

# Dye-Affinity Microbeads for Removal of Phenols and Nitrophenols from Aquatic Systems

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**ABSTRACT:** Alkali Blue 6B attached poly(2-hydroxyethyl methacrylate) (PHEMA) microbeads were investigated as dye-affinity adsorbents for the removal of phenol and nitrophenols (i.e., 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol) from aqueous solutions. PHEMA microbeads were prepared by radical-suspension polymerization of HEMA in the presence of azobisisobutyronitrile as the initiator. These microbeads with a swelling ratio of 55% and carrying 23.6  $\mu\text{mol}$  Alkali Blue 6B/g polymer were then used in the removal of phenol and nitrophenols from aqueous media. The adsorption was fast in all cases (20-min equilibrium time). The maximum adsorptions of phenols onto the microbeads carrying Alkali Blue 6B were 145.2  $\mu\text{mol/g}$  for phenol, 87.8  $\mu\text{mol/g}$  for 2,4-dinitrophenol, 112.6  $\mu\text{mol/g}$  for 4-nitrophenol, and 104.3  $\mu\text{mol/g}$  for 2-nitrophenol. The affinity order was phenol > 4-nitrophenol > 2-nitrophenol > 2,4-dinitrophenol. The adsorption of nitrophenols decreased with increasing pH. Desorption of nitrophenols was achieved using a 30% (v/v) methanol solution. The microbeads carrying Alkali Blue 6B are suitable for repeated use for more than five cycles without a noticeable loss of adsorption capacity. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2411–2418, 2002

**Key words:** Alkali Blue 6B; poly(2-hydroxyethyl methacrylate) microbeads; phenol and nitrophenol removal

## INTRODUCTION

Phenolic compounds are very toxic, and many are known or suspected human carcinogens.<sup>1–3</sup> Loss of appetite, marasmus, headache, rapid fatigue, and severe chronic insomnia are the symptoms of chronic phenol intoxication in humans after long-term intake of excessive phenol concentrations. Phenolic compounds are present in the wastewater generated from petroleum and petrochemical,

coal-conversion, pharmaceutical, plastics, rubber-proofing, disinfectants, steel, and phenol-production industries. Large-scale coal gasification and carbonization plants generate huge quantities of high strength phenolic wastewater.<sup>4</sup> The U.S. Environmental Protection Agency (EPA) and European Union have included phenol and various chlorophenols and nitrophenols in their lists of priority pollutants to be monitored in the aquatic environment. The maximum level allowed for these compounds in publicly supplied water is 0.5  $\mu\text{g/mL}$ . EPA regulations call for lowering the phenol content in wastewater to <1  $\mu\text{g/mL}$  from the several thousand milligrams per liter that is often present.

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Different approaches to the purification of phenolic effluents have been developed. These techniques are based on chemical–biological oxidation and solvent extraction.<sup>5</sup> The main limitation of these methods is their low efficiency in the removal of trace levels of phenols. Adsorption technology is currently being extensively used for the removal of phenolic compounds in a low concentration such as the parts per million level.<sup>6</sup> Nonspecific adsorbents such as activated carbon, metal oxides, silica, and ion-exchange resins have been used.<sup>7–9</sup> However, specific adsorbents have recently been considered as one of the most promising techniques.<sup>10</sup> Specific adsorbents consist of a ligand (e.g., ion-exchange material) that specifically interacts with the organic and inorganic pollutants and a carrier matrix that may be an inorganic material (e.g., aluminum oxide, silica, or glass) or polymer microbeads [e.g., polystyrene, starch, chitosan, cellulose, poly(maleic anhydride), or poly(methyl methacrylate)].<sup>11–16</sup>

A wide variety of complexing agents may be used as ligands in the design of novel adsorbents.<sup>6–16</sup> These ligands are extremely specific in most cases. However, they are expensive because of the high cost of production and/or extensive preparation steps. In the process of adsorbent preparation, it is difficult to immobilize them onto the supporting matrix with retention of their original activity. Numerous precautions are also needed in their use (at the adsorption, desorption, and regeneration steps) and storage. Dye-ligands have been considered as one of the important alternatives to the conventional adsorption chromatography to circumvent many of their drawbacks mentioned above. Dye-ligands are able to bind most of pollutants including heavy metals and organic species in a remarkably specific manner. They are commercially available, inexpensive, and can be easily immobilized, especially matrices bearing hydroxyl groups. Another advantage of dye-affinity systems is good operational stability during the consecutive adsorption–regeneration stages.

Recently, we prepared water swellable microbeads made of hydroxyethyl methacrylate (HEMA) as an adsorbent matrix to prepare specific adsorbents.<sup>17</sup> Several dye-ligands were attached on these sorbents covalently and used for selective removal of heavy metal ions and biomolecules from aqueous media.<sup>18–22</sup> The objective of this study is to investigate the adsorption behavior of phenol and nitrophenols on the poly(HEMA) (PHEMA) microbeads with Alkali Blue 6B at-

tached. Phenol, 4-nitrophenol, 2-nitrophenol, and 2,4-dinitrophenol were used as model adsorbates because they are some of the most challenging species of priority organic pollutants that need to be removed from wastestreams and groundwater.

## EXPERIMENTAL

The details of the preparation and characterization of the PHEMA microbeads were reported elsewhere.<sup>17</sup> The PHEMA microbeads were selected as the carrier matrix for the synthesis of affinity sorbents for the removal of phenol and nitrophenols. The microbeads were produced by radical-suspension polymerization of the respective HEMA (Sigma, St. Louis, MO) and ethylene glycol dimethacrylate (EGDMA, Rohm) comonomers in an aqueous media as described in our previous articles.<sup>18–20</sup> Benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA,  $M_n = 100,000$ , 98% hydrolyzed, Aldrich, Rockford, IL) were used as the initiator and the stabilizer, respectively. Toluene (Merck AG, Darmstadt, Germany) was utilized as the diluent and as received. The dispersion medium was distilled water. In order to produce polymeric microbeads of about 150–200  $\mu\text{m}$  in diameter and with a narrow size distribution, the amounts of HEMA, EGDMA, toluene, water, BPO, and PVA were 4.0 mL, 8.0 mL, 12.0 mL, 50.0 mL, 0.06 g, and 0.20 g, respectively. Polymerizations were carried out at an agitation rate of 600 rpm at 65°C for 4 h and at 90°C for 2 h. At the end of the polymerization reaction, soluble components were removed from the polymer by repeated decantation with water and ethyl alcohol.<sup>19</sup>

Alkali Blue 6B was used as the dye-ligand (Sigma). Three grams of microbeads were magnetically stirred at 400 rpm in a sealed reactor at a constant temperature of 80°C for 4 h with 100 mL of the Alkali Blue 6B aqueous solution containing 4.0 g of NaOH. Under these experimental conditions, a condensation reaction took place between the amino group of the Alkali Blue 6B and the OH groups of the PHEMA microbeads, resulting in the covalent attachment of Alkali Blue 6B to the polymer matrix. The initial concentration of the Alkali Blue 6B in the medium was 4.0 mg/mL. After incubation, the microbeads carrying Alkali Blue 6B were filtered and washed with distilled water and methanol several times until all the physically attached Alkali Blue 6B molecules were removed. The leakage of the Alkali Blue 6B

from the microbeads was followed by treating the microbeads with adsorption and desorption media for 24 h at room temperature. After this treatment the Alkali Blue 6B concentration in the liquid phase was measured spectrophotometrically at 630 nm.

The amount of Alkali Blue 6B immobilized on the microbeads was evaluated by using an elemental analysis instrument (CHNS-932, Leco) and considering the nitrogen and sulfur stoichiometry.

### Phenol and Nitrophenols Adsorption–Desorption

Adsorption of phenol and nitrophenols (i.e., 4-nitrophenol, 2-nitrophenol, and 2,4-dinitrophenol) from the single species aqueous solutions was investigated in batch adsorption–equilibrium experiments. The phenol and nitrophenols for the adsorption studies were obtained from Sigma and used without further purification. The effects of the initial concentration of the nitrophenols and the pH of the medium on the adsorption rate and capacity were studied. Twenty milliliters of aqueous nitrophenol solutions with different concentrations (25–1000 mg/L) were treated with the unmodified and/or Alkali Blue 6B carrying microbeads (100 mg microbeads/batch) at different pH values (2.0–12.0, adjusted with HCl–NaOH) at room temperature in flasks agitated magnetically at 600 rpm. Sodium azide (final  $\text{NaN}_3$  concn = 0.1%) was added to the solution to prevent microbial contamination. Stock solutions of nitrophenols 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 microbeads were separated from the adsorption medium at the end of each experiment, and the concentration of the nitrophenols in the aqueous phase was measured by high performance liquid chromatography (HPLC). The LC equipment consisted of a Cecile CE1100 liquid chromatograph pump and a Hewlett–Packard 3395 integrator. A Cecile CE1220 LC UV variable-wavelength monitor was used as the detector. In the chromatographic determination a Spherisorb ODS1 column (25-cm length, 4.6-mm inside diameter) containing 5- $\mu\text{m}$  particles was used. Samples were injected through a Rheodyne injector with a 20- $\mu\text{L}$  loop. The wavelength was set at a high absorption wavelength for the detection of the

nitrophenols. The mobile phase was prepared by the addition of phosphoric acid to deionized water until a pH of 2.35 was obtained. The aqueous phosphoric acid was modified with 38% methanol. Tetrabutylammonium bromide was used as the ion-pair reagent with the concentration of  $1.4 \times 10^{-4} \text{ M}$ . The mobile phase was degased in an ultrasonic water bath immediately before use. Prior to use, the mobile phase was also filtered through a 0.45- $\mu\text{m}$  filter. A flow rate of 1.2 mL/min was used in all experiments. The concentration of adsorbed phenol and nitrophenols was obtained by using the following expression:

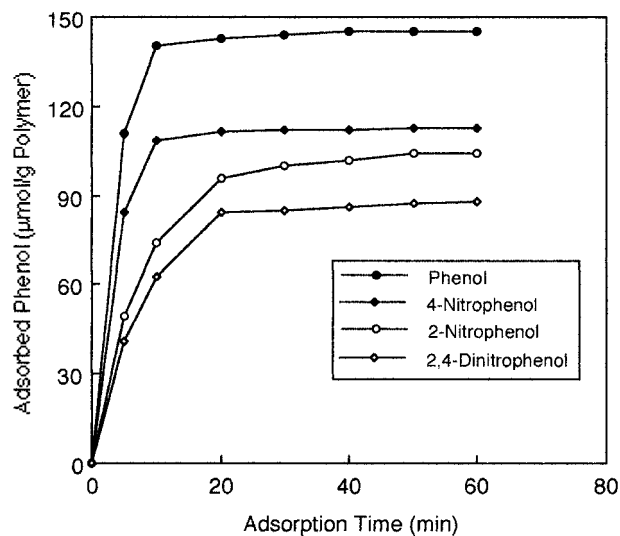
$$q = [(C_0 - C_A)/V]/m \quad (1)$$

where  $q$  is the amount of phenols adsorbed onto the unit amount of the microbeads ( $\mu\text{mol/g}$ );  $C_0$  and  $C_A$  are the concentrations of the phenols in the initial solution and in the aqueous phase after adsorption, respectively ( $\mu\text{mol/L}$ );  $V$  is the volume of the aqueous phase (L); and  $m$  is the weight of the microbeads (g).

In order to determine the reusability of the Alkali Blue 6B carrying microbeads, consecutive adsorption–desorption cycles were repeated 5 times by using the same sorbent. The desorption of phenol and the nitrophenols was achieved by using a methanol solution (30% v/v). The Alkali Blue 6B microbeads loaded with 145.2  $\mu\text{mol/g}$  for phenol, 87.8  $\mu\text{mol/g}$  for 2,4-dinitrophenol, 112.6  $\mu\text{mol/g}$  for 4-nitrophenol, and 104.3  $\mu\text{mol/g}$  for 2-nitrophenol were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final phenol and nitrophenol concentration in the aqueous phase was determined by using HPLC. The desorption ratio was calculated from the amount of nitrophenols initially loaded on the microbeads and the final phenol concentration in the desorption medium.

## RESULTS AND DISCUSSION

The PHEMA microbeads are hydrophilic and have a crosslinked structure. The equilibrium swelling ratio was about 55%. Alkali Blue 6B was selected as the hydrophobic dye-ligand. A condensation reaction took place between the amino group of the Alkali Blue 6B and the OH groups of the PHEMA microbeads, resulting in covalent attachment of Alkali Blue 6B to the polymer matrix.<sup>23,24</sup> Elemental analysis was also performed,



**Figure 1** The adsorption rates of phenol and nitrophenols on the PHEMA microbeads carrying Alkali Blue 6B. The initial concentration of phenols is 400 mg/L at 20°C and pH 6.0.

and the attachment of the Alkali Blue 6B was found as 23.6  $\mu\text{mol/g}$  from the sulfur and nitrogen stoichiometry. This was the maximum dye-attachment value that was achieved. Alkali Blue 6B leakage from the microbeads was also monitored continuously. There was no Alkali Blue 6B leakage in any of the adsorption and desorption media used, which assured that the washing procedure was good enough for removal of physically adsorbed Alkali Blue 6B molecules from the microbeads.

## Phenol and Nitrophenol Adsorption

### Adsorption Time

The equilibrium adsorption time of phenol and nitrophenols (i.e., 2,4-dinitrophenol, 4-nitrophenol and 2-nitrophenol) on the Alkali Blue 6B carrying PHEMA microbeads was investigated (Fig. 1). We define equilibrium here as the point at which no further compound was adsorbed from solution. Note that these batch experiments were performed by using single aqueous solutions of the considered phenol and nitrophenols. The initial concentrations of the phenol and nitrophenols within the aqueous phase were kept constant at 400 mg/L. As seen from Figure 1, the adsorption was very fast at the beginning of adsorption, and saturation levels are gradually reached within 10 min for all nitrophenolic compounds. Note that

phenol was adsorbed much faster than other nitrophenolic compounds because of the much higher affinity of the ligand (i.e., Alkali Blue 6B) molecules. The adsorption rate order is phenol > 4-nitrophenol > 2-nitrophenol > 2,4-dinitrophenol. The dimensions of each phenolic molecule are also important in the adsorption process. An increase in the molecular mass of the phenolic compounds will increase their molecular dimensions and the porosity of the polymeric microbeads (i.e., in the swollen form) plays an important role in the adsorption process. As a result, those molecules with smaller molecular dimensions attain equilibrium at a faster rate. A similar result for substituted phenols of increasing molecular dimensions being adsorbed from aqueous solution on activated carbon is proposed in the literature.<sup>25</sup>

The adsorption of phenolic species was quite fast, especially when the initial solution concentration was high. Data on the adsorption kinetics of phenolic compounds by various sorbents show a wide range of adsorption rates. For example, Yenkie and Natarajan considered 4 h as the equilibrium time in their phenol adsorption kinetic studies in which they used granular activated carbon as the sorbent.<sup>26</sup> Ravi et al. investigated phenol and cresol isomers adsorption on activated carbon and they reported a 20-h equilibrium adsorption time.<sup>6</sup> Furuya et al. investigated the adsorption of chloro- and nitrophenols on granular activated carbon and reported that the equilibrium adsorption time is 2 weeks.<sup>7</sup> Shu et al. considered 48 h as a short equilibrium time in their chlorophenol adsorption kinetic studies; they used aluminosilicate-based microporous materials as the sorbents.<sup>9</sup> Streat and Sweetland studied phenol and chlorophenols adsorption on a new series of hypercrosslinked porous polymeric ion-exchange sorbents (Hypersol-Macronet<sup>TM</sup>), and they reported 20-day equilibrium adsorption time.<sup>27</sup> 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.<sup>28</sup> Note that there are several parameters that determine the adsorption rate such as the stirring rate (or flow) in the aqueous phase, the structural properties of the adsorbent (e.g., porosity, surface area), the amount of sorbent, the adsorbate properties (e.g., molecular mass and dimensions), the initial concentration of the phenolic species, and of course the existence of other species that may compete with the phenolic species of interest for the active

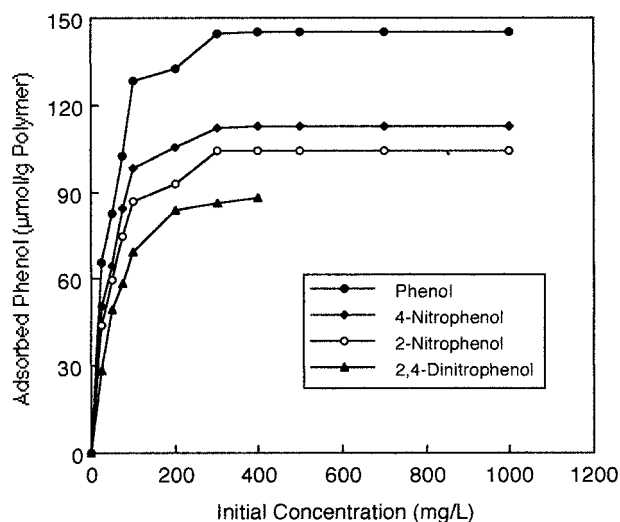


adsorption sites. Therefore, it is too difficult to compare the adsorption rates that are reported. However, the adsorption rates obtained with the Alkali Blue 6B microbeads that we produced seem to be very fast.

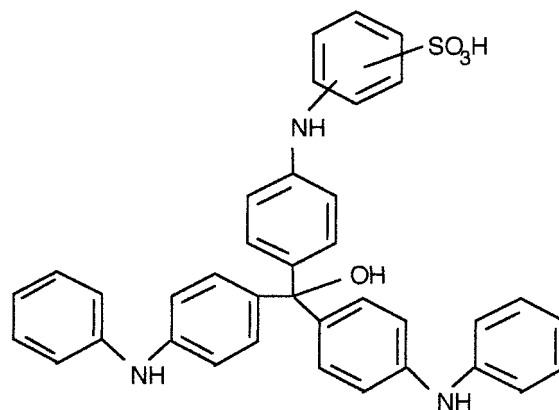
### Effects of Initial Concentration of Phenol and Nitrophenols

The amount of phenol and nitrophenolic compounds adsorbed was measured over a wide range of equilibrium compound concentrations from 0 to 1000 mg/L. The phenol and nitrophenols adsorption capacities of the Alkali Blue 6B carrying microbeads are given as a function of the initial concentration of phenols within the aqueous phase in Figure 2. In general, the adsorption curves were characterized by a gradual rise and a flattening at higher adsorbate concentrations. The maximum adsorption capacities of the Alkali Blue 6B microbeads in the studied range are 145.2  $\mu\text{mol/g}$  for phenol, 87.8  $\mu\text{mol/g}$  for 2,4-dinitrophenol, 112.6  $\mu\text{mol/g}$  for 4-nitrophenol, and 104.3  $\mu\text{mol/g}$  for 2-nitrophenol at pH 2.0, which correspond to an initial concentration of 400 mg/L. The results suggest that the affinity of nitrophenols toward adsorption follows the order phenol > 4-nitrophenol > 2-nitrophenol > 2,4-dinitrophenol.

We expected that we would obtain higher adsorption capacities for nitrophenols than phenol due to their lower solubilities in water. However, in contrast, the adsorption capacity for the phenol



**Figure 2** The phenol and nitrophenol adsorption capacity of the microbeads carrying Alkali Blue 6B at 20°C and pH 2.0.



**Figure 3** The chemical structure of Alkali Blue 6B.

is higher than that of the nitrophenols. This shows that solubility is not important in this system. The difference in the adsorption behavior of the phenol and nitrophenol species compared to each other can be explained by the different affinities of the phenolic species for the reactive functional groups in the ligand Alkali Blue 6B. A difference in geometrical structure is most probably also the case for the immobilized Alkali Blue 6B ligand, resulting in a relatively high adsorption of phenol. These results also suggest that the molecular size of the adsorbates controls the degree of adsorption.

The structure of Alkali Blue 6B consists of six aromatic rings (Fig. 3). It is assumed that when a phenolic molecule is adsorbed on Alkali Blue 6B attached polymer microbeads, the aromatic  $\pi$  electrons of the phenolic molecule interact directly with the  $\pi$  electrons of the Alkali Blue 6B aromatic ring. In other words, adsorption is a result of the interaction (or overlapping) of the two  $\pi$ -electron orbitals. Note that the sulfonate and amino groups of Alkali Blue 6B are also available for interaction with phenolic compounds. The nitrophenols' adsorption on the unmodified microbeads (carrying no Alkali Blue 6B) is relatively low, being about 2.8  $\mu\text{mol/g}$  for phenol, 1.6  $\mu\text{mol/g}$  for 2,4-dinitrophenol, 1.2  $\mu\text{mol/g}$  for 4-nitrophenol, and 1.4  $\mu\text{mol/g}$  for 2-nitrophenol at pH 2.0. Note that these microbeads are highly swellable and porous; therefore, they may absorb (or entrap) phenol and nitrophenols within the matrix of the swollen microbeads.

As mentioned before, 1 g of the sorbent carries 23.6  $\mu\text{mol}$  Alkali Blue 6B, which was found by elemental analysis. From the stoichiometry it seems that one immobilized Alkali Blue 6B molecule interacts with from one to six nitrophenol

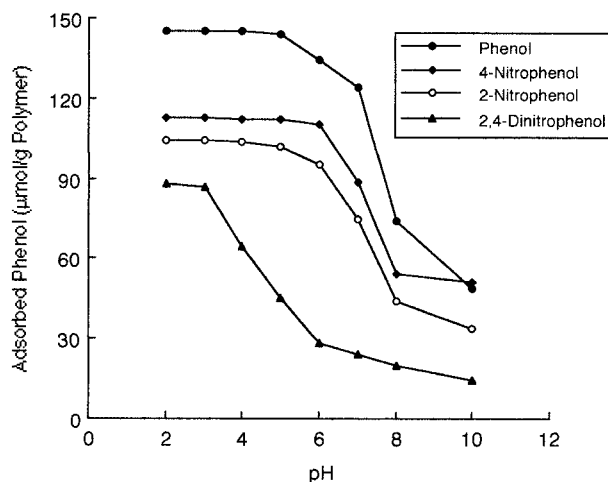
molecules, depending on the type of phenolic compounds (Table I).

In the literature studies different adsorbents were used with a wide range of adsorption capacities for phenolic compounds. Singh and Misra studied iron(III) hydroxide-loaded marble as an adsorbent to remove phenolic compounds (i.e., phenol, 2-chlorophenol, *p*-nitrophenol, pyrogallol, resorcinol, quinol, pyrocatechol) from aqueous solutions.<sup>1</sup> They reported adsorption capacities between 14.7 and 76.5  $\mu\text{mol/g}$ . Ravi et al. reached an adsorption capacity of between 3.2 and 4.4 mmol/g with activated carbon for phenol and cresol isomers.<sup>6</sup> Furuya et al. used chloro- and nitrophenols as the test adsorbates, and granular activated carbon was used as the adsorbent.<sup>7</sup> They achieved up to a 4 mmol/g adsorption capacity. Dargaville et al. found up to a 100  $\mu\text{mol/g}$  adsorption capacity for multinuclear phenolic compounds by activated carbon.<sup>8</sup> Shu et al. used aluminosilicate-based microporous materials (pillared clays, silicalite, and zeolite  $\beta$ ), and they reported selective nitrophenol adsorption capacities up to 0.45 mmol/g.<sup>9</sup> Streat and Sweetland reported up to a 1.5 mmol/g adsorption capacity for phenol and chlorophenols with a new series of hypercrosslinked porous polymeric ion-exchange sorbents (Hypersol-Macronet<sup>TM</sup>).<sup>27</sup> Gupta et al. showed a 60  $\mu\text{mol/g}$  adsorption capacity for phenol and *p*-nitrophenol with a low cost adsorbent (i.e., bagasse fly ash, a waste generated in local sugar plants).<sup>28</sup> Liu and Huang studied the adsorption of monosubstituted phenols including *m*- and *p*-nitrophenols onto hydrous ZnS and they obtained 59.2  $\mu\text{mol/g}$  as the maximum adsorption capacity for nitrophenols.<sup>29</sup> Tewari and Kamaluddin studied the removal of *o*-aminophenol and *o*-nitrophenol from aqueous solutions by copper, zinc, molybdenum, and chromium ferrocyanides

**Table I** Comparison of Molar Ratios of Phenol and Nitrophenols Adsorbed per mole of Alkali Blue 6B

Species	Adsorption Capacity ( $\mu\text{mol/g}$ )	Molar Ratio Species/Alkali Blue 6B (mol/mol)
2,4-Dinitrophenol	87.8	3.7
2-Nitrophenol	104.3	4.4
4-Nitrophenol	112.6	4.8
Phenol	145.2	6.2

The Alkali Blue 6B loading was 23.6  $\mu\text{mol/g}$ .



**Figure 4** The effect of pH on the adsorption of phenol and nitrophenols on the microbeads carrying Alkali Blue 6B at 20°C with initial phenol concentrations of 400 mg/L.

and they reported adsorption capacities in the range of 107–256  $\mu\text{mol/g}$  for nitrophenols.<sup>30</sup> However, note that the adsorption capacities that we achieved are comparable with the values reported in previous publications.

#### Effects of pH

The most critical parameter in the treatment of phenolic compounds by the synthetic adsorbent that affects the adsorption capacity is the pH of the adsorption medium. The effect of the initial pH on the adsorption of phenol and nitrophenols is shown in Figure 4. The pH primarily affects the degree of ionization of the phenolic adsorbate and the surface properties of the adsorbent (i.e., surface charge of the dye molecules). It was observed that the adsorption capacities decreased with increasing pH. The highest adsorption of phenol and nitrophenols occurred at pH 2.0 for all species. However, within the pH range of 2.0–6.0 there is no change in the equilibrium adsorption capacity, beyond which a sharp decline in the adsorption is observed. As the pH was lowered, the protonation of the dye molecules led to electrostatic attractions between the dye molecules and negatively charged phenols. As the pH increased the adsorption decreased because of the deprotonation of the dye molecules. The interaction forces between nitrophenols and attached Alkali Blue 6B molecules are rather weak in the neutral solutions. The decrease in the adsorption

**Table II** Adsorption–Desorption Cycles for Phenols

Cycle No.	Phenol		2,4-Dinitrophenol		2-Nitrophenol		4-Nitrophenol	
	Adsorption ( $\mu\text{mol/g}$ )	Desorption (%)	Adsorption ( $\mu\text{mol/g}$ )	Desorption (%)	Adsorption ( $\mu\text{mol/g}$ )	Desorption (%)	Adsorption ( $\mu\text{mol/g}$ )	Desorption (%)
1	145.2	95.6	87.8	93.2	104.3	92.8	112.6	92.7
2	144.6	93.8	87.0	89.5	103.8	94.5	112.0	91.5
3	144.0	89.7	86.5	88.6	102.9	92.4	111.2	90.1
4	143.1	88.5	86.1	89.0	102.5	90.6	110.0	89.9
5	142.2	91.2	84.9	91.0	101.3	88.8	109.4	87.8

The initial concentration of nitrophenols was 400 mg/L at pH 2.0 and 20°C.

capacity may also be due to the competing hydroxide ions.

### Regeneration of Microbeads

The regenerability of the adsorbent is likely to be a key factor in improving the process economics. Desorption experiments were performed with a 30% (v/v) aqueous methanol solution as the desorption agent. The Alkali Blue 6B microbeads loaded with nitrophenols were placed within the desorption medium and the amount of phenols desorbed in 30 min was measured. Table II shows the adsorption–desorption values of phenols and nitrophenols by Alkali Blue 6B carrying microbeads after several cycles of consecutive adsorption and desorption. This table clearly shows that the Alkali Blue 6B carrying microbeads can be used repeatedly without losing significant adsorption capacities for all nitrophenols studied here.

### CONCLUSION

Wastewaters containing phenolic compounds present a serious public problem. Phenols can cause bad taste and odor in drinking water, even at low concentrations. Some phenolic compounds have been found to accelerate tumor formation and to be ciliostatic. Phenol-containing wastewater may not be conducted into open water without treatment because of the high toxicity of phenolic compounds. At present, polymeric adsorbents are widely employed for the removal of phenolic compounds. In this study, PHEMA microbeads carrying 23.6  $\mu\text{mol}$  Alkali Blue 6B/g polymer were used for adsorption–desorption of phenol and nitrophenols (i.e., 2-nitrophenol, 4-nitrophenol, and

2,4-dinitrophenol) from aqueous solution. The present study leads to the following conclusions: the maximum adsorption capacities of these dye-affinity microbeads from their single solutions were 145.2  $\mu\text{mol/g}$  for phenol, 87.8  $\mu\text{mol/g}$  for 2,4-dinitrophenol, 112.6  $\mu\text{mol/g}$  for 4-nitrophenol, and 104.3  $\mu\text{mol/g}$  for 2-nitrophenol. The affinity order of phenol > 4-nitrophenol > 2-nitrophenol > 2,4-dinitrophenol suggests that the molecular size of the adsorbates controls the degree of adsorption. The adsorption of phenol and nitrophenols decreased with increasing pH. Consecutive adsorption and desorption cycles showed the feasibility of these Alkali Blue 6B carrying microbeads for nitrophenol removal from aqueous solutions. In conclusion, the adsorbent system suggested here is simple, rapid, and inexpensive on a laboratory scale. These results make the dye-affinity adsorbent system suitable for reduction of the contents of phenolic and nitrophenolic compounds in wastewater.

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