 48.7 μmol/g; pH 6.0; *T*: 20 °C.

of the chlorophenol species compared to each others can be explained by the different affinity of the phenolic species for the reactive functional groups in the ligand Reactive Green HE 4BD. Adsorption capacity is also affected by the position of –Cl group on the ring. Adsorption of *p*-chlorophenol having a chlorine in the para position tended to be lower than *o*-chlorophenol containing chlorine in only ortho position. This may be a result of streic hindrance between the –Cl and –OH group in the case of *p*-chlorophenol [30]. The adsorption capacity for the chlorophenols is higher than that of phenol, possibly due to the higher solubility of phenol (solubility: 638.4 mol/L) in water. The solubility values are 198.4 mol/L for *o*-chlorophenol, 186.0 mol/L for *p*-chlorophenol and 4.3 mol/L for 2,4,6-trichlorophenol.

As mentioned before, one gram of the adsorbent carries 48.7 μmol Reactive Green HE 4BD which was found by elemental analysis. From the stoichometry, it seems that one attached Reactive Green HE 4BD molecule interact from one to five chlorophenol molecules depending on the type of chlorophenols.

Note that the SO_3 groups of Reactive Green HE 4BD are available for ionic interactions with phenolic acids. The chlorophenols adsorption on the unmodified hollow fibers (carrying no Reactive Green HE 4BD) are relatively low, about 2.8 μmol/g for phenol, 4.1 μmol/g for 2,4,6-trichlorophenol, 3.5 μmol/g for *o*-chlorophenol and 2.6 μmol/g for *p*-chlorophenol. Polyamide hollow fibers are swellable and porous, which therefore may absorb (or entrap) chlorophenols within the swollen matrix.

In recent years, a number of studies have focused on some solid supports and microorganisms which are able to adsorb phenols and chloro- and nitro-phenols. Aksu and Yener investigated the biosorption of phenol, *o*- and *p*-chlorophenol from aqueous solutions on dried activated sludge [12]. Maximum adsorption capacity was found to be 1.7 mmol/g. Streat and Sweetland reported up to 1.5 mmol/g adsorption capacity for phenol and chlorophenols with a new series of hypercrosslinked porous polymeric ion-exchange sorbents (Hypersol-Macronet^{TM}) [13]. Azanova and Hradil investigated the adsorption of phenol by porous copolymers of different porous structure and polarity with hyper-crosslinked poly(ethylene glycol dimethacrylate) and commercial samples including Lewatit EP63 and Amberlite XAD4 [14]. They obtained maximum adsorption capacity in the range of 0.46–1.6 mmol/g. Denizli et al. used dye affinity beads for removal of phenolic compounds [16,17]. Maximum adsorption capacities were in the range of 87.8–145.2 μmol/g for nitrophenols and 88.8–109.1 μmol/g for chlorophenols. Ravi et al. reached an adsorption capacity between 3.2 and 4.4 mmol/g with activated carbon for phenol and cresol isomers [23]. Furuya et al used chloro- and nitro-phenols as the test adsorbates, and granular activated carbon was used as the adsorbent [24]. They achieved up to 4 mmol/g adsorption capacity. Shu et al. used aluminosilicate-based microporous materials (pillared clays, silicalite and zeolite beta) and they reported selective phenol adsorption capacity up to 1 mmol/g [25]. Gupta et al. showed 60 μmol/g adsorption capacity for phenol and *p*-nitrophenol with a low cost adsorbent, i.e., bagasse fly ash (a waste generated in local sugar plants) sorbents [26]. Dargaville et al found up to 0.1 mmol/g adsorption capacity for multinuclear phenolic compounds by activated carbon [31]. Lin and Cheng reported that organobentonite is rather effective adsorbent in removing phenol and chlorophenol pollutants from industrial wastewaters [32]. They determined that the adsorption capacity was in the range of 14.7–76.5 μmol/g. The adsorption capacity in the present study is comparable to other adsorbents reported in the literature.

4.4. *Effects of pH*

The effect of pH on adsorption of chlorophenols is shown in Fig. 5. It was observed that the adsorption capacities decreased with increasing pH. The highest adsorption of chlorophenols occured at pH 2.0 for all species. However within the pH range of 2.0–6.0 there is no significant decrease in the equilibrium adsorption capacity. But, adsorption capacity was considerably decreased when the pH of the initial solution was above 6.0. The interaction forces between chlorophenols and Reactive Green

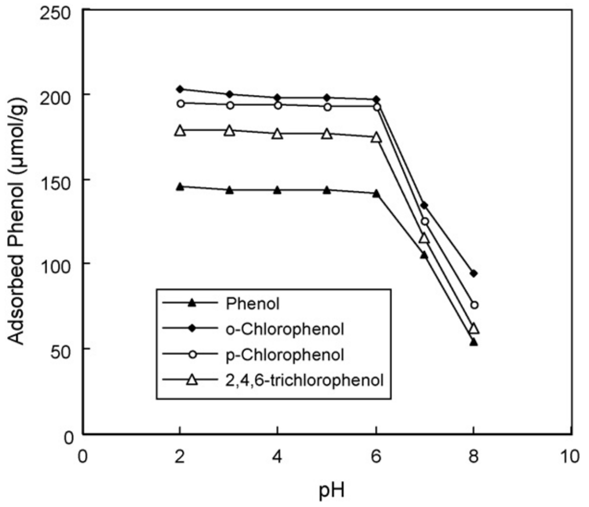

Fig. 5. Effect of pH on adsorption of chlorophenols on the Reactive Green HE 4BD-carrying hollow fibers: dye loading: 48.7 μmol/g; concentrations of chlorophenols: 500 mg/L; *T*: 20 °C.

Table 4
Adsorption–desorption cycles for phenol or chlorophenols

Cycle no.	Phenol		2,4,6-Trichlorophenol		*p*-Chlorophenol		*o*-Chlorophenol	
	Ads (μmol/g)	Des (%)	Ads (μmol/g)	Des (%)	Ads (μmol/g)	Des (%)	Ads (μmol/g)	Des (%)
1	145.9	97.6	179.2	95.5	194.5	96.5	202.8	98.1
2	145.7	95.3	179.0	96.2	194.2	96.8	202.5	99.3
3	145.1	95.8	178.4	96.4	194.0	97.0	202.0	99.0
4	144.6	96.0	178.2	98.0	193.5	97.2	201.8	97.5
5	144.0	96.4	178.0	97.5	193.0	98.0	201.5	97.8
6	143.2	96.8	177.9	97.0	192.7	98.1	201.2	98.5
7	143.0	96.9	177.5	96.9	192.0	98.7	201.0	98.1
8	142.8	96.5	177.2	96.2	191.8	98.3	200.6	98.0
9	142.6	95.2	176.8	96.6	191.5	97.8	200.4	98.4
10	142.2	95.8	176.1	96.7	191.0	98.0	200.0	98.6

Concentrations of chlorophenols: 500 mg/L; pH 6.0; *T*: 20 °C.

HE 4BD are rather weak in the neutral solutions. The decrease in adsorption capacity may also be due to the competing hydroxide ions.

4.5. Effect of dye loading

In order to study the effect of dye loading on adsorption of chlorophenols, polyamide hollow fibers with different dye contents were evaluated. Fig. 6 provides the effect of dye loading on the chlorophenols adsorption. The highest chlorophenols adsorbed was observed in the case with the highest dye loading. This may be explained as follows, when the dye loading increases the attached amount of reactive functional groups on the hollow fiber surface which will interact with the chlorophenols will increase leading to higher phenols adsorption.

4.6. Regeneration of hollow fibers

To be useful in removal processes, adsorbed species should be easily desorbed under suitable conditions and adsorbents should be used many times in order to reduce material costs. Main advantages of dye-attached polyamide hollow fibers used as an adsorbent are the regeneration and recycling properties of this matrix. To remove phenol molecules adsorbed, methanol solution (30%, v/v) was used as the desorption agent. The Reactive Green HE 4BD-carrying hollow fibers loaded chlorophenols were placed within the desorption medium and the amount of chlorophenols desorbed in 30 min was measured. Successive sequences of adsorption–regeneration cycles were performed, and Table 4 shows the adsorption-desorption values of chlorophenols by Reactive Green HE 4BD-carrying hollow fibers. This table shows that the Reactive Green HE 4BD-carrying hollow fibers can be used repeatedly without loosing significantly their adsorption capacities for all chlorophenols studied here. This means that methanol breaks down the interaction forces between chlorophenols and binding sites onto the surface of the dye-attached hollow fibers.

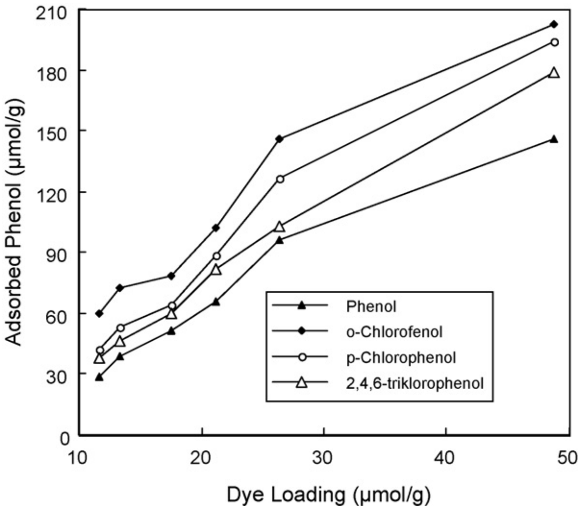

Fig. 6. Effect of dye loading on adsorption of chlorophenols on the Reactive Green HE 4BD-carrying hollow fibers—concentrations of chlorophenols: 500 mg/L; pH 6.0; *T*: 20 °C.

5. Conclusion

Very fast increase in the population rate and also transition to the modern life have brought a rapid increase in water pollution problems, especially in municipal areas. Phenol containing wastewater may not be conducted into open water without treatment because of the toxicity of phenol. Thus to eliminate phenol from waste streams has become a major environmental problem. Off all removal approaches, adsorption appears to be most prominent. Due to their adjustable funtionality, high surface area and porosity and ease of regeneration, polymeric adsorbents have been increasingly viewed as an alternative to activated carbon for eliminating organic pollutants from contaminated water streams. Reusable polyamide hollow fibers carrying Reactive Green HE 4BD were used for adsorption/desorption of chlorophenols (i.e., phenol, *o*-chlorophenol, *p*-chlorophenol and 2,4,6-trichlorophenol) from aqueous solutions. The present study leads to the following conclusions: The maximum adsorption capacities of these dye-affinity hollow fibers from their single solutions were 145.9 μmol/g for phenol, 179.2 μmol/g for 2,4,6-trichlorophenol, 194.5 μmol/g for *p*-chlorophenol and 202.8 μmol/g for *o*-chlorophenol. The affinity order was as follows: *o*-chlorophenol > *p*-chlorophenol > 2,4,6-trichlorophenol > phenol. The adsorption of chlorophenols decreased with increasing pH. Consecutive adsorption and desorption cycles showed the feasibility of this Reactive Green HE 4BD-carrying hollow fibers for chlorophenol removal from aqueous solutions.

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