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Removal of selected pharmaceutical compounds from water by an organic polymer resin

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This study presents adsorption performances for Carbamazepine, Propyphenazone, and Sulfamethoxazole using polymer resin, Lewatit VP OC 1163. Adsorption capacities followed: Carbamazepine> Sulfamethoxazole> Propyphenazone. Lewatit VP OC 1163 showed a larger adsorption for pharmaceuticals having low solubility, with Freundlich adsorption parameter, K_f, reaching 46.068 [(mgg^{-1}) (mgl^{-1})] for Carbamazepine (solubility, 179 mgl^{-1}). SAC_{254} (Spectral Absorption Coefficient at 254 nm) can be used as a control parameter for pharmaceutical adsorption studies.

Keywords: SAC_{254}, Adsorption, Freundlich isotherm, Pharmaceuticals, Polymer resin

Introduction

Pharmaceutical compounds (approx. 3000), approved as constituents for medicinal products in European Union[1], are inherently biologically active and can have unforeseen adverse effects on nontarget ecological species when released into environment[2,3]. Wastewater treatment studies[4-8] have shown that pharmaceuticals are released directly into environment. Three pharmaceuticals [Carbamazepine (CBZ), Propyphenazone (PP) and Sulfamethoxazole (SMX)] are used worldwide, with a production volume estimated to be many hundreds of tons annually, and are present in environment all over the world[9-17]. An effective treatment technology for removal of pharmaceuticals is by adsorption onto activated carbons[18-20]. Polymer resins are becoming more common in wastewater treatment due to low costs, easy regeneration, and selective removal of pollutants[21-23]. Lewatit VP OC 1163, a microporous, hypercrosslinked adsorber resin with good chemical and mechanical stability, has been characterized as having very high adsorption capacity[24].

This study assesses potential use of Lewatit VP OC 1163 as an adsorbent, both in batch and in column experiments, for removal of pharmaceuticals (CBZ, PP, and SMX) from aqueous solution.

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Materials and Methods

Materials

Carbamazepine [5H-Dibenz(b,f)azepine-5-carboxamide), Propyphenazone (4-isopropyl-1,5-dimethyl-2phenyl-1,2-dihydro-3H-pyrazol-3-one], and Sulfamethoxazole [4-amino-*N*-(5-methylisoxazol-3-yl)-benzene sulfonamide] were obtained[25,26] in e"99% purity from pharmaceutical-manufacturing units in Istanbul, Turkey. Stock solutions were prepared by dissolving pharmaceuticals in distilled water. Experiments were carried out at pH values of pharmaceuticals in solutions as follows: CBZ, 5.75-6.07; PP, 6.17-6.79; and SMX, 5.12-5.51.

A commercial organic polymer resin (Lewatit VP OC 1163) obtained from Bayer AG was used as an adsorbent. Lewatit VP OC 1163, a microporous, brown-red, translucent, hypercrosslinked adsorber resin without functional groups, has following properties[27]: mean bead size, 0.45-0.55 mm; density, 1.09 gml^{-1}; surface area, >1300 m^2g^{-1}; pore volume, 0.6-0.8 cm^3g^{-1}; pore diam, 0.5-10 nm, and Zeta Potential (measured by Brookhaven Instruments BIC 90 Plus at pH 2-12) 0 mV.

Adsorption Studies

Batch Experiments

Batch experiments were carried out at 25±2°C in a thermostated orbital shaker at an agitation speed of 150 rpm. Pharmaceutical solution (100 ml) was added to a

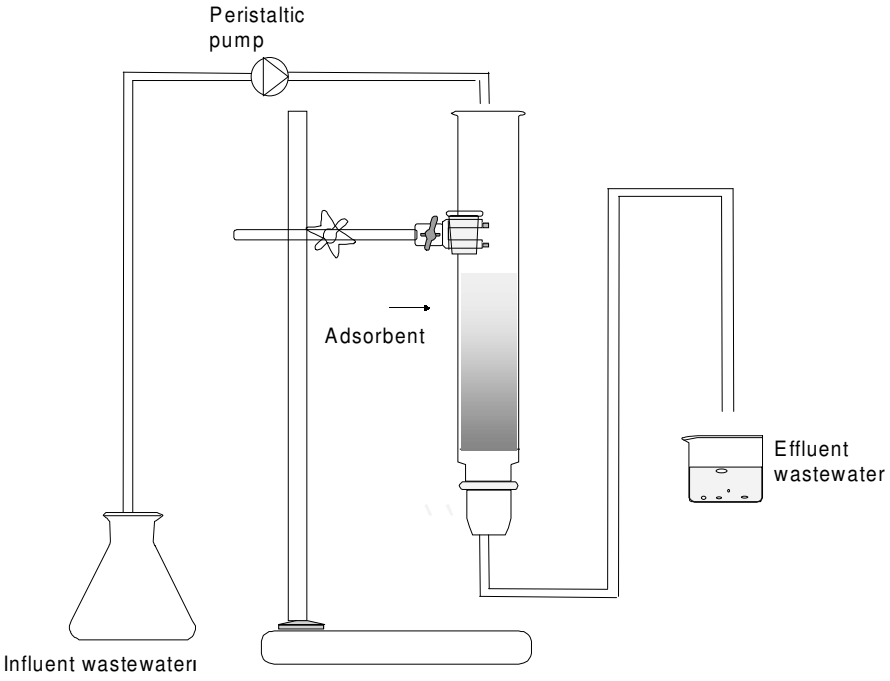

Fig. 1—Schematic representation of fixed bed column experimental setup

standard amount of adsorbent in stoppered Erlenmeyer flask. Blanks using distilled water were prepared to assess loss of solutes to flask components during adsorption tests. Results from duplicate flasks showed that average solution phase concentrations were within 96-102% of respective initial concentrations of same solutions analyzed in a similar manner. Hence, loss of compound was negligible. Supernatants were filtered through 0.45 ¼m Whatman filter paper to determine contaminant concentration by two methods, $KMnO_4$ Demand[28] and SAC_{254}[29] (Spectral Absorption Coefficient at 254 nm). Adsorption studies from aqueous solutions involve measurement of adsorbate concentration as a function of time, and amount of adsorbent used. SAC_{254} method was used for pharmaceutical adsorption studies. Spectrophotometric measurements were carried out using a Jenway 6105 UV-Vis spectrophotometer. Pharmaceutical amounts were determined from initial and final concentrations of solution. $KMnO_4$ Demand and SAC_{254} data were converted into concentration data using calibration relations for each pharmaceutical. Adsorbed amounts of pharmaceuticals were calculated as[30]

$$\mathbf{q_e = (C_0 - C_e)\frac{V}{W}} \qquad \ldots(1)$$

where q_e is amount of pharmaceutical adsorbed on adsorbent, C_0 is initial pharmaceutical concentration, C_e is equilibrium concentration of pharmaceutical solution, V is volume of pharmaceutical solution used and W is weight of adsorbent used. Removal efficiency, R, has also been calculated from batch experiments as

$$R = [(C_0 - C_e)/C_0].100 \qquad \ldots(2)$$

Column Experiments

Column tests were carried out using a column of glass (diam, 2 cm; ht, 45 cm). Column (Fig. 1) was packed with a 10 ml of adsorbents (12.7-13.2 cm ht). Glass wool was used as a support for adsorbents. Adsorbate solution was fed by a peristaltic pump (ISMATEC, MV–CA4). Column was charged in downflow mode with a volumetric flow rate [1.5 $mlmin^{-1}$ (~5 $m^3/m^2/h$)]. Pharmaceutical solutions with initial concentrations of 20 mgl^{-1} and 50 mgl^{-1} were used. Samples were collected at different time intervals and contaminant concentrations were determined by SAC_{254}. Temperature (T) was maintained at 25 ± 2°C, and all studies were conducted at existing pH of solutions, which in turn depend on their concentration. To facilitate calculation of fixed bed adsorption capacity, breakthrough bed volume is often fixed at 50% or 10% of inlet concentration according to target quality of final effluent. Loading of adsorbents was continued until breakthrough

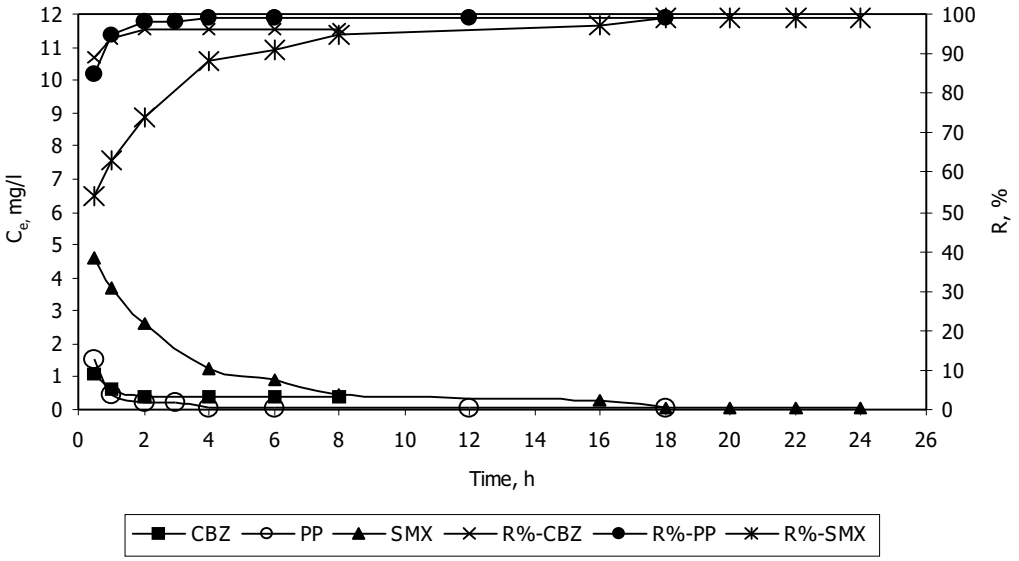

Fig. 2—Effect of contact time on pharmaceutical adsorption by VP OC 1163 (C_0 = 10 mgl^{-1}, T = 25°C, 150 rpm, W = 0.1 g, V = 20 ml)

was 10% of feed concentration. Quantity of adsorbed contaminant at breakpoint (q_b in mgg^{-1}) can be obtained as[31]

$$q_b = \frac{Q_v\, t_{10\%}\, C_0}{m_c} \qquad \ldots(3)$$

where $t_{10\%}$ is service time (min) at outlet concentration 10% of inlet concentration, C_0 is inlet pharmaceutical concentration (mgl^{-1}), Q_v is effluent flow rate ($lmin^{-1}$), and m_c is adsorbent amount (g).

Results and Discussion

Batch Experiments

Experiments were conducted for various time intervals to determine duration required to reach adsorption equilibrium (Fig. 2). Adsorption increased with increasing contact time for all pharmaceutical solutions, due to a large number of vacant surface sites are available for adsorption during initial stage, and after a lapse of time, remaining vacant surface sites are difficult to be occupied because of the repulsive forces between solute molecules in solid and bulk phases[32]. Removals for CBZ and PP were 89% and 85% within 1½ h and then gradually increased up to 96% and 99% in 2 h and 4 h, respectively. Because of such a quick sorption rate, it can be inferred that in this instance, process is predominantly controlled by film diffusion, and this is triggered by high concentration difference between bulk solution and solid phase[33].

Compared with other pharmaceutical solutions, a slow (gradual) uptake of SMX and establishment of equilibrium after a long period (18 h) were observed. Most uptake occurred within first 8 h. Adsorption appeared to be governed by two transport processes. During first stage, SMX was rapidly adsorbed on organic polymer resin particles for 6-8 h. In second stage, slower migration of pharmaceutical to less accessible sites within resin matrix could be observed for a period totaling 18 h. Therefore, a large amount of SMX was expected to be progressively adsorbed by adsorbent matrices as contact time increases[34]. Slow uptake of adsorbates and establishment of equilibrium over a long period indicate strong chemical binding of adsorbate with adsorbent[32].

An increase in adsorbent dosage increased percentage removal of pharmaceuticals. Increase in R with increase of adsorbent dose can be attributed to increased number of sites available for adsorption[35]. Lewatit VP OC 1163 had a greater adsorption affinity for CBZ (0.1 g/20 ml) and SMX (0.1 g/20 ml) than that for PP (0.4 g/20 ml) (Fig. 3). Initial concentration affects both adsorption capacity of adsorbent and adsorption rate. With increasing concentrations, R values from SAC_{254} and $KMnO_4$ Demand measurements increased for CBZ and PP and decreased for SMX (Table 1).

Freundlich model is based on a monolayer adsorption and is expressed as

$$q_e = K_f\, C_e^n \qquad \ldots(4)$$

where K_f and n are noncompetitive Freundlich constant characteristics of the system. K_f and n are indicators of adsorption capacity and adsorption intensity,

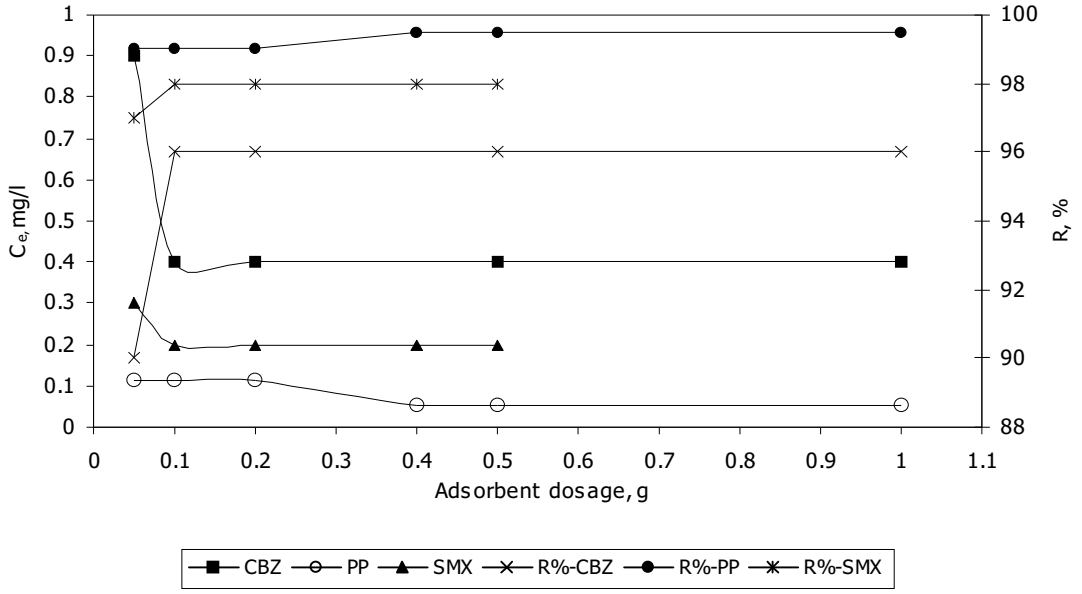

Fig. 3—Effect of adsorbent dosage on pharmaceutical adsorption by VP OC 1163 (C_0 = 10 mgl^{-1}, T = 25°C, 150 rpm, V = 20 ml)

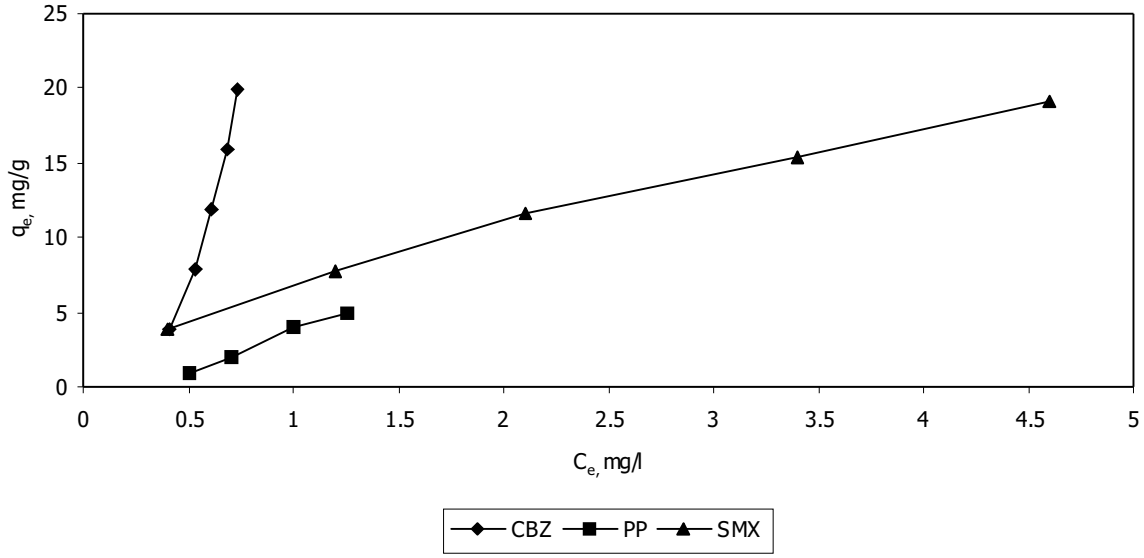

Fig. 4—Adsorption isotherms of pharmaceuticals onto VP OC 1163 at 25°C (obtained from SAC_{254} measurements)

respectively. Langmuir model, originally developed to represent monolayer sorption on a set of distinct localized sorption sites, is expressed as

$$q_e = \frac{Q^0\, b\, C_e}{1 + b\, C_e} \quad \text{(Non–linear form)} \qquad \ldots(5)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0\, b} + \frac{C_e}{Q^0} \quad \text{(Linear form)} \qquad \ldots(6)$$

where Q^0 is maximum amount of adsorbate per unit weight of adsorbent that forms a complete monolayer on the surface and b is a constant related to affinity of binding sites[30].

Experimental equilibrium data of pharmaceuticals adsorbed on Lewatit VP OC 1163 were obtained using SAC_{254} (Fig. 4) and $KMnO_4$ demand measurements (Fig. 5). Liquid adsorption isotherms have been classified into four categories (S, L, H, and C types) with subdivisions for each type[36-37]. Isotherms obtained from both parameters [SAC_{254} and $KMnO_4$ demand]

Table 1—Effect of initial pharmaceutical concentrations on the amount of adsorbed pharmaceuticals and corresponding removal efficiencies

C_o mgl^{-1}	R%					
	Carbamazepine		Propyphenazone		Sulfamethoxazole	
	SAC_{254}	$KMnO_4$ demand	SAC_{254}	$KMnO_4$ demand	SAC_{254}	$KMnO_4$ demand
20	98	99	97.5	n d	98	95.8
40	98.7	99.3	98.3	n d	97	95.3
60	99	99.4	-	n d	96.5	95.1
80	99.1	99.4	98.8	n d	95.8	95.3
100	99.3	99.5	98.8	n d	95.4	95

* n d: not determined

Table 2—Estimated parameters for Freundlich isotherm model at 25°C

Pharmaceuticals	SAC_{254}				$KMnO_4$ demand			
	K_f	n	R^2	Σ %	K_f	n	R^2	Σ %
Carbamazepine	46.068	2.7862	0.9984	1.18	11.792	1.3668	0.9922	0.91
Propyphenazone	3.573	1.7979	0.9856	1.73	n d	n d	n d	n d
Sulfamethoxazole	7.04	0.6474	0.9993	0.2	1.103	0.9054	0.9976	0.45

* n d: not determined

showed same shape. In studied concentration ranges, isotherms of CBZ and PP may be classified as belonging to S type, suggesting multilayer adsorption and vertical orientation of adsorbed pharmaceutical molecules on adsorbent surface, with availability of new sites to solvent as adsorption proceeds. It also indicates that solvent and solute compete with each other for adsorption sites on adsorbent surface. Upward nature of curves shows that, after complete adsorption on adsorbent surface, adsorbate molecules attract each other and become associated to a considerable extent[38]. According to the slope of initial portion of curves, isotherms of SMX may be classified as L type, indicating high affinity of adsorbent for adsorbate. This shows that no strong competition occurs for adsorption sites between solvent molecules (distilled water) and adsorbate molecules (pharmaceutical molecules). However, as active sites of adsorbent become saturated, adsorption of new molecules occurs with greater difficulty. Adsorption reaches a constant saturation value[39].

Estimated parameters of Freundlich model (Table 2) are given with average percentage errors. Langmuir equation did not reproduce equilibrium data satisfactorily for CBZ and PP, and estimated Langmuir parameters were negative. Langmuir isotherm values of $KMnO_4$ Demand measurements of PP batch experiments were not calculated due to lack of data because PP removal was below detection limit. Average percentage errors were calculated as[40]

$$\varepsilon\,\% = \frac{\sum_{i=1}^{N} \frac{\left|q_{e,i,exp} - q_{e,i,calc}\right|}{q_{e,i,exp}}}{N} \cdot 100 \qquad \ldots(7)$$

where N is number of measurements, 'exp' and 'calc' represent experimental and calculated q_e values.

Fit of experimental data obtained from both SAC_{254} and $KMnO_4$ Demand measurements for Freundlich equation is good for CBZ and PP in studied concentration range. Correlation coefficients showed that fit to Freundlich model is excellent. Average percentage error values calculated for fit of isotherm data of three pharmaceuticals to Freundlich equation are in accordance with correlation coefficients. For SMX adsorption, both Langmuir (R^2= 0.9885) and Freundlich model (R^2 = 0.9993) generated a satisfactory fit of experimental data. Applicability of both Langmuir and Freundlich isotherms to the system may indicate that both monolayer and heterogeneous surface conditions

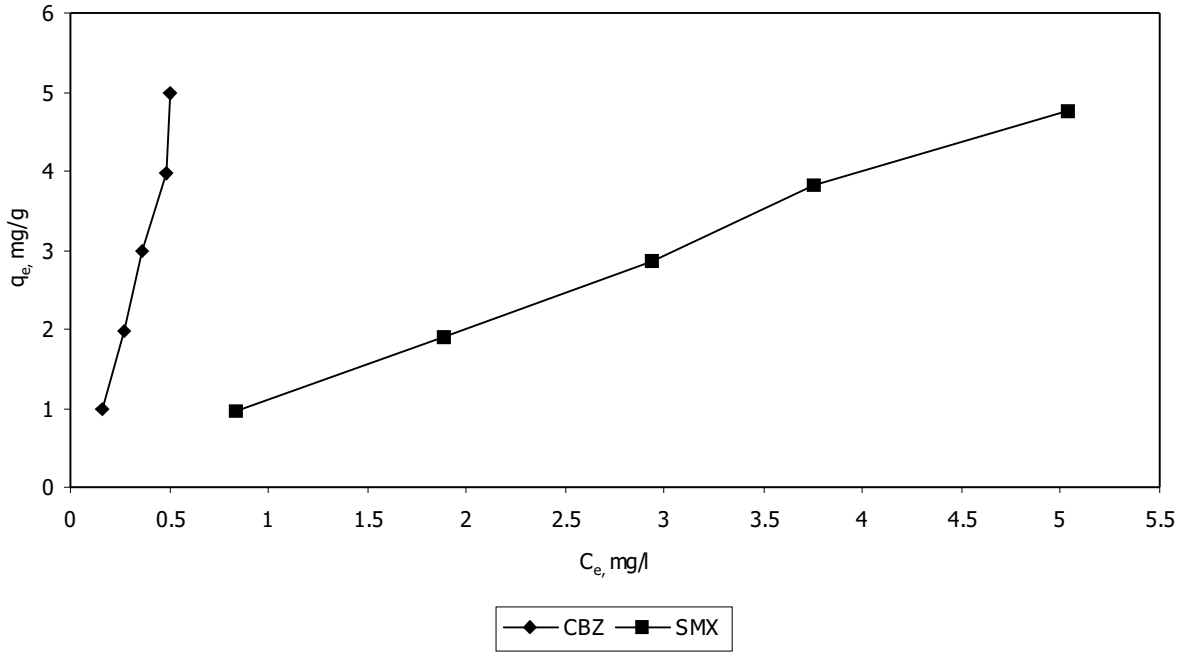

Fig. 5—Adsorption isotherms of pharmaceuticals onto VP OC 1163 at 25°C (obtained from $KMnO_4$ demand measurements)

Table 3—Adsorption capacity of Lewatit VP OC 1163 at different initial pharmaceutical concentrations (BV = 10 ml, Z = 12.7-13.2 cm, m_c = 6.7391 g, v = 5 mh^{-1}, and Q_v = 6.6 $mlmin^{-1}$)

Pharmaceuticals	Initial concentration, C_0 mgl^{-1}	Treated volume, v_b ml[a]	Breakthrough point, t_b min[a]	Adsorption bed capacity, q_b mgg^{-1}[b]
Carbamazepine	20	68700	10410	203.9
	50	30200	4576	224.08
Propyphenazone	20	57100	8652	169.47
	50	28000	4242	207.72
Sulfamethoxazole	20	64200	9727	190.53
	50	30100	4561	223.34

[a]Obtained experimentally
[b]Calculated according to Eq. (3)

exist under experimental conditions used[42]. However, higher values of correlation coefficient and lower percentage errors for Freundlich model, compared with Langmuir (£ % = 0.2 and 47.5, respectively) indicated that Freundlich model gave a better fit of the data.

Adsorbed amounts and K_f values of three pharmaceutical solutions (PP<SMX<CBZ) indicate higher adsorption capacity for CBZ. In general, adsorption increases with decreasing water solubility and increasing compound hydrophobicity, as represented by octanol-water partitioning coefficient (log K_{ow}). For CBZ, PP and SMX, main cause for variation in K_f was varying adsorbate solubility. This result is in agreement with Lundelius rule. A lower adsorption capacity was obtained for highly soluble compounds (PP and SMX) in comparison with less soluble compound (CBZ).

At a pH value between pK_a (dissociation constant) values of compounds, pharmaceuticals exist predominantly as neutral species. Nature of solid surface, either hydrophobic or hydrophilic, and electrical interactions play an important role in adsorption kinetics of contaminant at solid-liquid interface. In deionized water (pH 2, 4, 6, 8, 10, and 12), ζ-potentials of organic polymer resin particles were all zero. Therefore, resin

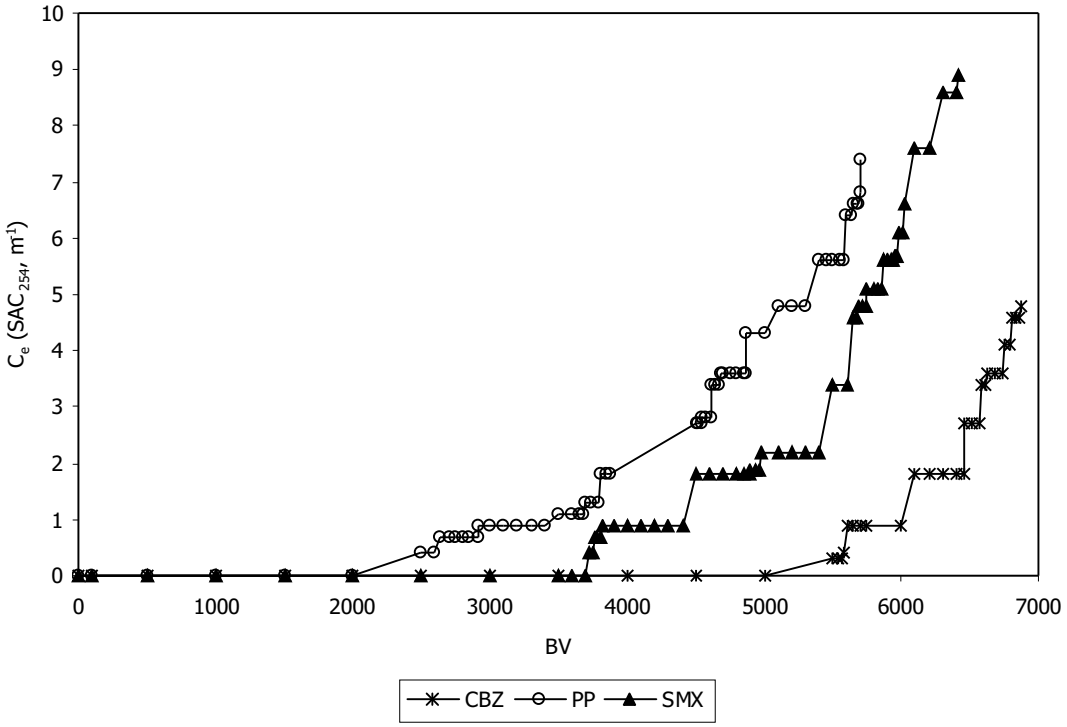

Fig. 6—Breakthrough curves of 20 mgl^{-1} pharmaceutical solutions using Lewatit VP OC 1163 (V = 10 ml, Z = 12.7–13.2 cm)

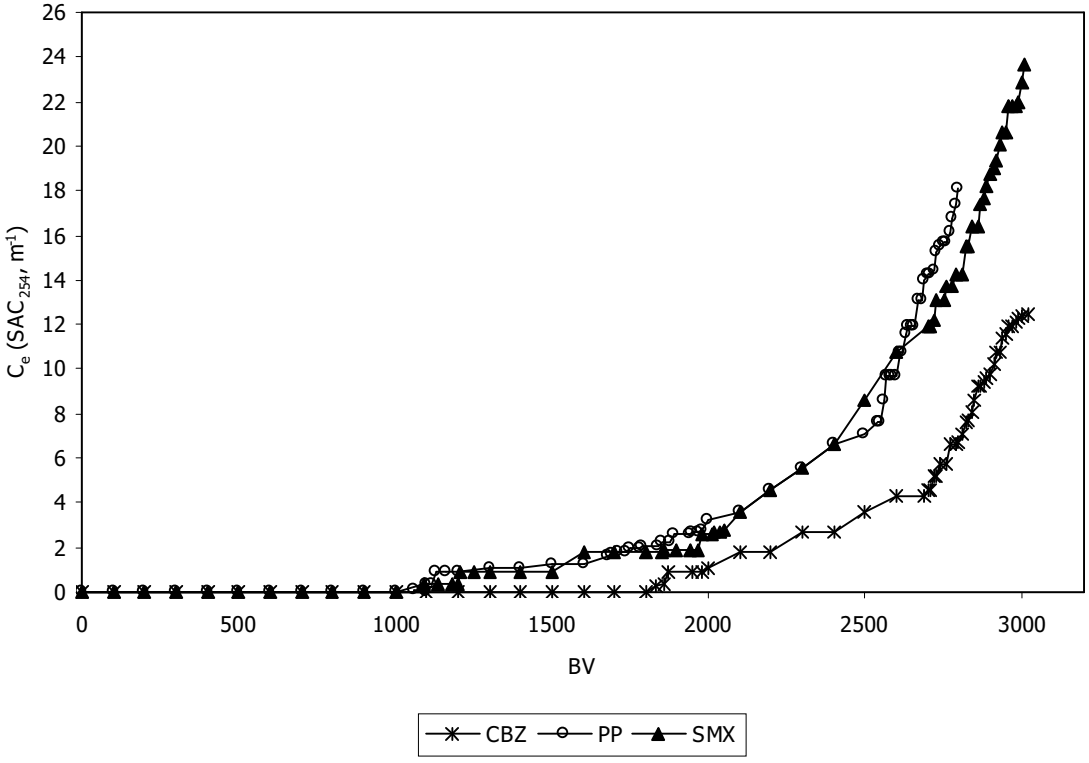

Fig. 7—Breakthrough curves of 50 mgl^{-1} pharmaceutical solutions using Lewatit VP OC 1163 (V = 10 ml, Z = 12.7–13.2 cm)

surface was uncharged in deionized water within a broad pH range. In this context, it could be assumed that electrostatic interaction might not significantly contribute to adsorption of pharmaceuticals. Lower the hydrophobicity (log K_{ow}) of a compound, higher is the expected adsorption onto organic polymer resin. Because organic polymer is a hydrophilic (weak polar), higher adsorption capacity was expected in the case of relatively hydrophilic (polar) PP. But estimated values of Freundlich parameter showed that adsorptive capacity of CBZ was higher than that of PP and SMX (K_f = 46.07, 3.573, and 7.04, respectively). However, adsorption of SMX was higher than that of PP despite log K_{ow} of SMX is lower than that of PP. Thus, for the studied system, no simple relationship was found between hydrophobicity of pharmaceuticals and adsorption affinity toward hydrophilic surface of the adsorbent. Freundlich fitting with n>1 for CBZ and PP would indicated conformity of the data to a multilayer formation on adsorbent surface. For SMX (n<1) implies that organic polymer resin-SMX systems correspond to a favorable adsorption process.

Column Experiments

Only SAC_{254} measurements could be used for evaluation of column experiments because of low outlet column concentrations. Table 3 shows treated volume (V_b), breakthrough time (t_b), and quantity of adsorbed contaminant at breakthrough point (q_b). Good adsorbability of CBZ on Lewatit VP OC 1163 could be confirmed by column experiments. 10% of initial CBZ concentration was reached after 68700 ml (6870 BV (bed volume) for 20 mgl^{-1} (Fig. 6) and 30200 ml (3020 BV) for 50 mgl^{-1} (Fig. 7). PP and SMX were generally less adsorbed than CBZ, can be attributed to physicochemical properties of solutes, mainly solubility. When initial concentrations were increased, breakthrough point was reached more quickly. A rise in initial pharmaceutical concentration reduced volume that was treated before 10 % of initial concentration was reached. S-shaped breakthrough curves obtained from column studies showed that less than half of adsorbent capacity was used until breakthrough point.

Conclusions

Experimental data of adsorption capacities under optimized conditions were best fitted to Freundlich model. Estimated values of Freundlich parameter showed that adsorptive capacity of CBZ was higher than that of PP and SMX (K_f = 46.068, 3.573, and 7.04, respectively), implying that adsorbate solubility has most impact on adsorption. After 2-4 h contact, a steady-state approximation was assumed and quasi-equilibrium was accepted for CBZ and PP. This is a very important aspect for pharmaceutical industry because less contact time could have a favorable impact on process economics. Good adsorbability of CBZ on Lewatit VP OC 1163 could be confirmed by column experiments. Relatively high solubilities of PP and SMX are responsible for short breakthrough times observed using Lewatit VP OC 1163 column. Breakthrough curves (S-shaped) show that less than half the adsorbent capacity was used until breakthrough point. SAC_{254} is a useful parameter for determining pharmaceutical concentration in aqueous solutions with advantage that no chemicals are used and measuring time is shorter compared to other organic matter parameters. Organic polymer resin is found effective for removing pharmaceuticals.

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