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Adsorption of phenol and *o*-chlorophenol on surface altered fly ash based molecular sieves

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Abstract

The contamination of water by organic pollutant viz. phenolic compounds is a worldwide environmental problem due to their highly toxic nature. Surface modified zeolite materials have been developed from a waste material like fly ash which are being used for adsorption of phenol and *o*-chlorophenol from wastewater. The comparison of adsorption of phenol and *o*-chlorophenol on commercial zeolite-Y, fly ash based zeolite (FAZ-Y) and surface modified fly ash based zeolite (SMZ-Y) were studied. It was observed that the adsorption of phenol on SMZ-Y was 4.05 and 3.24 times higher than the FAZ-Y and commercial zeolite-Y, respectively. For *o*-chlorophenol the efficiency is higher by a factor of 2.29 and 1.8 for FAZ-Y and commercial zeolite-Y, respectively. This may be attributed to the hydrophobicity imparted by surfactant molecules on the surface of fly ash zeolite, consequently leading to organic partitioning. The effect of various parameters like adsorbent dose, pH and initial concentration were studied for their optimization. The rate of adsorption of phenol and *o*-chlorophenol was found to be maximum at neutral pH. The effect of the presence of anions on adsorption of solute was also studied. It was found that the salts have a substantially detrimental effect on adsorption of phenol and *o*-chlorophenol. Equilibrium adsorption data for phenol and *o*-chlorophenol were analyzed by using Freundlich adsorption isotherms model.

Keywords: Adsorption; Fly ash; Surface modified fly ash based zeolite (SMZ-Y); Phenol; *o*-Chlorophenol; pH and anion effects

1. Introduction

Phenolic compounds are identified as highly toxic compounds from last several decades due to their carcinogenic nature and pungent odor. Phenol pollution is a serious problem in many countries including India. The major sources of phenolic waste are petroleum refineries, petrochemical, steel mills, coke oven plants, coal gas, synthetic resins, pharmaceuticals etc. Total phenol concentration in the wastewater of a typical Indian refinery processing 5.0 million tonnes of crude per year is around 135 mg l^{-1} and the discharge rate of wastewaters varies from 125 to 250 $m^3 h^{-1}$ with pH being in the range of 8.8–9.4 [1]. The Ministry of Environment and Forests (MOEF), Government of India and EPA, USA, have listed phenol and phenolic compounds on the priority-pollutants list. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances [2]. Phenol being highly toxic and difficult to degrade biologically, it has led to setting up of rigid limits on the acceptable level of phenol in the environment. While the MOEF has set a maximum concentration level of 1.0 mg l^{-1} of phenol in the industrial effluents for safe discharge into surface waters, the WHO recommends the permissible phenolic concentration of 0.001 mg l^{-1} in potable waters [1,2].

Various physicochemical methods have been proposed for the treatment of wastewaters containing phenolic wastes [3–8]. It is now widely recognized that sorption processes provide a feasible method for the removal of pollutants from wastewaters. Great effort has been exerted to develop new sorbents and stabilizers (e.g., organoclay, activated carbon and surfactant-modified zeolites) for nonionic organic contaminants and to immobilize them in situ [9–13]. The choice of treatment depends on effluent characteristics such as concentration of solute, pH, temperature, flow

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Nomenclature

C_0	initial concentrations of phenol and *o*-chlorophenol (mg l^{-1})
C_e	equilibrium concentration of phenol and *o*-chlorophenol (mg l^{-1})
C_t	concentrations of phenol and *o*-chlorophenol at any time t (mg l^{-1})
K_F	Freundlich constants related to adsorption capacity (mg g^{-1})
n	adsorption intensity (heterogeneity factor)
q_e	equilibrium adsorbate capacity (mg g^{-1})
V	volume of the solution (L)
W	weight of the adsorbent (g)

volume, biological oxygen demand, the economics involved and the social factor like standard set by government agencies. Activated carbon is widely used for removal of organic pollutants from wastewater [8,14–17]. The porous nature of this adsorbent material and its high internal surface area are suitable properties for adsorption. However, owing to its relatively high cost and restricted applications there has been a continuous attempt for locally available and cheaper adsorbents for removal of a variety of organic compounds such as phenol and *o*-chlorophenol.

Zeolites are attractive options for removal of organic compounds from the wastewater, because of its superior advantages [13]. Molecular sieves or zeolites are hydrated alumino-silicate minerals having cage like structures with internal and external surface area of about 500–600 m^2 g^{-1} and cation exchange capacities of up to several milliequivalents per kilogram. This material appears attractive because of its high affinity for cations and molecules with kinetic pore diameter less than 7 Å however; these materials can also be tailored to adsorb anions and molecules greater than 7 Å. There is a need for such versatile material for environmental remediation; the commercially available zeolites are finding restricted usage due to one of the problems that they can adsorb organic pollutants of kinetic diameters less than 7 Å only. To overcome this problem, we have developed a process for development of surface modified zeolite from fly ash, which can be exploited for wider array of organic pollutants making the process more economical. Fly ash being a waste residue generated in thermal power stations after combustion is having a great disposal problem due to its mega production and low percent utilization. However, fly ash contains oxides of silica and alumina as main constituents and can be effectively used as a source material for synthesis of zeolites A and Y, detailed elsewhere [18,19]. The first step towards synthesis of surface modified zeolites is development of fly ash-based zeolites followed by surface treatment to modify the surface chemistry of zeolite through a simple process of surface modification using surfactant and quaternary ammonium compounds.

Various investigators have given emphasis on use of natural zeolites, activated carbons, clays, etc., for sorption of phenolic compounds. The details of these are given in Table 1. In the present work a systematic study of the sorption of phenol and *o*-chlorophenol on surface modified fly ash based molecular sieves is reported. This article addresses to altering surface chemistry of fly ash based molecular sieve viz.; FAZ-Y by a suitable cationic surfactant namely hexadecyltrimethyl ammonium bromide (HDTMA-Br) to enhance its sorption properties for organic pollutants such as phenol and *o*-chlorophenol from water. The comparison of removal of phenol and *o*-chlorophenol using commercial zeolite-Y, FAZ-Y and SMZ-Y was also studied. The effect of various parameters such as pH, adsorbent dose and effect of concentration on adsorption of phenol and *o*-chlorophenol were studied in detail. The effect of the presence of anions on adsorption of phenol and *o*-chlorophenol was also investigated.

2. Experimental

2.1. Materials

All the reagents used for experimental studies were of analytical grade. Zeolite-Y having silica: alumina ratio of 2.5 and cation exchange capacity of 380–400 meq/100 g was synthesized from fly ash as per procedure reported elsewhere [20]. Fly ash was procured from Thermal Power Plant, Koradi, Nagpur, India for synthesis of surface modified fly ash zeolite (SMZ-Y). The commercial zeolite-Y was procured from Merck, Germany for comparative study. Phenol, *o*-chlorophenol, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate and cationic surfactant hexadecyltrimethyl ammonium bromide were obtained from Merck India Ltd., Mumbai, India. The stock solutions of phenol and *o*-chlorophenol were prepared in distilled water.

2.2. Synthesis of surface modified fly ash based zeolite (SMZ-Y)

Initially the fly ash-based zeolite-Y (FAZ-Y) was washed with distilled water several times till its pH reached to 10.0 to 10.5 and subsequently dried in an oven at 323–333 K. Pre weighed quantity of washed FAZ-Y sample was then mixed with different initial concentration of hexadecyl trimethyl ammonium bromide (HDTMA-Br) surfactant solution in 1:100 (solid:liquid) ratio. The surfactant concentration was ranging from 100 to 800 mg l^{-1} for 10 g of fly ash zeolite-Y. The solution was agitated for 7–8 h at 150 rpm on a gyratory shaker at pH 8.0 to 8.5. The pH of the system was maintained by addition of dilute nitric acid or hydrochloric acid. The solution was then filtered and the solid residue was washed thoroughly with double distilled water and air dried for 4–6 h. The SMZ-Y sample synthesized as such was then mechanically ground with a mortar and pestle to fine particle size. After that the adsorbents samples were stored in sealed flasks to prevent exposure to moisture. SMZ-Y having variable surfactant loading was then used for removal of phenolics. As the surfactant is the only source of carbon in the system, the surfactant loading was monitored by total organic carbon (TOC) analysis of the initial and final solutions obtained during the synthesis of SMZ-Y. The TOC analysis was carried

Table 1
Sorption of phenolic compounds on natural zeolites, activated carbon, clays, etc.

Phenolic compounds	Adsorbents	Concluding remarks	Authors
Phenol	Peat, fly ash and bentonite	The removal of phenol from wastewater on peat, fly ash and bentonite were studied by Viraraghavan and Alfaro [3]. From the batch kinetic it was observed that an equilibrium time of 16, 5 and 16 h was needed for the adsorption of phenol on peat, fly ash and bentonite respectively. It was observed that 40–45% of phenol was adsorbed in the pH range of 4 to 5 at equilibrium time	Viraraghavan and Alfaro [3]
Benzene, toluene and phenol	Synthesized MCM-41, organo-zeolites and natural clinoptilolite	The adsorption of benzene, toluene and phenol on organo-zeolites, as-synthesized MCM-41 and molecular sieve were investigated. Benzene and toluene almost showed similar sorption capacity on the organo-zeolites, whereas phenol showed the lowest sorption capacity among them. The experimental results were analyzed by using the Langmuir, Freundlich, Redlich–Peterson and Henry's equations. According to the Langmuir equation, the maximum organics adsorption by synthesized MCM-41 was much greater than that of the natural clinoptilolite and ZSM-5 zeolites	Ghiaci et al. [13]
Phenol	Zeolite-templated porous carbons	The adsorption behaviors of phenol in aqueous solution on zeolite-templated porous carbons with different pore structures and surface properties were studied. The adsorption capacity of phenol on the porous carbons after thermal treatment was markedly increased in spite of reduced surface area and pore volume. Possible reasons behind the experimental observations were also discussed	Su et al. [12]
Phenol, *o/m/p*-nitrophenol	Kaolinite-type clay	Adsorption behavior of phenol, *o/m/p*-nitrophenol on kaolinite-type clay has been investigated. Adsorption of the phenolic compounds in aqueous solution decreases in the following order: *o*-nitrophenol > phenol > *m*-nitrophenol ≅ *p*-nitrophenol. Influence of an anionic surfactant, sodium dodecylsulfate (SDS), on adsorption behavior of phenol and nitro-substituted phenols onto kaolinite is studied. It was observed that the adsorption of aromatic nitro compounds on kaolinite modified with SDS shows significant adsorption capacity as compared to bare kaolinite especially at high-concentration region	Pura and Atun [23]
o/*p*-Chlorophenol	Activated sludge and fly ash	Aksu and Yener [4] studied removal of *o*/*p*-chlorophenols using activated sludge and fly ash as a substitute for granular carbon. It was observed that the binding capacity of the adsorbent depends upon initial concentration, initial pH and functional group attached to the benzene ring	Aksu and Yener [4]
Phenol	Activated carbon, Filtrasorb (F-400), Activated alumina, Silica gel, HiSiv 3000 (Zeolite ZSM-5 and HiSiv 1000 (Zeolite-Y)	Adsorption of phenol from water using silica gel, HiSiv 3000, activated alumina, activated carbon, Filtrasorb-400, and HiSiv 1000 was studied by Roostaei and Tezel [6]. From the kinetic study they observed that HiSiv 1000 had the highest rate of adsorption among the adsorbents studied. From particle size experiments it appeared that adsorption capacity of HiSiv 1000 did not change by changing the particle size, but the rate of adsorption decreased considerably by increasing the particle size. It was also observed that adsorption capacity of HiSiv 1000 did not change after 14 regeneration cycles. Equilibrium experiments showed that the adsorption capacities of activated carbon and Filtrasorb-400 were several times higher than that of HiSiv 1000	Roostaei and Tezel [6]
Phenol and *o*/*p*/*m*-chlorophenol	Activated carbon and Na–Y and Ni/Na–Y zeolites	The adsorption of phenol and the three chlorophenol (CP) from aqueous solutions was studied in an agitated batch system using activated carbon and Na–Y and Ni/Na–Y zeolites as adsorbents. While equilibrium uptake on activated carbon was achieved within the first 2 to 4 h, extended treatment times were required to ensure an attainment of the maximum uptake on the zeolite samples; this was due to diffusion limitations. The experimental adsorption isotherms were analyzed using standard Langmuir and Freundlich equations	Okolo et al. [11]
Phenol and its derivatives	Activated carbons	Adsorption of phenol and its derivatives on activated carbons was critically reviewed by Dabrowski *et al.* [8]. The effects of carbon surface functionalities, pH of solution and heterogeneity effects on adsorption of phenolic compounds was discussed. The most important aspects are overviewed referring to irreversible adsorption of phenols and impact of different substituents of phenolic compounds on their uptake by activated carbons was also explained	Dabrowski et al. [8]
Phenol	Titanium oxide anatase (Degussa P25)	The adsorption of phenol, on a photocatalyst titanium oxide anatase (Degussa P-25) was experimentally investigated by Bekkouche et al. [26]. From the equilibrium adsorption study it was observed that, the kinetics of adsorption was slow and obeyed the Lagergren model. They also observed that adsorption was chemisorption in a monolayer	Bekkouche et al. [26]

Table 1(*Continued)*

Phenolic compounds	Adsorbents	Concluding remarks	Authors
Phenol	Chitin	Dursun and Kalayci [24] studied the adsorption of phenol onto chitin, a naturally occurring material as a function of initial pH, temperature and initial phenol concentration. The thermodynamic parameters of the adsorption process were estimated and it was observed that the adsorption of phenol on chitin was endothermic and spontaneous process	Dursun and Kalayci [24]
Phenol	Activated carbon from nuts of *Terminalia Arjuna*, an agricultural waste	Mohanty et al. [15] prepared activated carbon from nuts of *Terminalia Arjuna*, an agricultural waste, by zinc chloride activation under four different activation atmospheres. The developed activated carbon shows substantial capability to adsorb phenol from dilute aqueous solutions. The kinetic data were fitted to the models of intraparticle diffusion, pseudo-second order, and Lagergren model which followed more closely the pseudo-second-order chemisorption model. It was found that the isotherm equilibrium data were well fitted by the Langmuir and Freundlich models	Mohanty et al. [15]
Phenols and acid and basic dyes	Granular activated carbon prepared from coffee grounds	Namane et al. [16] studied the adsorption of different phenols and acid and basic dyes on granular activated carbon prepared from coffee grounds by chemical activation. They observed that, the coffee grounds based activated carbon may be promising adsorbent for removal of phenol and dye from aqueous streams	Namane et al. [16]
Phenol	Coal, residual coal, and residual coal treated with H_3PO_4; petroleum coke, coke breeze, rice husk, and rice husk char	The removal of phenol from wastewater by using coal, residual coal, and residual coal treated with H_3PO_4 was studied by Ahmaruzzaman and Sharma [7]. Other low-cost adsorbents such as petroleum coke, coke breeze, rice husk, and rice husk char have also been used. The effect of system variables such as pH, contact time, and temperature has been also investigated. The Freundlich, Langmuir, and Redlich–Peterson adsorption models were used to fit the equilibrium data for each phenol–adsorbent system and showed that the Redlich–Peterson model best fit. Kinetic modeling of removal of phenols was done using the Lagergren first-order rate expression	Ahmaruzzaman and Sharma [7]
Phenol and chlorophenols	Tris (2,2V bipyridine)ruthenium(II)-clay	The adsorptive properties of tris(2,2V-bipyridine)ruthenium(II)-clay was tested for removal phenols by Okada et al. [25]. The adsorption isotherms of phenols for the tris(2,2Vbipyridine) ruthenium(II)-clays from aqueous solutions followed Langmuir type, indicating strong adsorbate–adsorbent interactions. The adsorbed amounts of 2,4-dichlorophenol for the tris(2,2V-bipyridine)ruthenium(II)-saponite and the tris(2,2V-bipyridine)ruthenium(II)-montmorillonite were the largest among three phenols	Okada et al. [25]
Phenol	Granular activated carbon (GAC) prepared from mixing powered activated carbon (PAC)	The adsorption of phenol on granular activated carbon (GAC) prepared from mixing powered activated carbon (PAC), carboxymethyl cellulose as a binder, and kaolin as reinforcer was studied by Tancredi et al. [14]. The equilibrium adsorption data were fitted to Langmuir and Freundlich models, and corresponding parameters were determined. Maximum phenol uptakes for all carbons were determined and correlated with carbon characteristics	Tancredi et al. [14]
Phenol	Activated carbon prepared from waste tires and a commercial activated carbon	Adsorption of phenol on activated carbon prepared from waste tires and a commercial activated carbon was investigated by Tanthapanichakoon et al. [17]. Adsorption experiments reveal that the prepared activated carbon shows comparable phenol adsorption capacity as the commercial one but clearly larger adsorption capacity of two reactive dyes, Black 5 and Red 31. It was ascertained that the prepared activated carbon exhibited less irreversible adsorption of phenol and the two dyes than its commercial counterpart. Moreover, ethanol regeneration efficiency of the prepared AC saturated with either dye was higher than that of the commercial AC	Tanthapanichakoon et al. [17]

out using a Shimadzu TOC analyzer (model: TOC-VC$_{PH}$). The SMZ-Y has been characterized with respect to crystallinity using XRD (Model: Philips DW 1710 atomic diffractometer), particle size (Model: Laser particle sizer analysetter 22) and morphological characteristics through SEM (Model: Stereoscan S250 MK3 Cambridge instruments). The adsorbents used in this study, FAZ-Y and SMZ-Y were also characterized using a Perkin-Elmer FT-IR spectrometer with KBr pellets, BET surface area using Micromeritics BET surface area analyzer (Model: ASAP 2000).

2.3. Batch adsorption

Batch adsorption experiments were carried out in a 100 cm^3 stoppered conical flask. For single solute adsorption studies, model solutions were prepared using pure samples of the solutes. Fixed amounts of these aqueous solutions were taken in the conical flask containing known amounts of the adsorbent. The conical flasks were then kept on a shaker (150 rpm) at ambient temperature (303 K) for 24 h to attain equilibrium. Residual solution concentration of the phenol and *o*-chlorophenol were analyzed by Chemito make UV–vis spectrophotometer (Model UV 2100) at wavelength 270 and 274 nm, respectively. In order to reduce measurement errors, the UV absorption intensity of each equilibrium solution sample was measured twice and the average value was used to calculate the equilibrium concentration based on a standard calibration curve, whose correlation coefficient (R^2) was 0.99.

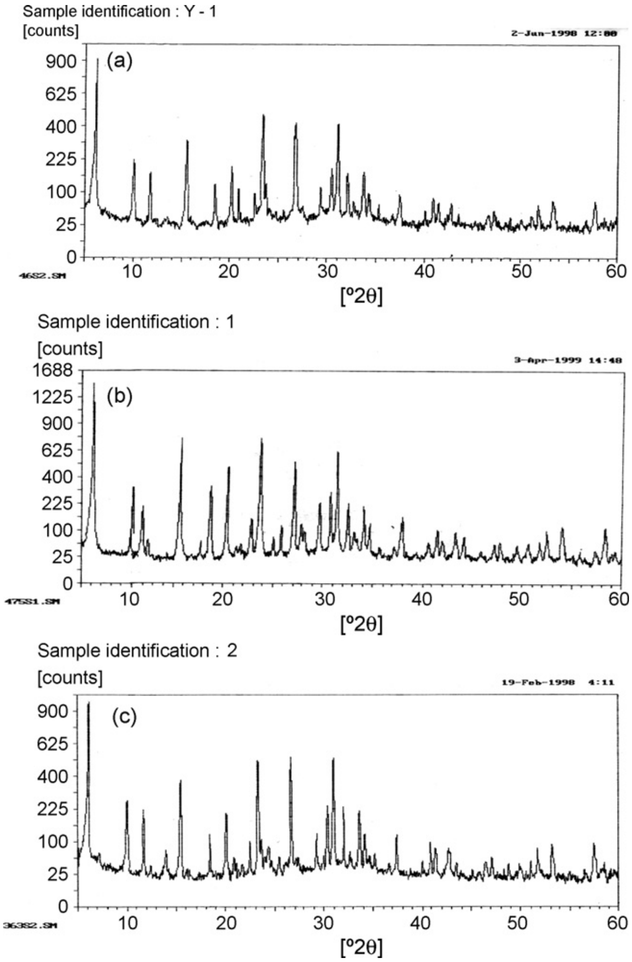

Fig. 1. The XRD patterns for (a) commercial zeolite-Y, (b) FAZ-Y and (c) SMZ-Y.

The amount of phenol and *o*-chlorophenol adsorbed onto the adsorbate q_e (mg g^{-1}) were calculated according to:

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

where V is the volume of the solution (l), C_0 the initial concentration (mg l^{-1}), C_e the equilibrium concentration (mg l^{-1}), and W is the weight of the adsorbent (g).

3. Results and discussions

3.1. Characterization of FAZ-Y and SMZ-Y

The zeolite structure stability was monitored during the characterization of the materials. Powder XRD analysis, using Cu Kα as the source for X-rays, and the sum total of relative intensities of *d*-spacing values of standard commercial zeolite-Y were compared to FAZ-Y and SMZ-Y to determine percent crystallinity. The *d*-spacing values used for reference are as follows: 14.15, 8.73, 7.46, 5.69, 4.78, 4.39, 3.79, 2.87 and 2.65 Å. The closely matching *d*-spacing values of all these zeolites prove

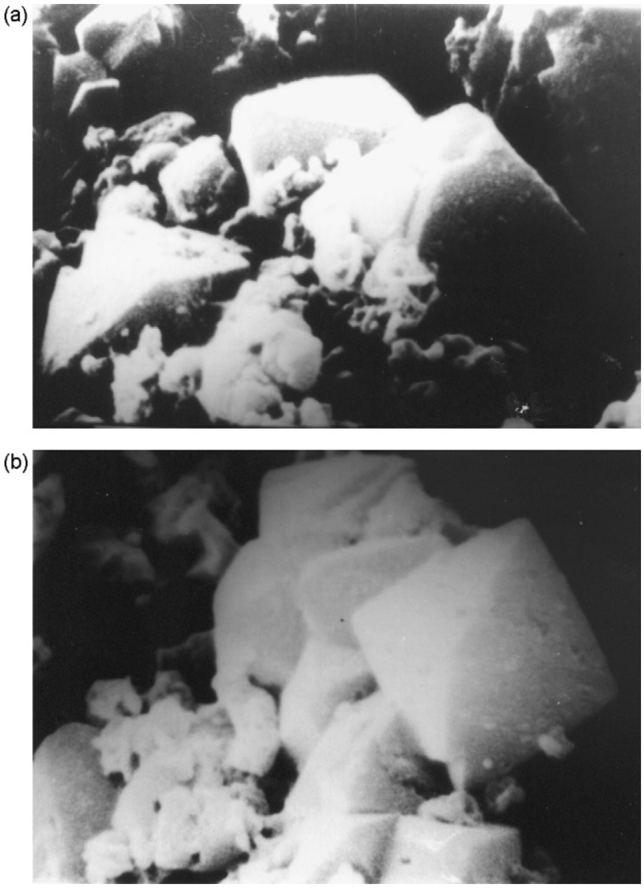

Fig. 2. Scanning electron micrographs for (SEM) of (a) FAZ-Y and (b) SMZ-Y.

that structure has been retained. The XRD patterns for commercial zeolite-Y, FAZ-Y and SMZ-Y are shown in Fig. 1. The surface morphology of FAZ-Y and SMZ-Y was examined by SEM and is presented in Fig. 2. The orthorhombic geometry of zeolites has not changed much; probably there are changes in sharp edges and corners. FT-IR spectra obtained using KBr pellets of HDTMA-Br, FAZ-Y and SMZ-Y are shown in Fig. 3. The IR patterns confirm that in SMZ-Y the characteristic peaks at wave numbers 3419, 2922, 2854, 1377 and 721 cm^{-1} are observed. These are similar to FAZ-Y. There is a slight shift in peaks at wave numbers 1458 and 983 cm^{-1} however; both the patterns are nearly the same. This further substantiates the structural stability of zeolite after surface modifications. FT-IR pattern of HDTMA-Br was obtained separately. The three most intense peaks in case of HDTMA-Br are observed at 725, 3427 and 964 cm^{-1}. Peaks at 3427 and 964 cm^{-1} are co-incident with that observed in FAZ-Y. The peaks may be overlapping. However, the most intense peak at 721 cm^{-1} is observed distinctly in SMZ-Y. This confirms the loading of HDTMA-Br on the zeolite.

The surfactant loading was confirmed by using TOC analysis, as mentioned earlier and was around 30–32 $\mathrm{mg\,g}^{-1}$ for a surfactant loading of 450 $\mathrm{mg\,l}^{-1}$ for 10 g of FAZ-Y. Substantial changes in specific surface area and micropore volume were observed in the case of SMZ-Y. Micropore volume, micropore area and external surface area estimated using nitrogen adsorption for FAZ-Y were 0.337 $\mathrm{cm}^3\,\mathrm{g}^{-1}$, 868.8 $\mathrm{m}^2\,\mathrm{g}^{-1}$, and 34.4 $\mathrm{m}^2\,\mathrm{g}^{-1}$ respectively. These were reduced to micropore vol-

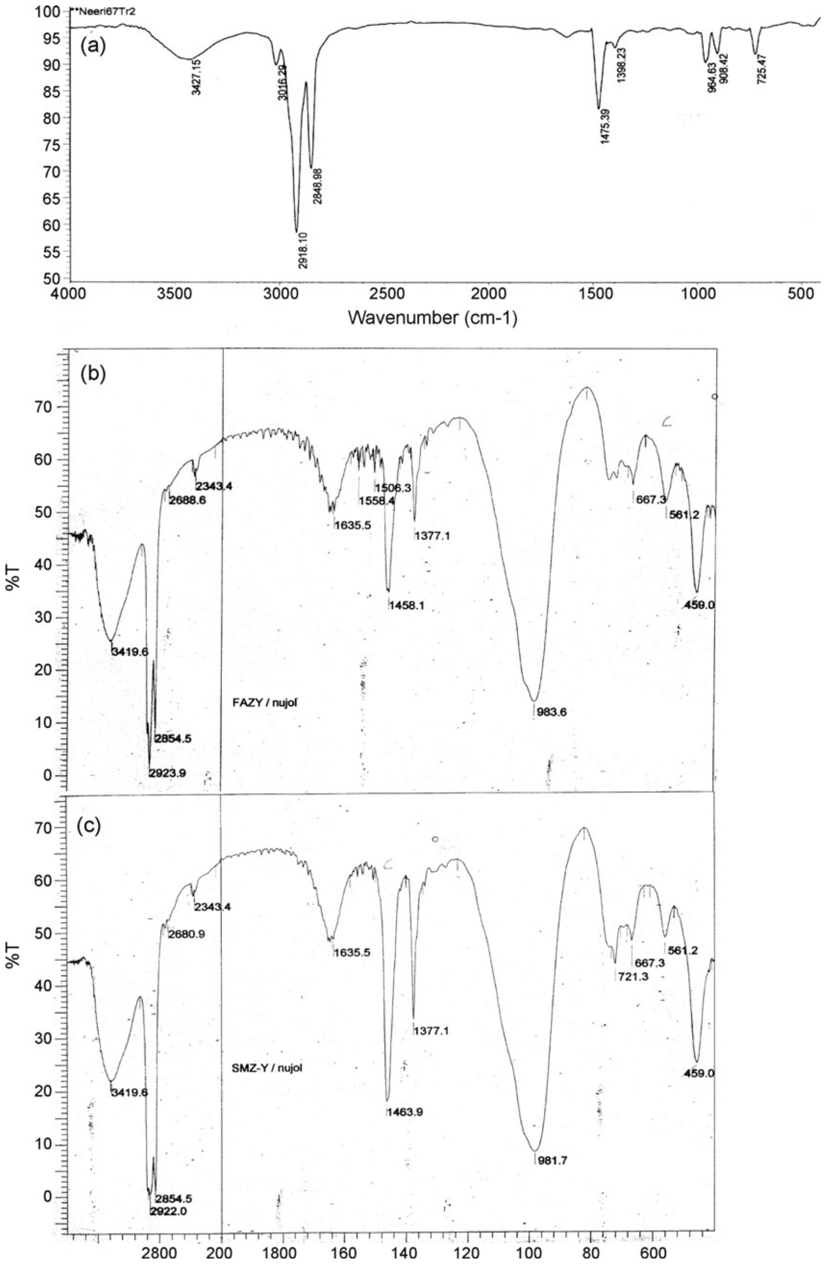

Fig. 3. FT-IR patterns for (a) HDTMA-Br, (b) FAZ-Y and (c) SMZ-Y.

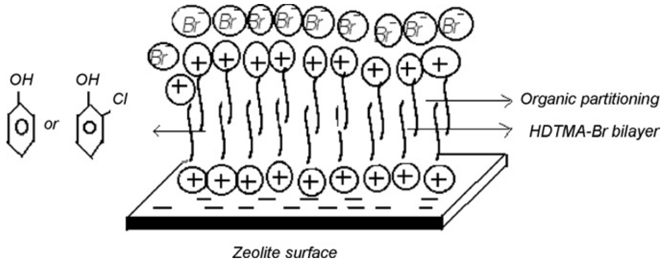

Fig. 4. Schematic representation of adsorption of phenol and *o*-chlorophenol on SMZ-Y.

ume of 0.283 $cm^3\,g^{-1}$, micropore area of 728.4 $m^2\,g^{-1}$ and external surface area of 28.08 $m^2\,g^{-1}$ for SMZ-Y. The surfactant molecules (head size of about 6 Å) have probably entered into the micropores of FAZ-Y and may be some of the molecules are present at the pore openings.

3.2. *Effect of surfactant loading on fly ash based zeolite*

When a fly ash based zeolite (FAZ-Y) is mixed with the surfactant solution having concentration less than its critical micelle concentration (CMC) then the surfactant molecule forms a monolayer on the external surface of zeolite via exchange. It is well known that CMC is the concentration below which the surfactant molecule exists as a monomer. The theoretical CMC of HDTMA-Br is about 9×10^{-4} mmoles l^{-1} [10,20,21]. If the concentration of surfactant is increased then it forms micelle which attaches itself in a patchy layer and subsequently rearranges to form a second layer over the first layer via hydrophobic tail to tail interaction of surfactant due to weak Van der Waals cohesive forces. Due to this tail-to-tail interaction, an organic fraction is created over the surface of zeolite crystal, which is responsible for trapping organic hydrophobic pollutants like phenolics. Fig. 4 reveals the schematic representation of mechanism of adsorption of phenol and *o*-chlorophenol by surface modified zeolite-Y. The effect of surfactant loading on removal of phenol, *o*-chlorophenol was given in Table 2. It was found that for surfactant treatment of 450 mg l^{-1} (i.e. SMZ-450), maximum removal of phenol and *o*-chlorophenol was observed. The steady decreasing trend for percentage removal efficiency of phenolics for SMZ-600 and SMZ-800 may be due to excessive crowding of monomers of surfactant molecule on external surface of FAZ-Y, which might have blocked the organic partitioning created by tails of long chain alkyl compound for sorption of organics.

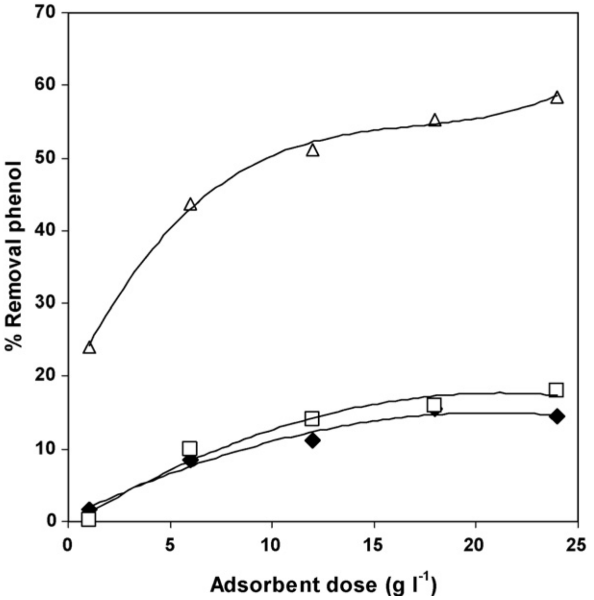

Fig. 5. Comparison of removal of phenol using commercial zeolite-Y, FAZ-Y and SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, contact time = 24 h). (♦) Commercial zeolite-Y, (□) FAZ-Y, (△) SMZ-Y.

3.3. *Effect of various parameters on adsorption of phenol and o-chlorophenol*

3.3.1. *Preliminary adsorption experiments*

The preliminary adsorption experiments under identical set of experimental conditions were carried out using commercial zeolite-Y, FAZ-Y and SMZ-Y. The percentage removal of phenol and *o*-chlorophenol by commercial zeolite-Y, FAZ-Y and SMZ-Y are shown in Figs. 5 and 6. It was observed that the removal efficiency of FAZ-Y and commercial zeolite-Y is significantly less as compared to SMZ-Y. This may be attributed to the hydrophobicity imparted by surfactant molecules on the surface of fly ash zeolite, consequently leading to organic partitioning. Therefore, further experiments were carried out using SMZ-Y for optimization of adsorption parameters.

3.3.2. *Effect of adsorbent dose*

The adsorption of phenol and *o*-chlorophenol on SMZ-Y were carried out at different adsorbent dose by keeping other parameters constants. The relationship between adsorbent dose and substrate removal for same initial concentrations of phenol and *o*-chlorophenol is presented in Figs. 7 and 8, respectively. It can be seen from Figs. 7 and 8 that percentage removal

Table 2
Effect of surfactant loading on fly ash based zeolite on percentage removal of phenol and *o*-chlorophenol

FAZ-Y dose (g)	HDTMA-Br concentration (mg l^{-1})	Surfactant loading (mg l^{-1})	% Removal of phenol	% Removal of *o*-chlorophenol
10	100	54.5	18.8	38.8
10	200	61.0	35.6	57.9
10	300	67.0	41.5	66.1
10	450	70.0	58.5	80.4
10	600	70.0	44.8	71.5
10	800	70.0	42.8	71.0

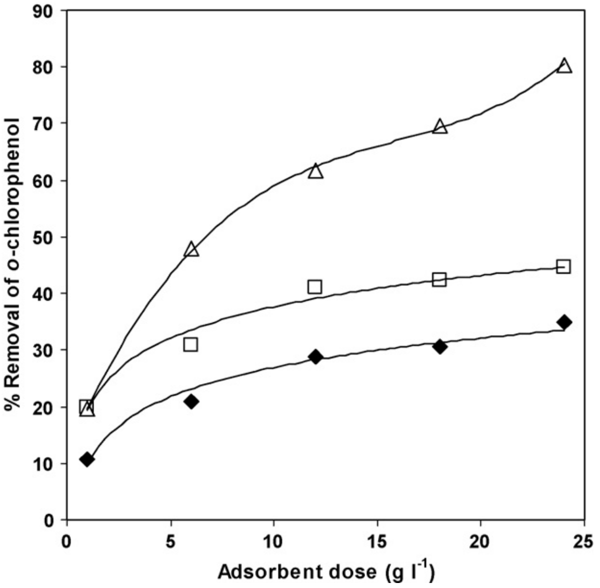

Fig. 6. Comparison of removal of *o*-chlorophenol using commercial zeolite-Y, FAZ-Y and SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, contact time = 24 h). (♦) Commercial zeolite-Y, (□) FAZ-Y, (△) SMZ-Y.

of phenol and *o*-chlorophenol increased with the increase in adsorbent dose while loading capacity (amount of phenol and *o*-chlorophenol loaded per unit weight of adsorbent) gradually decreased for the same. This increase in loading capacity is due to the availability of higher number of solutes (phenol and *o*-chlorophenol) per unit mass of adsorbent, i.e. higher solute/adsorbent ratio. These experiments were performed with initial concentration of 50 mg l^{-1} of solutes and neutral pH of the solution. It can be concluded that the rate of phenol/*o*-chlorophenol binding with adsorbent increases more rapidly in the initial stages and after some point the adsorption is marginal and becomes almost constant.

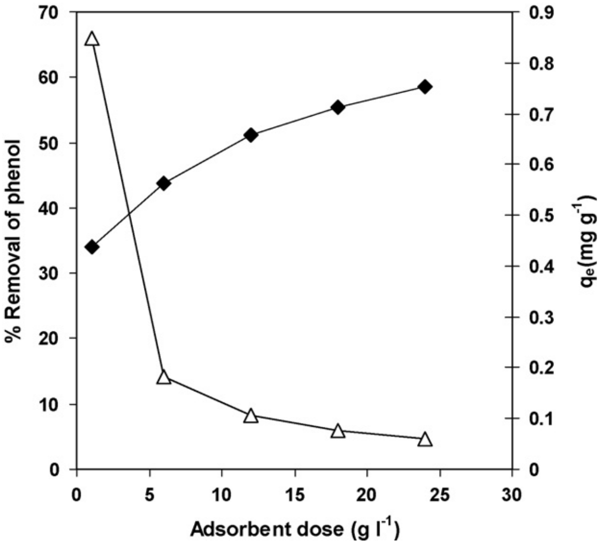

Fig. 7. Effect of adsorbent dose on removal of phenol on SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, contact time = 24 h). (♦) % removal of phenol, (△) equilibrium adsorption capacity (q_e) in mg g^{-1}.

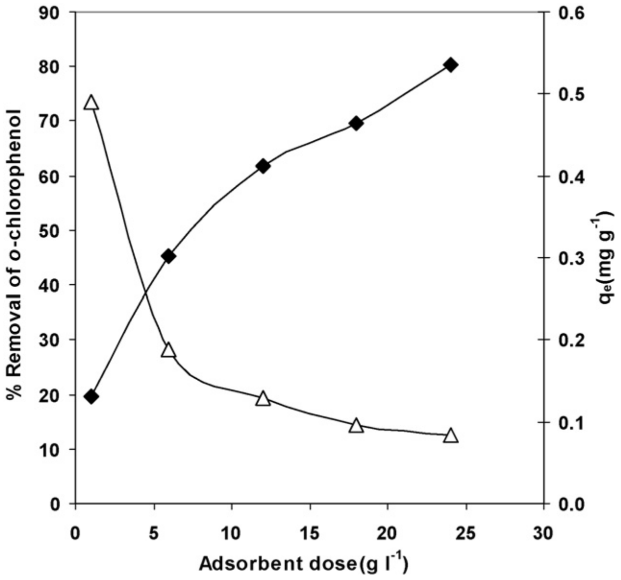

Fig. 8. Effect of adsorbent dose on removal of *o*-chlorophenol on SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, contact time = 24 h). (♦) % removal of *o*-chlorophenol, (△) equilibrium adsorption capacity (q_e) in mg g^{-1}.

3.3.3. Effect of pH

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. Effect of initial pH on adsorption of phenol and *o*-chlorophenol were studied with initial concentration of 50 mg l^{-1} and optimum dose of 2 g l^{-1}. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic range, pH was varied using $HClO_4$. The experimental result for the uptake of the phenol and *o*-chlorophenol on SMZ-Y in the pH range of 5, 7 and 11 are shown in Figs. 9 and 10. It was observed that the relative amount of phenol and *o*-chlorophenol adsorbed was significantly affected by pH. The maximum adsorption occurs at neutral pH. Significant decline in removal efficiency was observed for further increase in pH, which may be attributed to formation of phenolate anions. The effect of pH less than 5

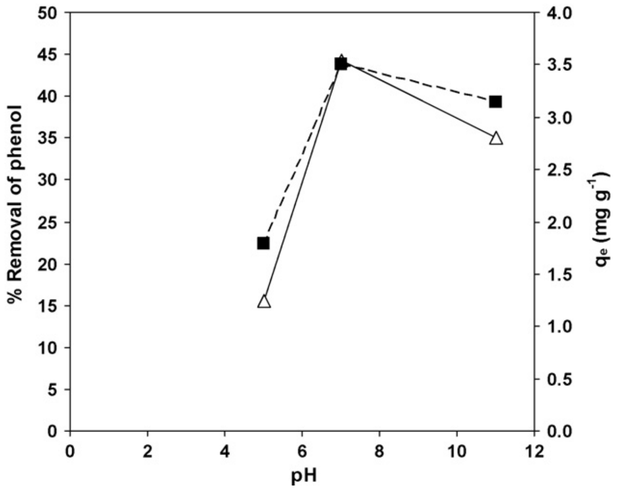

Fig. 9. Effect of pH on adsorption of phenol on SMZ-Y (initial concentration = 50 mg l^{-1}, optimum dose = 2 g l^{-1}, contact time = 24 h). (△) % removal of phenol, (■) equilibrium adsorption capacity (q_e) in mg g^{-1}.

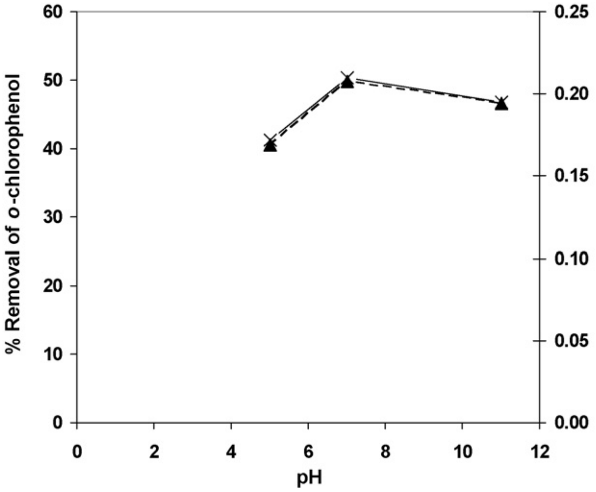

Fig. 10. Effect of pH on adsorption of *o*-chlorophenol on SMZ-Y (initial concentration = 50 mg l^{-1}, optimum dose = 2 g l^{-1}, contact time = 24 h). (×) % removal of *o*-chlorophenol, (▲) equilibrium adsorption capacity (q_e) in mg g^{-1}.

was not investigated because zeolites are not stable at pH below 5.0.

3.3.4. *Effect of concentration*

Effect of initial concentration on the percentage removal of phenol and *o*-chlorophenol on SMZ-Y were studied at different initial concentrations and variable adsorbent dose by keeping other parameters constant. From Figs. 11 and 12 it was observed that with the increase in initial substrate concentration, the % removal phenol and *o*-chlorophenol decreases. This may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in decrease in overall percent removal.

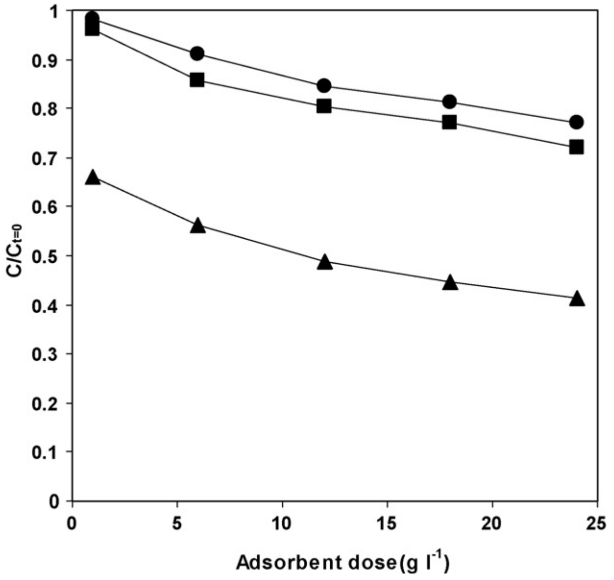

Fig. 11. Effect of initial concentration on adsorption of phenol on SMZ-Y (contact time = 24 h, pH 7, contact time = 24 h). (▲) Initial concentration of phenol = 50 mg l^{-1}, (■) initial concentration of phenol = 75 mg l^{-1}, (●) initial concentration of phenol = 100 mg l^{-1}.

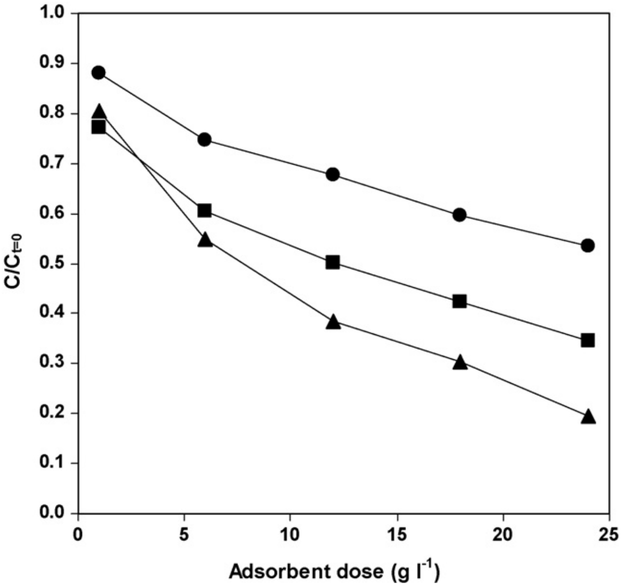

Fig. 12. Effect of initial concentration on adsorption of *o*-chlorophenol on SMZ-Y (contact time = 24 h, pH 7, contact time = 24 h0. (▲) Initial concentration *o*-chlorophenol = 50 mg l^{-1}, (■) initial concentration *o*-chlorophenol = 75 mg l^{-1}, (●) initial concentration *o*-chlorophenol = 100 mg l^{-1}.

3.3.5. *Effect of the presence of anions*

Industrial effluents contain apart from pollutants different salts at different levels of concentration. The anion and cation parts of the salt have different effects on the adsorption of substrate. The effect of the presence of various anions such as chloride, sulfate, bicarbonate and carbonate was studied using 0.1 M solution of their sodium salts at initial concentration of 50 mg l^{-1} of aqueous phenol and *o*-chlorophenol solution on SMZ-Y. The results are presented in Figs. 13 and 14. In the case of phenol the percentage removal in the presence of sodium chloride, sodium sulfate, sodium bicarbonate and sodium carbonate was 7.6%, 12.4%, 9.1% and 25.5%, respectively, whereas in the absence of anions the percentage removal was 43.8%. It can thus

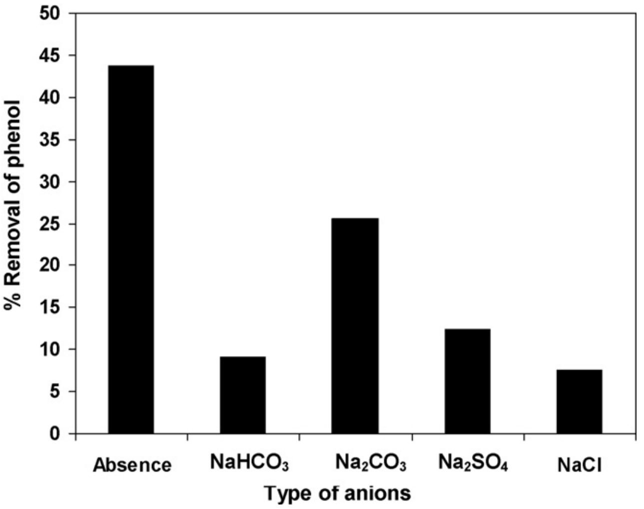

Fig. 13. Effect of the presence of anions on adsorption of phenol on SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, optimum dose = 2 g l^{-1}, contact time = 24 h).

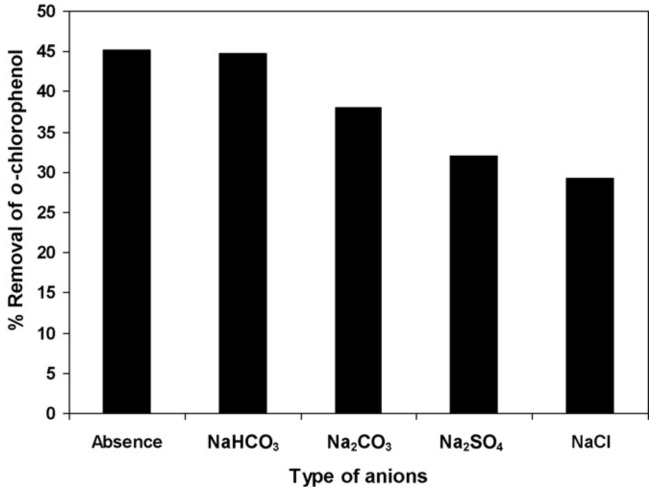

Fig. 14. Effect of the presence of anions on adsorption of *o*-chlorophenol on SMZ-Y (initial concentration = 50 mg l^{-1}, pH 7, optimum dose = 2 g l^{-1}, contact time = 24 h).

be seen that the Cl^-, $HCO_3{}^-$, $SO_4{}^{2-}$ significantly decrease the adsorption while $CO_3{}^{2-}$ affects adsorption to a lesser extent. In case of *o*-chlorophenol the percentage removal in presence of sodium chloride, sodium sulfate, sodium bicarbonate and sodium carbonate was 29.2%, 32.0%, 44.8% and 38%, respectively, and in the absence of anions was 45.15%. The effect of the salts on the adsorption of phenol and *o*-chlorophenol shown in Figs. 13 and 14 clearly indicates that the salts have a substantially detrimental effect on adsorption. The adsorption capacity in the presence these ions might also block the active sites of the adsorbent surface thus deactivating the adsorbent towards the organic molecules.

3.3.6. *Reusability of the adsorbent*

In order to determine the adsorptive capacity of the adsorbent after each cycle an experiment was performed with used adsorbent to determine its reusability. Significant decline in the removal efficiency was observed for subsequent adsorption. As the number of adsorption cycles increases the adsorptive capacity of the adsorbent decreases because with successive adsorption the active sites of the adsorbent decreases which results in the decrease in its removal efficiency. Fig. 15 shows the percentage removal for each cycle of adsorption for phenol and *o*-chlorophenol.

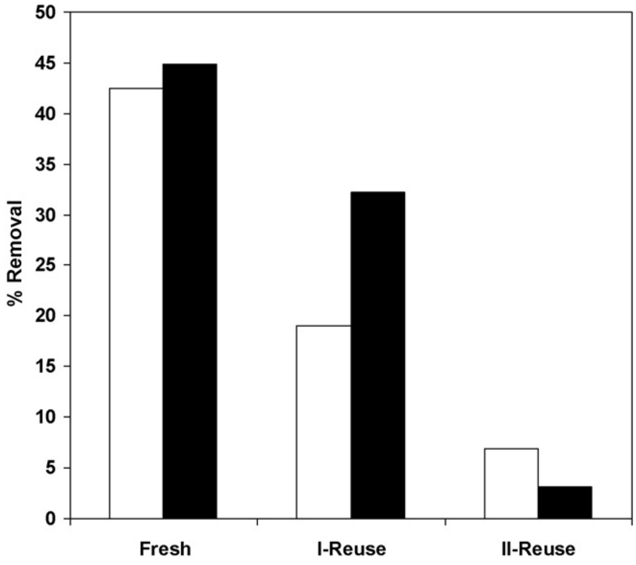

Fig. 15. Reusability of SMZ-Y adsorbent (initial concentration = 50 mg l^{-1}, pH 7, optimum dose = 2 g l^{-1}, contact time = 24 h). (□) Phenol, (■) *o*-chlorophenol.

4. Equilibrium modeling

Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Langmuir Equation or Freundlich Equation. The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants that indicate relative capacity and adsorption intensity, respectively. The Freundlich equation can be linearized by taking logarithms and constants can be determined (Figs. 7 and 8). To determine the equilibrium isotherms, adsorbent dose were varied, while the initial concentration of substrate was kept constant. The value of K_F for phenol and *o*-chlorophenol are 0.0020, 0.149 mg g^{-1}, respectively, and while $1/n$ is 5.47 and 0.798 for Freundlich isotherm. The value of Freundlich constants (K_F) for *o*-chlorophenol is high as compared to phenol, which indicates the higher adsorption capacity for *o*-chlorophenol due to its hydrophobicity.

5. Conclusions

- Surface modified zeolite (SMZ-Y) materials are proving to be an effective new class of adsorbents for the adsorption of phenolic compounds. It has good physical as well chemical stability; hence it can be used for various environmental applications.
- The SMZ-Y shows higher efficiency as compared to FAZ-Y and commercial zeolite for removal of phenol and *o*-chlorophenol. This may be attributed to the hydrophobicity imparted by surfactant molecules on the surface of fly ash zeolite, consequently leading to organic partitioning.
- The surfactant loading plays an important role on adsorption of solute on surface modified zeolite.
- The adsorption of phenol and *o*-chlorophenol on SMZ-Y is found to mainly depend on the pH of the solution as well as the type of co-existing anions. It was found that the presence of anions has a deleterious effect on the adsorption of phenol and *o*-chlorophenol. The removal of phenol and *o*-chlorophenol at neutral pH is high as compared to alkaline pH and this may be attributed to the fact that at higher pH it form phenolate ion, which decrease its adsorption.
- The sorption of *o*-chlorophenol was high as compared to phenol, which may be due to more hydrophobic nature of *o*-chlorophenol.

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