Removal of Atenolol (β-blocker) from Aqueous Phase by Sorption onto Activated Charcoal

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ABSTRACT
β-blockers used to treat hypertension are reported in surface water bodies. Atenolol (β-blocker) was selected to study it removal from aqueous phase by adsorption onto activated charcoal using agitated non-flow batch sorption experiments. Sorption experiments documented good removal of atenolol from aqueous phase by activated charcoal but was found to be dependent on the concentration loaded. Equilibrium data of atenolol-charcoal sorption system showed a reasonably good fit with pseudo first-order kinetic plot. The intra-particle diffusion plot indicates complex nature of atenolol-activated charcoal sorption system involving both boundary layer and intra-particle diffusions. Equilibrium sorption data confirmed to linear Freundlich's and dual mode model (DMM) corresponding to two and three parameter models respectively. Neutral redox condition documented higher sorption capacity of activated charcoal for atenolol. Operating temperature showed marked improvement in atenolol sorption onto activated charcoal up to 30 °C. Good desorption of atenolol from activated charcoal was observed with distilled water followed by inorganic solvents.

Keywords: desorption; Intraparticle diffusion model; Isothermal models; pharmaceutical products.

1. INTRODUCTION
Global concern about the persistence and occurrence of human-used pharmaceuticals in wastewaters and ambient surface waters is more evident[1-5]. Occurrence of these drugs in the watersheds of densely populated areas across Europe and North America was reported. Substantial amounts of these pharmaceuticals and their metabolites get into the wastewater after excretion and finally end up in the surface water[4]. Wastewater treatment plants (WWTPs) are the major sources for these "down-the-drain" chemicals. Further, human metabolism, removal in WWTPs, dilution in receiving waters and elimination processes in surface water play an important role in determining their surface water concentrations[2]. Ecotoxicological studies show that aquatic organisms are sensitive to these substances[4,6-9].
β-blockers are a group of drugs normally used to treat high blood pressure (hypertension) and to prevent heart attack recurrences. Studies documented the occurrence of β-blockers in surface water[2,10-21] and indicated incomplete degradability of these substances in sewage treatment plants[18,22-25]. Alder and co-workers[2] reported occurrence and fate of four β-blockers (atenolol, sotalol, metoprolol and propranolol) in wastewater and surface water (Glatt Valley Watershed, Switzerland). About 50% of orally administered atenolol normally gets absorbed and the rest un-metabolized fraction gets excreted mainly as the parent compound with approximately equal fractions in feaces and urine[2]. Concentration of β-blockers in the surface waters of Europe and North America range from a few ng/L to 2.2 mg/L where, higher concentrations are measured in the rivers impacted by municipal wastewater[2]. The excreted β-blockers and/or their metabolites (microbial cleavage of conjugates) are partially removed in WWTPs[4,26-32]. Escher et al.[33,34] demonstrated that most β-blockers had a specific toxicity towards green algae. All β-blockers have the same mode of

toxic action in the aquatic organisms[34] and demonstrate a specific toxicity towards green algae[33,34]. To reduce the potential risk caused by β-blockers in water discharged to aquatic environment, their removal is significantly important. Therefore in this study, the potential of sorption process for the removal of atenolol, a widely used β-blocker drug was evaluated by activated charcoal as sorbent using agitated non-flow batch sorption experiments. Atenolol is a selective β$_1$ receptor antagonist drug used primarily in cardiovascular diseases as a replacement for propranolol in the treatment of hypertension.
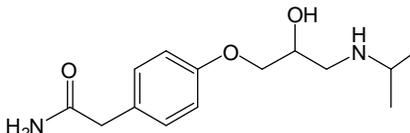
2 Experimental procedures

2.1 Activated charcoal
Activated charcoal (granular; Loba Chemie Pvt Ltd., India) with 1.5 mm average diameter [surface area, 99.5 m^2/g; bulk density, 0.4 g/ml; pore size, less than 5 nm (67%)] was used to evaluate its potential as sorbent to adsorb EE2 from aqueous phase.

2.2 Atenolol
Atenolol ((*RS*)-2-{4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl}acetamide) was purchased from Sigma-Aldrich (≥ 90% purity) and used in the adsorption studies after diluting to predetermined concentrations with distilled water (Table 1).

Table 1: Structure and properties atenolol

Formula	Molecular Mass	pKa[a]	Water Solubility (mg/L)	Sorption coefficient of sludge[b] (K_d, l/Kg)	Degradation rate constant WWTP[b] (l/d-g)	Structure
C$_{14}$H$_{22}$N$_2$O$_3$	266.336 g/mol	9.6	26700	40	0.69	

[a] [35], [b] [4]

2.3 Experimental design
Agitated batch sorption experiments were designed and performed to evaluate the potential of activated charcoal to adsorb atenolol from aqueous phase and to understand the adsorption behavior of the atenolol-activated charcoal system. Independent bottles were used to represent a single point on the graph. Each 250 mL glass bottle was loaded with 250 mg of activated charcoal followed by required concentration of 50 mL of atenolol solution. Effect of contact time on adsorption was evaluated by taking 50 mL of atenolol spiked solution (5.0 μg/L) and 250 mg of activated charcoal. The atenolol-activated charcoal reaction mixture after adjusting to neutral pH was agitated at 120 rpm on a horizontal shaker for predetermined time intervals of 15, 30, 60, 120, 180, 240 and 400 min. The resulting sorption data was used to estimate the equilibrium time required for sorption and for the kinetic evaluation of atenolol-activated charcoal sorption system. Effect of sorbate concentration on adsorption was studied by varying atenolol concentration (1.0, 2.5, 5.0 and 7.0 μg/L). The requisite concentration of atenolol solution was loaded with 250 mg of activated carbon and the reaction mixture was adjusted to pH 7 prior to subjecting for constant agitation (120 rpm; 28±2 ^{0}C) for 120 min. Isothermal studies were performed by varying concentrations of atenolol (1.0–7.0 μg/L) and agitating the reaction mixture at 120 rpm for equilibrium time at pH 7. Influence of aqueous phase redox condition on atenolol sorption was studied by adjusting the initial pH of the reaction mixture (atenolol, 5 μg/L; activate charcoal, 250 mg) from 2 to 10.5. The reaction mixture after adjusting pH was agitated at 120 rpm for 120 min. The required pH was adjusted using 0.1 N HCl and 0.1 N NaOH solutions. Influence of temperature on sorption was evaluated based on the batch sorption experiments carried out at predetermined temperature (19 to 40 °C; pH 7; atenolol,

5 µg/l; activate charcoal, 250 mg; equilibrium time, 120 min). Desorption studies were performed by suspending the atenolol loaded activated charcoal (up to equilibrium) in 0.1 N H_2SO_4, 0.1 N NaOH, 0.1 N methanol and distilled water separately followed by agitation (120 rpm; contact time, 30 min) and analyzed for desorbed atenolol concentration. All the experiments were carried out at room temperature (28 ± 2^0C) in a temperature controlled shaking incubator.

2.4 Analysis

Residual atenolol concentration present in the aqueous phase was estimated by employing colourimertic procedure based on the oxidation–bromination reaction of the drug by bromine, generated *in situ* by the action of acid on a brominated-bromide mixture [36]. Atenolol solution (4 mL) was mixed with 5 M HCl (2 mL) followed by 1 ml of bromate-bromide reagent (10 mg/mL with respect to $KBrO_3$) and the contents were mixed well. The reaction mixture was set aside for 10 min with occasional shaking. Finally, 1 ml of 50 mg/mL methyl orange solution was added and the absorbance was measured at 520 nm against a reagent blank after 5 min. The concentration of the unknown was read from the calibration graph or calculated using the regression equation obtained by using the Beer law. Atenolol concentration was calculated based on the prepared calibration curve ($R^2 = 0.9612$). Infrared spectral (IR) studies were performed on the virgin (non-adsorbed) and atenolol sorbed activated charcoal to elucidate the role of functional groups on sorption process. IR spectra were recorded on Thermo Nicolet Nexus 670 Spectrometer at ambient conditions using KBr as diluents.

3. RESULTS AND DISCUSSION
3.1. Batch sorption studies
3.1.1. Effect of contact time

Atenolol-activated charcoal sorption profile during 400 minutes of operation documented typical behavior (Fig. 1). Initially up to 30 min, the rate of atenolol sorption was relatively rapid which subsequently leveled off at 120 min (sorption was relatively negligible (less than 1% change) after this phase). Rapid and instantaneous sorption of atenolol observed during initial phase might be attributed to a sort of chemical reaction between the sorbate molecule and the sorbent surface (chemisorptions type of sorption interaction). Active surface sites/specific functional groups present on the surface of the activated carbon might have participated in the sorption interaction during this phase of operation. After progressive sorption reaction, the rate of EE2 sorption decreased gradually and leveled off due to more and more occupation of the active sites and eventually reached saturation due to exhaustion of active sites for sorption reaction and this denotes the establishment of equilibrium. Large fraction of atenolol was adsorbed between 0 and 30 min of contact time. Stabilized in sorption was observed in between 30 and 120 m, hence an equilibrium time of 120 min was considered for subsequent experiments.
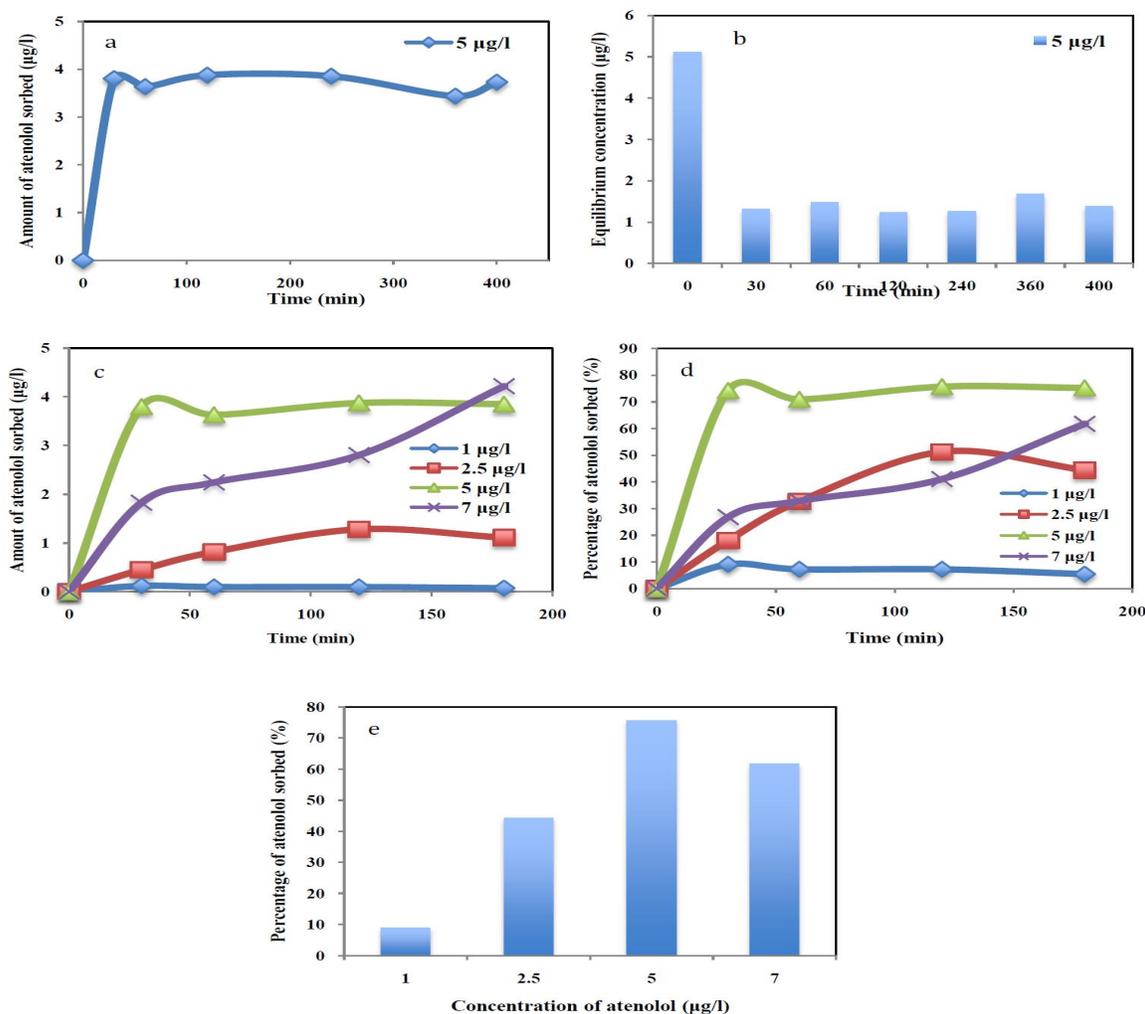
Fig. 1: (a, b) Effect of contact time on atenolol sorption; (c-f) Effect of initial atenolol concentration on sorption

3.1.2. Effect of atenolol concentration

Influence of initial aqueous phase concentration of atenolol on adsorption was evaluated by varying concentration (employing the same operational conditions (sorbent mass, 250 mg/L; contact time, 120 min; agitation, 120 rpm; pH, 7.0; temperature, 28±2°C). Initial concentration of atenolol showed significant influence on the adsorption process (Fig. 1). A marked improvement in sorption capacity of activated charcoal was observed with increase in E3 concentration from 1 to 5 µg/L and dropped thereafter. At 7 µg/L of atenolol concentration, sorption process started rapidly and leveled of up to 120 min. Subsequently after 120 minutes of contact time sorption rate showed significant raise. The differential sorption observed might be the manifestation of available atenolol in aqueous phase at the point of time might have influenced the sorption behavior. Irrespective of atenolol loading concentration, rapid and instantaneous sorption was observed in between 0 to 30 minutes of contact time. It can be presumed from the sorption data that the activated charcoal system showed higher sorption rates specifically in the range of 1–5 µg/L of atenolol concentration.

3.1.3 IR-spectral analysis

FT-IR spectra of virgin activated carbon showed spectral peaks at wave numbers of 3418 cm^{-1} (O–H stretch and carboxylic bands), 2922 cm^{-1} (carboxylic/phenolic stretching bands), 1585 cm^{-1} (quinine and OH bands) and 1041 cm^{-1} (=C–Nb). Significant changes in the FT-

IR spectra after the atenolol sorption were observed indicating surface change on the activated carbon (Fig. 2). New peaks at wave numbers 2300 cm^{-1} and 1719 cm^{-1} (NC=N–, NC=C, C=O stretch) were noticed on activated carbon after atenolol sorption. Strong adsorptions were observed at 1487 cm^{-1} and 1418 cm^{-1}. Two additional peaks were also observed on the plane deformation area in the region 777 cm^{-1} and 573 cm^{-1}. The strong adsorption pertaining to O–H stretch carboxylic bands in the region 3412 cm^{-1}, carboxylic/phenolic stretching bands in the region of 2924 cm^{-1} and the presence of new peaks at 2300 cm^{-1} and 1719 cm^{-1} indicates chemical type of sorption reaction. FT-IR results also confirm that hydrogen atoms in the carboxylic groups might have involved in the sorption interaction.
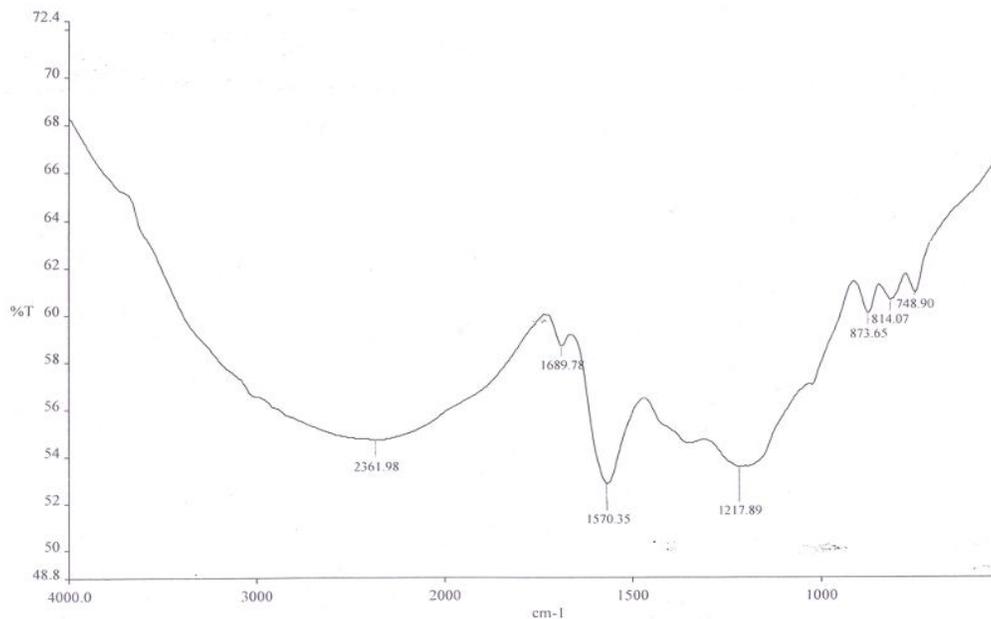
Activated charcoal
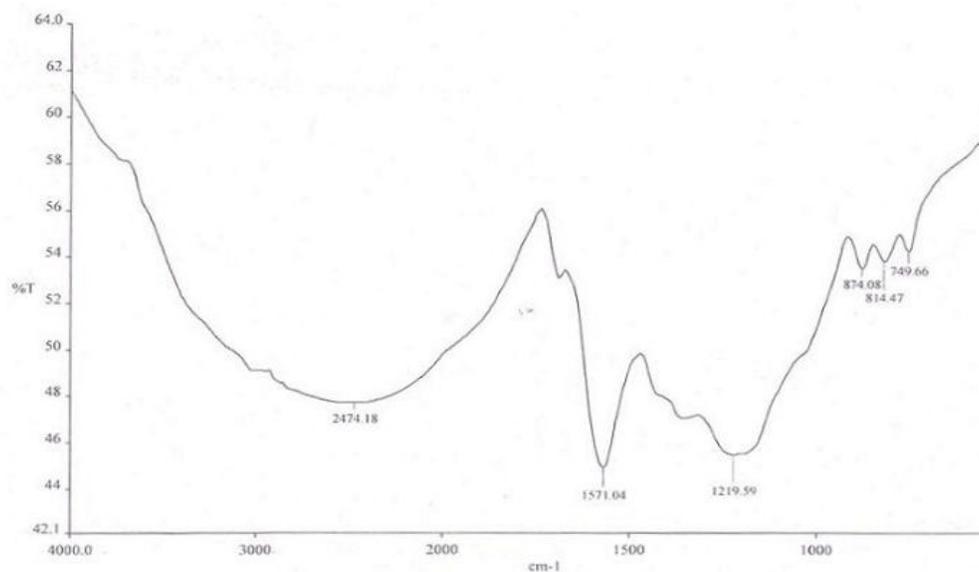
Atenolol sorbed activated charcoal
Fig. 2: FT-IR spectra of (a) virgin and (b) Atenolol adsorbed activated charcoal

3.2. Sorption kinetics

Linear forms of different kinetic models based on the aqueous phase concentration of adsorbate were used to evaluate the sorption mechanism. The sorption kinetic data obtained from the batch studies (sorbent mass, 250 mg; agitation, 120 rpm; pH 7.0; temperature, 28 ± 2^0C) was employed to study the linear forms of kinetic models viz., the intra-particle diffusion model[37-40], the pseudo-first-order kinetic model and the pseudo-second-order kinetic model[5,38-40].

3.2.1 Kinetic models

Sorption rate can be estimated based on the pseudo-first-order (Lagergren's equation) and pseudo-second order kinetic equations by assuming atenolol-activated charcoal sorption process as pseudo-chemical reaction[5,41] as represented by Eqs. (4) and (5).

$$dq_t/dt = k_1(q_e - q_t) \qquad (2)$$
$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (3)$$

A plot of ln (q_e-q_t) against contact time 't' should be a straight line if the sorption follows the pseudo first-order (Eq. (2); Fig 3). If the sorption process obeys the pseudo-second-order chemisorptions kinetic rate equation (Eq. (3)), t/qt should change linearly with time 't'. The best fit obtained by processing the kinetic data into pseudo first- and second-order kinetic equations, respectively are depicted in Fig. 3. Both the kinetic plots showed a reasonably good fit with sorption equilibrium data especially at higher concentrations. The rate constant for the sorption of atenolol from the aqueous phase by activated charcoal was obtained by the slope of the respective curves (K_1=-0.022 g/µg/min (R^2, 0.984 at 2.5 µg/L); K_2= 0.976 g/µg/min (R^2, 0.976 at 7.0 µg/L)) (Table 2).
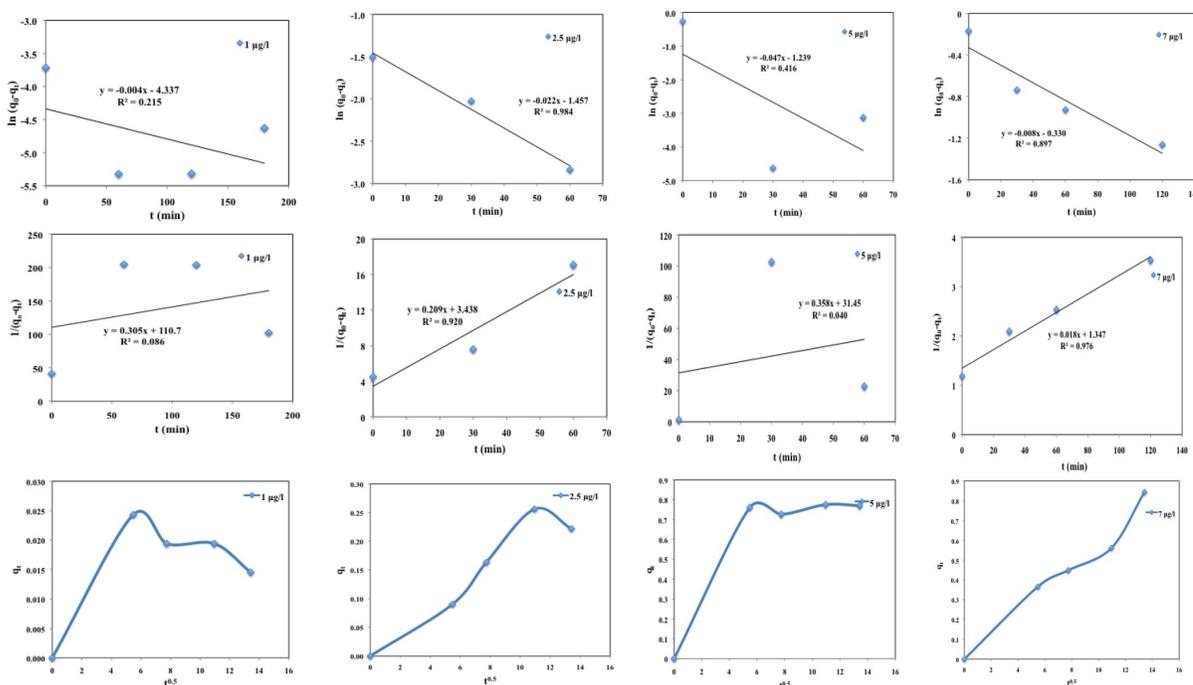

Fig. 3: (a) Pseudo first-order; (b) Pseudo second-order and (c) Intra-particle diffusion model plot for various concentrations of atenolol-activate charcoal sorption system

3.2.2 Intra-particle diffusion model

Intra-particle diffusion model is a single-resistance model derived from Fick's second law which can be expressed mathematically by the Eq. 1.

$$q_t \approx k_p t^{0.5} \dots (1)$$

Intra-particle diffusion was plotted between the amounts of atenolol adsorbed per unit mass (q_t) versus the square root of contact time ($t^{0.5}$) (Fig. 3). The intra-particle diffusion plot is observed to be of general type with a initial sharp portion and final linear portion. The initial portion might be attributed to the boundary layer diffusion effect; while the final linear portions might be due to the intra-particle diffusion. The initial sharp portion might be due to the boundary layer diffusion of the atenolol from aqueous phase to the external surface of the activated charcoal or the boundary layer diffusion of the atenolol molecule. The final portion represents the gradual sorption stage where, intra-particle diffusion is rate limiting. Straight line plot without passing through the origin was noticed with atenolol-activated charcoal system. This indicates some degree of boundary layer control which further shows that the intraparticle diffusion is not the only rate-controlling step, but also other processes may control the rate of adsorption[5,38,39,41]. The intraparticle diffusion plot of atenolol-activated charcoal sorption system indicates the complex nature involving both boundary layer and intra-particle diffusions with respect to initial atenolol concentration. Intra-particle diffusion model assumes that the diffusion (internal surface and pore diffusion) of adsorbate molecules inside the adsorbent is rate limiting and the film diffusion is considered negligible[41, 42].

Intra-particle diffusion rate constant (k_p,) calculated through the slope of the linear portions of the plot indicates the characteristic of sorption rate where intra-particle diffusion was rate limiting (Table 2).

Table 2: Summary of atenolol sorption data evaluated by different kinetic models

Initial atenolol concentration (µg/l)	First order rate constant		Second order rate constant		Intra particle rate constant	
	K_1 (g/µg/min)	R^2	K_2 (g/µg/min)	R^2	K_P (µg/g/min$^{0.5}$)	R^2
1	-0.004	0.215	0.305	0.086	-0.001	0.860
2.5	-0.022	0.984	0.209	0.920	0.018	0.763
5	-0.047	0.416	0.358	0.040	0.008	0.736
7	-0.008	0.897	0.018	0.976	0.056	0.910

3.3 Adsorption equilibrium

Equilibrium isotherm models express relationship between the quantity of adsorbate adsorbed and the concentration in solution at equilibrium and are especially important in optimizing the use of sorbent. The parameters derived from these equations and the underlying thermodynamic assumptions of these equilibrium isotherm models provide insight into the sorption mechanism and the surface properties and affinity of the sorbent. Two and three parameter equilibrium sorption models were employed to estimate sorption capacities at various atenolol concentrations (Fig. 4). Sorption (isothermal) experiments were performed under variable atenolol concentrations (1.0–7.0 µg/L) keeping other conditions constant (sorbent mass, 250 mg; agitation, 120 rpm; pH 7.0; temperature, 28±2^{0}C).

3.3.1 Two parameter models

Langmuir and Freundlich isothermal models are the most commonly used two parameters models describing the non linear equilibrium adsorbent surface (*q*) and adsorbate concentration in solution (*C*) at a constant temperature. The Langmuir model can be represented as

$$q = \frac{q_{mL}b_L C}{1+b_L C} \qquad (4)$$

Where, q_{mL} (µg/g) and b_L are the Langmuir parameters that represent the maximum sorption capacity and the site energy factor, respectively. A non-linear regression of sorption data for the atenolol was applied and the resulting Langmuir parameters are sorption capacity (q_{mL}, 1.13 µg/l) and site energy factor (b_L, 0.41), calculated from slope and intercept of the plot respectively. The Langmuir model showed reasonably good fit with the sorption data (R^2, 0.847; SSE, 0.276) (Table 2). The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor R_L, which describes the type of isotherm.

$$R_L = \frac{1}{1+b_L C_0} \qquad (5)$$

Where, b_L is the Langmuir constant (site energy factor) and C_0 is the initial concentration of the atenolol solution. The values of R_L indicate the type of isotherm to be unfavorable ($R_L>1$), linear ($R_L = 1$) and favorable ($0 <R_L< 1$) or irreversible ($R_L = 0$). The values of R_L were ranging between 0.25 and 0.64 representing that the sorption of atenolol onto activated charcoal is favorable.

The Freundlich model is represented as

$$q = K_F C^N \qquad (6)$$

Where, C (µg/L) is the aqueous phase concentration, q (µg/g) is the solid phase concentration, and K_F [(µg/g)/(µg/L)^N] and N are the Freundlich sorption coefficient and the Freundlich exponent, respectively. The Freundlich model parameters (K_F, 0.064 (µg/g)/(µg/L)^N; N, 1.408) were calculated. The Freundlich model showed best fit with the sorption data (R^2, 0.973; SSE, 0.037) (Table 3).Considering these two parameter models, Freundlich model showed best fit as represented by R^2/SSE (Freundlich, 0.973/0.037) (Fig 4)

3.3.2 Three parameter models
The three parameter models viz., Dual mode and Song were evaluated due to the feasibility of involving more number of parameters which may expect for better fit than the two parameter models. Also the three parameter models obey the correct thermodynamics boundary condition of Henry's law over infinity dilute concentration range [43]. The dual mode model (DMM) assumes that some of the solute dissolves in the partition medium and the rest absorbs in the sorption sites as shown below[43,44].

$$q = K_p C + \frac{q_{mD}b_D C}{1+b_D C} \qquad (7)$$

Where, K_p is the partition coefficient (L/g) and q_{mD} and b_D are the model parameters. The DMM was fitted to the single solute sorption data to estimate the three parameters using a non-linear regression technique. The DMM model didn't show reasonably good fit with the sorption data (R^2, 0.749; SSE, 1.262) (Table 3).The partition coefficient (K_p) of atenolol was 0.17 l/g.
Song model satisfies the Henry's law and the Freundlich isotherm models[44,45] in low and high concentration ranges, respectively (similar to DMM) and can be described as per Eq (8).

$$q = KC(1 + \beta C^2)^{\frac{n-1}{2}} \qquad (8)$$

Where, K (L/g), B (L/µg) and n are model parameters. Sorption data showed reasonably good fit with the Song model (R^2, 0.901; SSE, 0.254) (Table 3). The Freundlich index (n) can be estimated from the slope of asymptote in the high concentration region and the parameter (B) corresponding to the cross over point can be estimated from the intersection point of the two asymptotes. The Freundlich index (n) of atenolol was 1.408. Considering the three parameter models, the Song model appeared to be a better fit for estrogens because its R^2/SSE is 0.901/0.254.

Table 3: R^2 and SSE values for atenolol sorption predictions from two and three parametric models

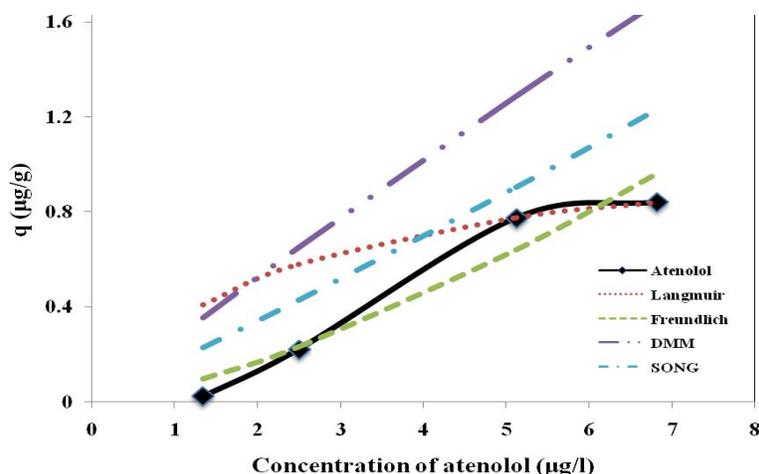| Sorption model	R^2	SSE
Langmuir	0.847	0.276
Freundlich	0.973	0.033
DMM	0.749	1.262
SONG	0.901	0.254

Fig. 4: Two (Langmuir and Freundlich) and three (DMM and Song) dimensional isothermal plots of atenolol-activated charcoal sorption system

3.4 Effect of pH

The influence of pH on atenolol sorption (atenolol concentration, 5 µg/L; temperature, 28 ± 2^0C; agitation, 120 rpm; adsorbent mass, 250 mh/L; contact time, 120 min) was evaluated. Aqueous phase pH showed significant influence on atenolol sorption on to activated charcoal (Fig. 5). Neutral conditions depicted the highest atenolol sorption capacity (95.40%) of activated charcoal. The ionic form of sorbate in solution and the activity and function of electrical charge on the activated charcoal (functional groups) mostly depend on the solution redox condition. The sorption in both acidic and neutral conditions was relatively low compared to neutral redox conditions. Lower sorption observed at basic pH range might be attributed to the increase in hydroxyl ion leading to the formation of aqua-complexes thereby retarding the sorption phenomena[37]. β-Blockers are secondary amines with acidity constants (pKa) above 9 and therefore predominantly present as positively charged species at operating pH values of around 7–8[2,4,35]. For all practical purposes and up-scaling of the process, aqueous phase pH 7.0 might be used for the atenolol-activated charcoal sorption system. Sorption to sewage sludge, which at those pH values usually carries a net negative charge[2].
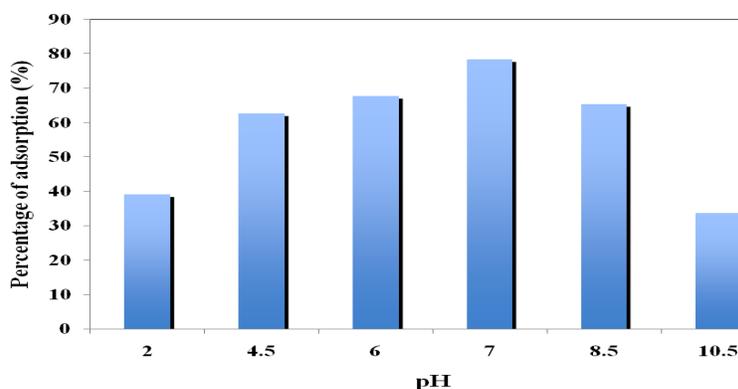
Fig. 5: Influence of aqueous phase pH on atenolol sorption

3.5 Effect of temperature

The sorption of EE2 was evaluated at different aqueous phase temperatures by keeping all other experimental conditions constant (atenolol concentration, 5 μg/L; pH 7.0; agitation, 120 rpm; sorbent, 250 mg/l; contact time; 120 min). Temperature plot showed a marked improvement in atenolol sorption onto activated charcoal with the increase in temperature up to 30 °C but sorption dropped gradually thereafter (Fig. 6). Thermodynamic parameters associated with the sorption process such as change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were determined using Eqs. ((9)–(10))[46].

$$K_C = Ceq / C_S \tag{9}$$
$$\Delta G^0 = -RT \, InK_C = \Delta H^o - T \, \Delta S^o \tag{10}$$
$$InK_C = \Delta G^0/RT = -\Delta H^0/RT + \Delta S^0/R \tag{11}$$

The Van't Hoff equation is used to evaluate the variation of equilibrium constant with the temperature. Entahalpy (ΔHo) and entropy (ΔSo) changes were determined as 29.45 kJ/mol and 0.0859 kJ/mol/K respectively, from plot of ln K_L Vs 1/T (Fig 6). Positive value of ΔHo suggests the endothermic nature of sorption while the positive values of ΔSo indicates the increasing randomness of activated charcoal and aqueous phase interface during the sorption process (Table 4). Temperature can also influence desorption and consequently the reversibility of the sorption equilibrium[47].

Table 4: Thermodynamic parameters at different temperature of atenolol-activated charcoal sorption system

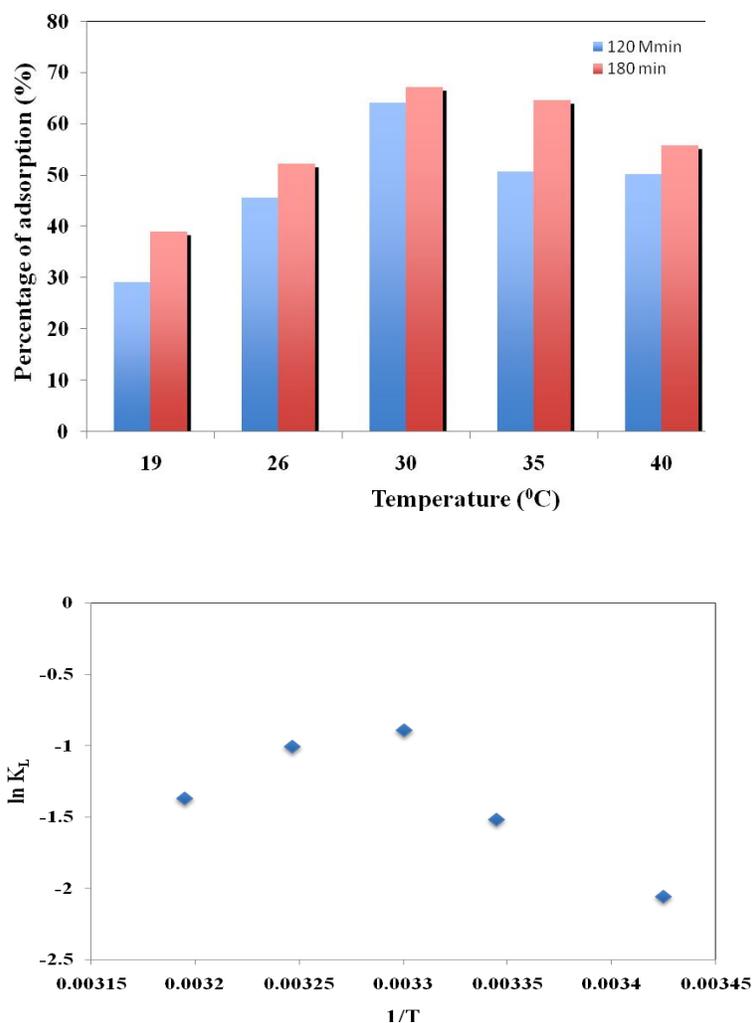| Temperature (°K)	ΔG^o (K J/mol)	ΔH^o (K J/mol)	ΔS^o (K J/mol/K)
292	-4.995		
299	-3.771		
303	-2.250	29.456	0.0859
308	-2.279		
313	-3.571		

Fig. 6: Effect of operating temperature on atenolol sorption

3.6. Desorption/Regeneration studies

Desorption/regeneration experiments are useful to understand the sorption mechanism of particular system with respect to regeneration capacity of the sorbent for reuse. The amount of desorption also provides an insight into the nature of adsorbent-adsorbate bonding and also on the ion exchange property of the adsorbent. Desorption studies were performed by suspending the atenolol loaded activated charcoal (up to equilibrium) in 0.1 N H_2SO_4, 0.1 N NaOH, 0.1 N methanol and distilled water separately followed by agitation (120 rpm; contact time, 30 min) and analyzed for desorbed atenolol concentration. Activated charcoal showed significant variation in atenolol desorption based on the solvent used (Fig 7). Marginal variation in desorption was observed among the solvents used in this study. Higher desorption of atenolol from activated charcoal was observed in distilled water (30.2%) followed alkaline (29.6%) and acid solutions (28.94%). Atenolol desorption in methanol (28.9%) was almost similar to acid solution. Desorption of atenolol observed in distilled water might be attributed to the physical type of interaction while desorption in inorganic solvents might be attributed to the chemical type of interaction. From the desorption data, it can be presumed that sorption interaction between atenolol and activated carbon is rather weak.
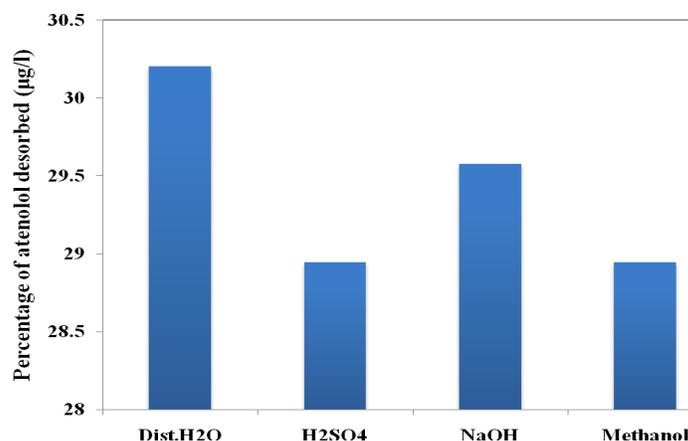
Fig. 7: Degeneration profile of atenolol-activated charcoal sorption system

4. CONCLUSIONS

Experiments documented the efficacy of activated charcoal as adsorbent in removing atenolol from aqueous phase. Sorption kinetic studies performed on atenolol-activated carbon sorption system showed good fit with both pseudo first and second order rate models. Isothermal data showed good fit with linear Freundlich's and dual mode model (DMM) corresponding to two and three parameter models respectively. Neutral redox conditions depicted highest atenolol sorption. Among the temperature parameters followed, operating temperature of 30 °C showed higher sorption capacity of atenolol onto activated charcoal. Atenolol showed good desorption from activated charcoal with distilled water.

REFERENCES

1. Khetan SK and Collins TJ. Human pharmaceuticals in the aquatic environment: a challenge to green chemistry. Chem Rev. 2007;107:2319.
2. Alder AC, Schaffner C, Majewsky M, Klasmeier J and Fenner K. Fate of b-blocker human pharmaceuticals in surface water: Comparison of measured and simulated concentrations in the Glatt Valley Watershed, Switzerland. Wat Res. 2010;44:936.
3. Kim SD, Cho J, Kim IS, Vanderford BJ and Snyder SA. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters, Wat Res. 2007;41:1013.
4. Maurer M, Escher BI, Richle P, Schaffner C and Alder AC. Elimination of b-blockers in sewage treatment plants. Wat Res. 2007;41:1614.
5. A.Kiran Kumar, S. Venkata Mohan, Endocrine disruptive synthetic estrogen (17α-ethynylestradiol) removal from aqueous phase through batch and column sorption studies: Mechanistic and kinetic analysis. Desalination, 2011, 276, 66.
6. Huggett DB, Khan IA, Foran CM and Schlenk D. Determination of beta-adrenergic receptor blocking pharmaceuticals in United States wastewater effluent. Environ Pollut. 2003;121:199.
7. Navarro VA, Rosas LE and Reyes JL. The heart of Daphnia magna: Effects of four cardioactive drugs. Comp Biochem Physiol Toxicol Pharmacol. 2003;136:127.
8. Ferrari B, Mons R, Vollat B, Fraysse B, Paxeus N, Lo G, Pollio AR and Garric JJ. Environmental risk assessment of six human pharmaceuticals: are the current environmental risk assessment procedures sufficient for the protection of the aquatic environment? Environ Toxicol Chem. 2004;23:1344.

9. Fent K, Weston AA and Caminada D. Ecotoxicology of human pharmaceuticals. Aquat Toxicol. 2006;76:122.

10. Vieno NM, Harkki H, Tuhkanen T and Kronberg L. Occurrence of pharmaceuticals in river water and their elimination a pilot-scale drinking water treatment plant. Environ Sci Technol. 2007;41:5077.

11. Ternes T, Bonerz M and Schmidt T. Determination of neutral pharmaceuticals in wastewater and rivers by liquid chromatography– electrospray tandem mass spectrometry. J. Chromatogr A. 2001:938:175.

12. Calamari D, Zuccato E, Castiglioni S, Bagnati R and Fanelli R. Strategic survey of therapeutic drugs in the rivers Po and Lambro in northern Italy. Environ. Sci. Technol. 2003;37:1241.

13. Stolker AAM, Niesing W, Hogendoorn EA, Versteegh JFM, Fuchs R and Brinkman UAT., Liquid chromatography with triple-quadrupole or quadrupole-time of flight mass spectrometry for screening and confirmation of residues of pharmaceuticals in water. Anal Bioanal Chem. 2004;378:955.

14. Hilton MJ and Thomas KV. Determination of selected human pharmaceutical compounds in effluent and surface water samples by high-performance liquid chromatography electrospray tandem mass spectrometry. J Chromatogr A. 2003;1015:129.

15. Fono LJ and Sedlak DL. Use of the chiral pharmaceutical propranolol to identik sewage discharges into surface waters. Environ Sci Technol. 2005;39:9244.

16. Gros M, Petrovic M and Barcelo D. Development of a multi residue analytical methodology based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) for screening and trace level determination of pharmaceuticals in surface and wastewaters. Talanta. 2006;70: 678.

17. Gros M, Petrovic M and Barcelo D. Wastewater treatment plants as a pathway for aquatic contamination by pharmaceuticals in the Ebro river basin (northeast spain). Environ Toxicol Chem. 2007;26:1553.

18. Bendz D, Paxeus NA, Ginn TR and Loge FJ. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Hoje River in Sweden. J Haz Mater. 2005;122:195.

19. Ashton D, Hilton M and Thomas KV. Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. Sci Tot Environ. 2004; 333:167.

20. Hordern KB, Dinsdale RM and Guwy AJ. Multiresidue method for the determination of basic/neutral pharmaceuticals and illicit drugs in surface water by solid phase extraction and ultra performance liquid chromatography-positive electrospray ionisation tandem mass spectrometry. J Chromatogr A. 2007;1161:132

21. Hordern KB, Dinsdale RM and Guwy AJ. The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Wat Res. 2009;43:363.

22. Ternes TA. Occurrence of drugs in German sewage treatment plants and rivers. Wat Res. 1998;32:3245.

23. Thomas KV and Hilton MJ. The occurrence of selected human pharmaceutical compounds in UK estuaries. Mar Pollut Bull. 2004;49:436.

24. Castiglioni S, Bagnati R, Fanelli R, Pomati F, Calamari D and Zuccato E. Removal of pharmaceuticals in sewage treatment plants in Italy. Environ Sci Technol. 2006; 40:357.

25. Roberts PH and Thomas KV. The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Sci. Total Environ. 2006;356:143.

26. Lee HB, Sarafin K and Peart TE. Determination of betablockers and beta (2)-agonists in sewage by solid-phase extraction and liquid chromatography-tandem mass spectrometry. J Chromatogr A. 2007;1148:158.

27. Vieno NM, Tuhkanen T and Kronberg L. Analysis of neutral and basic pharmaceuticals in sewage treatment plants and in recipient rivers using solid phase extraction and liquid chromatography-tandem mass spectrometry detection. J Chromatogr. A. 2006;1134:101.

28. Wick A, Fink G, Joss A, Siegrist H and Ternes TA. Fate of beta blockers and psycho-active drugs in conventional wastewater treatment. Wat Res. 2009;43:1060.

29. Andersen H, Siegrist H, Sorensen HB and Ternes TA. Fate of estrogens in a municipal sewage treatment plant. Environ Sci Technol. 2003;37:4021.

30. Belfroid AC, Horst VA, Vethaak AD, Schafer AJ, Rijs GBJ, Wegener J and Cofino WP. Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and waste water in The Netherlands. Sci. Total Environ. 1999;225: 101.

31. Gomes RL, Scrimshaw MD and Lester JN. Fate of conjugated natural and synthetic steroid estrogens in crude sewage and activated sludge batch studies. Environ Sci Technol. 2009;43:3612.

32. Ternes TA, Kreckel P and Mueller J. Behaviour and occurrence of estrogens in municipal sewage treatment plants—II. Aerobic batch experiments with activated sludge. Sci. Total Environ. 1999a;225:91.

33. Escher BI, Bramaz N, Eggen RIL and Richter M. In vitro assessment of modes of toxic action of pharmaceuticals in aquatic life. Environ Sci Technol. 2005;39:3090.

34. Escher BI, Bramaz N, Richter M and Lienert J. Comparative ecotoxicological hazard assessment of beta-blockers and their human metabolites using a mode-of-action-based test battery and a QSAR approach. Environ Sci Technol. 2006;40:7402.

35. Moffat AC, Osselton MD and Widdop B. Clarke's Analysis of Drugs and Poisons. Pharmaceutical Press, London, UK. 2004.

36. Basavaiah K, Chandrashekar U and Nagegowda P. Titrimetric, spectrophotometric and kinetic methods for the assay of atenolol using bromate–bromide and methyl orange. J Serb Chem Soc. 2006;71: 553.

37. Kiran Kumar A, Venkata Mohan S and Sarma PN. Sorptive removal of endocrine disruptive compound (estriol, E3) from aqueous phase by batch and column studies: kinetic and mechanistic evaluation, J Haz Mater. 2009;164:820.

38. Venkata Mohan S and Karthikeyan J. Removal of lignin and tannin aqueous solution by adsorption onto AC, Environ Pollut. 1997;1:183.

39. Yalcin M, Gurses A, Dogar C and Sozbilir M.The adsorption kinetics of cethyl tri methyl ammonium bromide (CTAB) onto powdered active carbon, Adsorption. 2004; 10:339.

40. Ho Y. Review of second-order models for adsorption systems, J Haz Mater. 2006; 136:681.

41. Yang X and Duri BA. Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. J Colloid Interface Sci. 2005;287:25.

42. Bulut E, Ozacar M and Sengil IA. Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, Microporous Mesoporous Mater. 2008;115:234.

43. Vieth WR and Sladek KJ. A model for diffusion in a glassy polymer. J Coll sci. 1965; 20:1014.

44. Shin WS. Competitive sorption of anionic and cationic dyes onto cetyl pyridinium modified montmorillonite. J Environ sci Health Part A. 2008;43:1459.

45. Song DI and Shin WS. Three – parameter empirical isotherm model: its application to sorption on to organo clays. Environ Sci Technol. 2005;39:1138.

46. Battacharya AK and Venkobachary C. Removal of cadmium (II) by low cost adsorbents. J Environ Eng Div ASCE Proc. 1984;110.

47. Chu BS, Baharin BS, Che Man YB and Quek SY. Separation of vitamin E from palm fatty acid distillate using silica: I. Equilibrium of batch adsorption. J Food Eng. 2004; 62:97.