



Sorptive removal of endocrine-disruptive compound (estriol, E3) from aqueous phase by batch and column studies: Kinetic and mechanistic evaluation

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ABSTRACT

Endocrine disruptive compounds (EDC) are a wide variety of chemicals which typically exert effects, either directly or indirectly, through receptor-mediated processes. They mimic endogenous hormones by influencing the activities of hormone activities even at nanogram concentrations and reported to disrupt the vital systems (e.g., the endocrine system) in aquatic organisms. The EDC are present in aquatic water bodies and sediments mainly due to the release of human and animal excreted waste. Estriol (E3) removal by adsorption process was investigated in this study to evaluate the potential of activated charcoal as adsorbent. Agitated non-flow batch sorption studies showed good E3 removal efficiency. Sorption kinetic data illustrated good fit with pseudo-first-order rate equation. Experimental data confirmed to linear Langmuir's isotherm model. Neutral pH condition showed comparatively good sorption of E3. Adsorption capacity showed a consistent increasing trend with increase in the operating temperature [ΔH° , -9.189 kJ/mol]; ΔS° , 0.492 J/mol K) suggesting exothermic nature of E3 sorption process. Free energy (ΔG°) increased from 2.51 to 2.97 kJ/mol with increase in temperature from 0 to 50°C . Further, E3 spiked distilled water, untreated domestic sewage and treated domestic sewage were studied in fixed bed column to assesses the potential of sorption process as tertiary unit operation in the ETP system. Total E3 concentration was determined quantitatively by employing direct competitive enzymatic-immuno assay (EIA) procedure.

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1. Introduction

More recently considerable interest is being focused on the aquatic toxicity due to the release of endocrine-disruptive compounds (EDC). EDC are a wide variety of chemicals that are excreted by humans and animals through their urine as inactive polar conjugates such as glucuronides and sulphates [1,2]. They typically exert effects, either directly or indirectly, through receptor-mediated processes mimicking endogenous hormones and inhibit the normal hormone activities [3]. They also disrupt vital systems (e.g., the endocrine system) in aquatic organisms [4,5] and increase the risk of cancer [6–8], even at nanogram levels. Waterborne ethinylestradiol (EE2) was reported to alter hormone-mediated biological indicators and increase plasma vitellogenin. They also found to decrease egg and sperm production, reduce gamete quality and tend to complete feminization of male fish [8]. Estriol (E3)

along with other steroid hormones was reported to be involved in the amelioration of autoimmune reactions [9].

The presence of EDC in surface water bodies and sediments was attributed primarily to the release of human and animal excreta and their incomplete removal in the sewage treatment plants [10,11]. Endocrine disrupting activity caused by natural steroid estrogens [17 β -estradiol (E2), estrone (E1), and estriol (E3)] and the synthetic estrogen [17 α -ethinylestradiol (EE2)] was detected in the effluent generated from the sewage treatment plants and in their receiving water bodies [12]. Conventional treatment plants are not designed to remove trace EDC and many of these conjugates are cleaved to free estrogens through microbial processes before or during sewage treatment [13,14]. Natural or synthetic estrogens exhibit two or three orders of magnitude higher estrogenic activity than the chemical compounds and are considered to be dominant contributors to estrogenic activity in the treated wastewater [15–17] causing abnormalities in aquatic organisms at very low concentrations [4,18]. Residues of EDC in secondary effluent may pose either acute or chronic adverse effects on the aquatic organisms in receiving waters, and on humans if the reclaimed water is returned to

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Nomenclature

EDC	endocrine-disruptive compounds
E3	estriol
TDIS	total dissolved inorganic solids (mg/l)
COD	chemical oxygen demand (mg/l)
q_t	amount of E3 adsorbed per unit mass of activated charcoal ($\mu\text{g/g}$)
k_p	intra-particle diffusion rate constant ($\mu\text{g/g min}^{-0.5}$)
t	contact time (min)
C_{eq}, q_e	solid phase concentration of E3 at equilibrium ($\mu\text{g/g}$)
C_S	equilibrium concentration of E3 in solution ($\mu\text{g/l}$)
C_0	initial E3 concentration at time '0' ($\mu\text{g/l}$)
q_t	solid phase concentration of E3 at contact time (t , min) (mg/g)
k_1	pseudo-first-order rate constants (min^{-1})
k_2	pseudo-second-order rate constants ($\text{g}/\mu\text{g min}$)
D_p	pore diffusion coefficient (cm^2/s)
D_f	film diffusion coefficient (cm^2/s)
R_p	radius of activated charcoal (0.11 cm)
ε	film thickness (10^{-3} cm)
$t_{1/2}$	half time required for sorption (min)
Q_m	sorption capacity of activated charcoal as derived from linearized plot of Langmuir's sorption isotherm ($\mu\text{g/g}$)
k_a	Langmuir's sorption isotherm constant ($1/\mu\text{g}$)
R_s	dimensionless separation factor
k_f	sorption capacity as derived from Freundlich's isotherm model ($1/\mu\text{g}$)
$1/n$	sorption intensity as derived from Freundlich's isotherm model
ΔG°	change in free energy (kJ/mol)
ΔH°	change in enthalpy (kJ/mol)
ΔS°	change in entropy (J/mol K)
K_C	equilibrium constant
Q_w	flow rate (l/h)
V_E	total volume of wastewater treated to the point of exhaustion (l)
V_B	total volume of wastewater treated to the point of breakthrough (l)
h_z	height of exchange zone (cm)
h_z	total bed depth (cm)
t_f	time required for the exchange zone to initially form (h)
t_z	time required for the exchange zone to move along the length of its own height up/down (h)
t_E	time required for exchange zone to become established and move completely out of bed (h)
S_z	amount of E3 removed by adsorption zone from breakthrough to exhaustion
S_{max}	amount of E3 removed by adsorption zone after completely exhausted
U_z	rate at which the exchange zone is moving up or down through bed (cm/h)

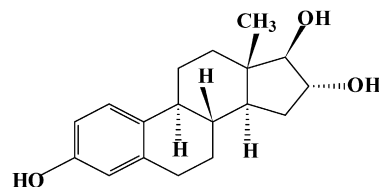


Fig. 1. Molecular structure of estriol (E3).

brane bioreactors [24,25] and reverse osmosis [25] were reported with different degree of efficiencies. Estrogens degradation efficacy under anaerobic conditions was reported to be significantly lower than under aerobic microenvironment [26]. Lee et al. [27] studied removal of EDC in pilot scale sewage treatment processes. Esperanza et al. [28] studied the fate of seven sex hormones in two pilot-scale wastewater treatment plants operated under conventional loading conditions. Due to low Henry's Law coefficients, high octanol-water partition coefficients (K_{ow}) and low biodegradable nature, removal of estrogens may be mainly attributed to the adsorption onto activated sludge by a combination of biosorption and biodegradation interaction [23].

Therefore, an attempt was made in this study to evaluate the potential of adsorption process for the treatment of estriol (E3), one of the important EDC normally found in sewage treatment plants. Agitated non-flow batch sorption experiments were performed employing activated charcoal as adsorbent. Fixed bed column studies were also operated with E3 spiked water and wastewater to evaluate the design parameters.

2. Materials and methods

2.1. Estriol (E3)

Estriol [E3; 1,3,5(10)-estratriene-3,16 α ,17 β -triol; $C_{18}H_{24}O_3$; Sigma-Aldrich] was used as model EDC after diluting to the required concentrations in water (Fig. 1). It is a white crystalline odorless solid (off-white; specific gravity 0.965) having molecular weight of 288.38 g/mole. It has melting point in the range of 284–285 °C and has solubility of 0.5 mg/ml in water at 25 °C (insoluble in cold and hot water). E3 is one forms of estrogen metabolized from estradiol through estrone from women ovary and is generally used for the treatment of menopausal symptoms as an alternative to estradiol, estrone or a combination of the two.

2.2. Activated charcoal

Activated charcoal (SD fine chemicals, India; surface area: 99.5 m²/g) was used to evaluate its potential to adsorb E3 from aqueous phase. Prior to use activated charcoal was grounded, sieved to the size of 0.71–1.4 mm, washed (double distilled water) and dried in hot air oven (120 °C).

2.3. Experimental design

2.3.1. Batch adsorption studied

Agitated non-flow batch adsorption experiments were designed and performed by bottle point method at room temperature (30 ± 1 °C), taking 0.25 g of activated charcoal in a 250 ml glass bottle containing 50 ml of E3 solution of required concentration. Each of the independent bottles used represents a single point on the graph. Effect of contact time on adsorption was evaluated by taking 50 ml of E3 spiked solution (5 $\mu\text{g/l}$) and 0.25 g of

the water supply [19]. To reduce the potential risk caused by EDC in treated wastewater discharged to aquatic environments, their removal is significantly important.

Treatment of EDC by, enzyme mediated treatment employing horseradish peroxidase [20], ultrasound destruction [21], ozonation and sand filtration [19], potassium ferrate treatment [22], adsorption by thermally deactivated activated sludge [23], mem-

activated charcoal at aqueous phase pH of 7.0. The reaction mixture was then subjected to agitation on a horizontal shaker for predetermined time intervals of 10, 15, 30, 60, 120, 240, 300, 700 min (temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm) and was used for kinetics and mechanistic evaluation of E3-activated charcoal sorption system. Effect of E3 concentration on adsorption was studied by varying E3 concentration between 5 and $25 \mu\text{g/l}$ (activated carbon 250 mg/l ; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 300 min). Isothermal studies were performed by adding various doses of E3 ($5\text{--}25 \mu\text{g}$ at increment of $5 \mu\text{g}$) and agitating reaction mixture for a period of equilibrium time of 300 min (temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; pH 7.0). Influence of the aqueous phase pH on E3 adsorption was studied by adjusting the initial pH of the reaction mixture from 3 to 11 ($5 \mu\text{g}$ estriol/l; activated carbon, 5 g/l ; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 300 min). pH was adjusted using 0.1 N HCl and 0.1 N NaOH solutions. Desorption studies were performed by suspending the activated charcoal adsorbed with E3 (up to equilibrium) in 0.1 N HCl, 0.1 N NaOH and distilled water separately followed by agitation (temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 30 min) and analyzed for desorbed E3 concentration in the resulting aqueous phase. Influence of temperature on adsorption and thermodynamic properties was evaluated based on the batch adsorption experiments carried out at variable temperature between 0 and 50°C ($5 \mu\text{g}$ estriol/l; activated carbon, 5 g/l ; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 300 min). Effect of TDIS on adsorption was studied by varying concentration between 500 and 2000 mg/l ($5 \mu\text{g}$ estriol/l; activated carbon, 5 g/l ; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 300 min).

2.3.2. Fixed bed column sorption studies

Down-flow fixed bed column studies were conducted using glass columns having 29 mm diameter and 15 cm length. The columns were packed with activated charcoal (bed depth of 12.5 cm) between two supporting layers of glass wool. Three adsorption columns were operated parallelly by loading E3 spiked separately in distilled water, untreated domestic sewage and treated domestic sewage. The column experiments were performed in down-flow mode at room temperature ($30 \pm 1^\circ\text{C}$) with a volumetric flow rate of 18 l/h ($5 \mu\text{g}$ estriol/l), 16.5 l/h ($5.11 \mu\text{g}$ estriol/l; 360 mg COD/l) and 16.5 l/h ($5 \mu\text{g}$ estriol/l; 160 mg COD/l), respectively. The samples were collected at different time intervals and were analyzed for the remaining E3 and COD concentrations.

2.4. E3 estimation

Residual E3 concentration present in the aqueous phase was estimated by employing direct competitive enzymatic-immuno assay (EIA) procedure normally used for the determination of total E3 concentration in serum and plasma using kits purchased from EQUIPAR srl, Italy (www.equipar.it). Total E3 (antigen) in the sample compete with horseradish-peroxidase E3 (enzyme-labeled-antigen) for binding onto the limited number of anti E3 (antibody) sites on the microplates. After incubation (30 min; 37°C), the plates were subjected to solid-phase washing followed by addition of enzyme (H_2O_2) and tetramethylbenzidine (TMB) as substrates and the absorbance (colour development) was determined at 450 nm employing UV-vis microplate/ELISA reader (Molecular Devices, USA) within 30 min. Total E3 concentration was calculated based on already prepared calibration curve using a series of standards, where colour intensity is inversely proportional to the total E3 concentration in the sample ($R^2 = 0.9899$).

2.5. Analysis

COD, TDIS and pH were determined according to the procedures outlined in the standard methods [29]. Infrared spectral (IR) studies were performed on the virgin (non-adsorbed) and E3 adsorbed AC to determine the functional groups present on the surface of the adsorbents and finally to elucidate the role of functional groups on adsorption. IR spectra were recorded on Thermo Nicolet Nexus 670 Spectrometer at ambient conditions using KBr as diluent.

3. Results and discussion

3.1. Batch adsorption studies

3.1.1. Effect of contact time

The influence of contact time on adsorptive removal of E3 from aqueous phase was evaluated by activated charcoal [$5 \mu\text{g}$ estriol/l; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; adsorbent mass, 5 g/l ; pH 7.0] (Fig. 2a). Adsorption profile showed typical behavior with marked variation. The rate of E3 sorption showed a rapid increase with the function of contact time prior to approaching equilibrium (adsorption is relatively negligible at this phase). The profile evidenced three variable equilibrium points at 30, 90 and 180 min during 300 min of the cycle operation. Subsequent to first equilibrium, the adsorption equilibrium plateau showed extension (30–60; 90–150; 180–300 min) leading to multiple equilibrium phases. A large fraction of E3 (>90%) was adsorbed within 180 min of contact time. Rapid and instantaneous sorption of E3 observed during initial phase of operation might be due to chemisorption interaction, where active surface sites/specific functional groups present on the adsorbent surface tend to participate. Reduction in E3 adsorption rate observed after achieving equilibrium might be due to the utilization of active sites on the adsorbent surface. Equilibrium time of 300 min was considered for subsequent experiments due to the multiple equilibrium points observed in the study.

3.1.2. Effect of initial E3 concentration

Influence of E3 concentration on the adsorption was evaluated by varying E3 concentration ($5\text{--}25 \mu\text{g/l}$) by employing uniform operational conditions [adsorbent mass, 5 g/l ; contact time, 300 min; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; pH 7.0]. E3 concentration showed significant influence on the adsorption phenomena (Fig. 2b). A marked improvement in sorption capacity of activated charcoal was observed with increase in E3 concentration from 5 to $20 \mu\text{g/l}$. However, a steady decrease in specific E3 sorption (per unit mass of activated charcoal) was observed after increase in E3 concentration from 10 to $25 \mu\text{g/l}$. It can be presumed from the experimental data that the system showed higher sorption rates specifically in the range of $5\text{--}10 \mu\text{g/l}$ of E3 concentration.

Influence of dissolved solids on adsorptive uptake of E3 was evaluated at variable TDIS concentration of 500, 1000 and 2000 mg/l [$5 \mu\text{g}$ estriol/l; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; adsorbent mass, 5 g/l ; pH 7.0]. With increase in TDIS concentration a marginal reduction in E3 removal was observed especially at higher concentrations (Fig. 2c). This might be attributed to the interference of salts or due to competitive adsorption phenomena between TDIS and E3.

3.1.3. Adsorption mechanics

Predicting the rate at which sorption takes place for a given system is probably the most important factor in the adsorption system design. In order to investigate the mechanisms of adsorption, various kinetic models were reported based on the aqueous phase concentration of adsorbate. The sorption kinetic data [$5 \mu\text{g}$ estriol/l; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; adsorbent mass,

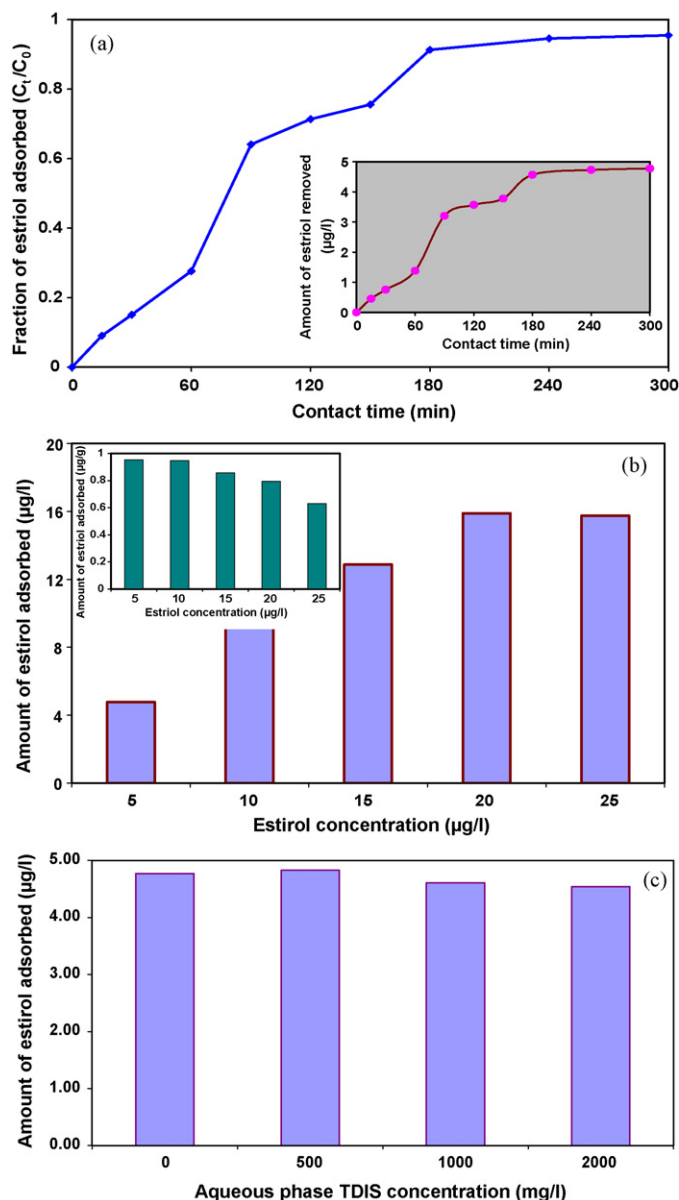


Fig. 2. (a) Effect of contact time on E3 adsorption [E3 concentration, 5 µg/l; temperature, 30 °C; agitation, 200 rpm; adsorbent mass, 5 g/l; pH 7.0]; (b) effect of initial E3 concentration on sorption [contact time, 300 min; temperature, 30 °C; agitation, 200 rpm; adsorbent mass, 5 g/l; pH 7.0]; (c). influence of TDIS concentration on E3 sorption [E3 concentration, 5 µg/l; temperature, 30 ± 1 °C; agitation, 200 rpm; adsorbent mass, 5 g/l; pH 7.0].

5 g/l; pH 7.0] was evaluated with the linear forms of different kinetic models, viz., the intra-particle diffusion model [30–34], first-order kinetic model [30], the pseudo-first-order kinetic model [31] and the pseudo-second-order kinetic model [30–33].

Table 1
Summary of E3 sorption data evaluated by different kinetic models

Kinetic model	Equation	Rate constant	R ²
Intra-particle diffusion mode	$y = 0.0422x + 0.2434$ (first)	$4.22 \times 10^{-2} \mu\text{g/g min}^{0.5}$	0.9853
	$y = 0.0109x + 0.7696$ (second)	$1.09 \times 10^{-2} \mu\text{g/g min}^{0.5}$	0.9088
Pseudo-first-order kinetic models	$y = -0.0124x + 1.6784$	$1.24 \times 10^{-2} \text{ min}^{-1}$	0.9334
Pseudo-second-order kinetic model	$y = 0.0825x + 30.391$	$8.25 \times 10^{-2} \text{ g}/\mu\text{g min}$	0.5813
First-order kinetic models	$Y = -0.0056x + 2.2869$	$5.6 \times 10^{-3} \text{ min}^{-1}$	0.8962

3.1.3.1. Intra-particle diffusion model. Intra-particle diffusion model assumes that the film diffusion is negligible and intra-particle diffusion is the only rate-controlling step [35]. The intra-particle diffusion model is a single-resistance model and can be derived from Fick's second law under two assumptions, viz., first, the intra-particle diffusivity (D) is constant; second, the uptake of adsorbate by the sorbent is small relative to the total quantity of sorbate present in the solution and can be expressed mathematically as follows [30–32,34,36,37]

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

According to Eq. (1), the plot of the amount of E3 adsorbed per unit mass (q_t) versus the square root of contact time ($t^{0.5}$) would yield a straight line passing through the origin if the sorption process obeys the intra-particle diffusion model. The intra-particle diffusion plot is observed to be of general type, i.e., initial curved portion with a final linear portion (Fig. 3a). The initial curved portion might be attributed to the boundary layer diffusion effect, while the final linear portions might be due to intra-particle diffusion [38,39]. It is apparent from intra-particle diffusion plot, that the straight line did not pass through the origin and this further indicated that the intra-particle diffusion was not the only rate-controlling step [30,31,33,35,36,40–44]. It is also observed from the plot that the sorption removal of E3 from aqueous phase on to activated charcoal is rather complex process, involving both boundary layer diffusion and intra-particle diffusion. The slope of the linear portion was defined as the rate parameter (k_p). It is characteristic of the rate of sorption in this region where intra-particle diffusion was rate limiting and is depicted in Table 1. Multi-linearity (two equilibrium states) was observed during the study period. The boundary layer diffusion depends on several parameters, including the external surface area of the sorbent, which is mainly controlled by the particle size, shape and density of the sorbent, the concentration of the solution and the agitation velocity. Greater particle size of adsorbent generally cause higher intra-particle diffusion resistance in the adsorption process [45].

3.1.3.2. Pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order and pseudo-second-order kinetic models assume that sorption is a pseudo-chemical reaction. Adsorption rate could be determined, respectively, by the first-order and second-order reaction rate equations [35] as represented by Eqs. (2) and (3)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

If the sorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ against contact time ' t ' should be a straight line. Similarly, t/q_t should change linearly with time ' t ' if the adsorption process obeys the pseudo-second-order rate equation. The derived rate constants together with the correlation coefficient are depicted in Table 1. Fig. 3 depicts best fit obtained by processing the kinetic

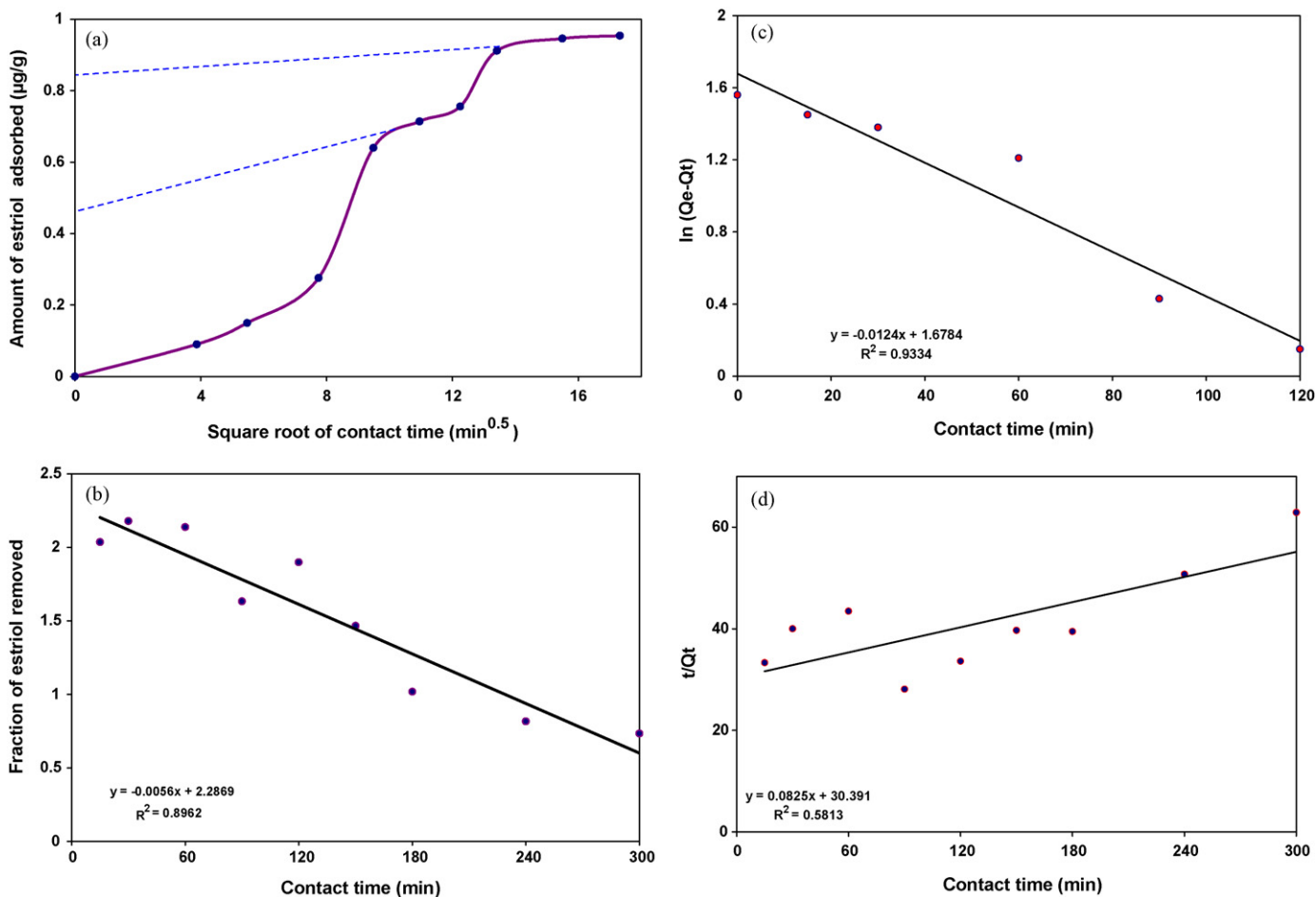


Fig. 3. (a) Intra-particle diffusion model plot; (b) first order kinetic plot; (c) pseudo-first-order kinetics plot; (d) pseudo-second-order kinetics plot of E3-carbon sorption system [temperature, 30 °C; agitation, 200 rpm; adsorbent mass, 5 g/l; pH 7.0].

data into pseudo-first- and second-order kinetic equations, respectively. The rate constant for the sorption of E3 from aqueous phase by activated charcoal was also obtained by assuming a first order reaction (Fig. 3b). Kinetic plots showed a reasonably good fit of sorption equilibrium data with respect to the pseudo-first-order kinetic model when compared to the first-order rate equation (Table 1).

3.1.3.3. Diffusion mechanism. In order to assess the nature of the diffusion process responsible for adsorption of E3, an attempt was made to calculate the coefficients of the process [46]. Assuming spherical geometry of the adsorbent, the overall rate constant of the process can be correlated with the pore diffusion coefficient (D_p) and the film diffusion coefficient (D_f) independently [47] as described below

$$D_p = 0.03 \left[\frac{R_p^2}{t_{1/2}} \right] \quad (4)$$

$$D_f = 0.23 \left[\left(\frac{R_p \varepsilon}{t_{1/2}} \right) \times \left(\frac{q_e}{C_0} \right) \right] \quad (5)$$

If film diffusion is the rate-determining step, the value of the film diffusion coefficient (D_f) should be in the range 10^{-6} to 10^{-8} cm²/s and if pore diffusion is the rate limiting step, the pore diffusion coefficient (D_p) should be in the range 10^{-11} to 10^{-13} cm²/s [48–50]. Experimental data showed that the E3 adsorption on activated carbon was controlled by film diffusion process since the coefficient values were observed to be around 10^{-8} cm²/s.

3.1.4. Adsorption equilibrium

The isotherms are useful in understanding the sorption interaction and also to estimate design parameters. The equilibrium sorption data were analyzed using both Langmuir's and Freundlich's sorption isotherm models. The rearranged Langmuir's isotherm model for evaluating the monolayer sorption phenomena is as depicted in Eq. (6)

$$\frac{C_{eq}}{Q_e} = \frac{Q_m}{k_a} + \frac{C_{eq}}{Q_m} \quad (6)$$

The experimental data produced a straight line fit with a correlation coefficient ($R^2 = 0.9789$) indicating the acceptability of Langmuir's model (Fig. 4a). Conformation of experimental data into linear plot indicated the formation of monolayer coverage of E3 molecules on the surface of the adsorbents. Sorption capacity (Q_m , 3.34 µg/g) and constant (k_a , 23.58 l/µg⁻¹) were calculated from slope and intercept of the plot. Hall and co-workers [51] and Venkata Mohan and co-workers [34] showed that essential characteristics of Langmuir's sorption isotherm equation could be expressed in terms of a dimensionless constant called as separation factor or equilibrium factor or equilibrium parameter, (R_s) defined by the Eq. (7), where k_a represents Langmuir's constant as defined earlier and C_0 denotes the initial E3 concentration.

$$R_s = \frac{1}{1 + k_a C_0} \quad (7)$$

The separation factor was calculated using the Langmuir's constants [51]. From the value of the separation factor obtained,

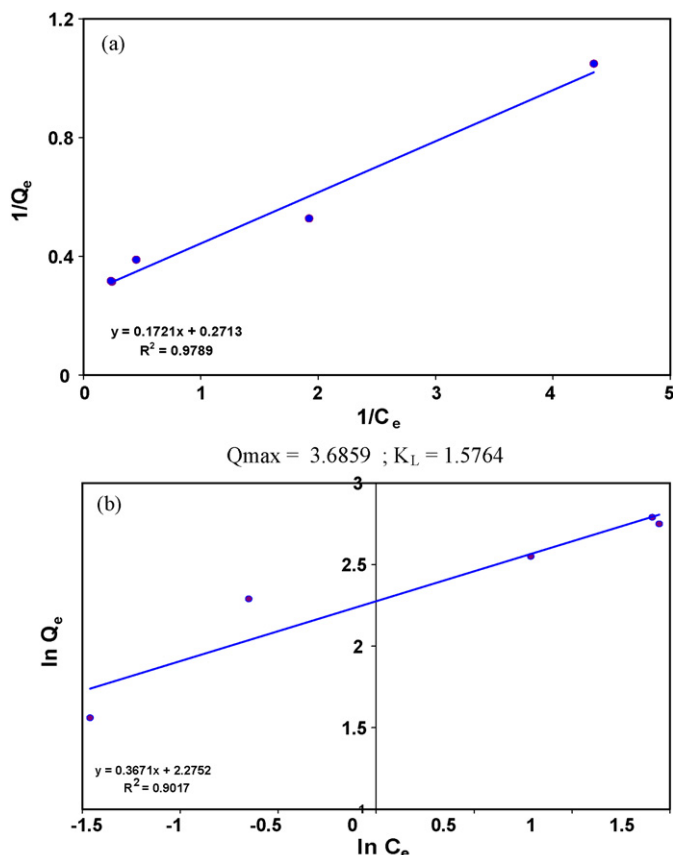


Fig. 4. (a) Langmuir's linearized sorption isotherm plot for E3-activated charcoal sorption system; (b) Freundlich's sorption isotherm plot for E3-activated charcoal sorption system [temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; contact time, 300 min; pH 7.0].

the isotherm can be assessed by classification, $R_s > 1$: unfavorable isotherm; $R_s = 0$: linear isotherm; $0 < R_s < 1$: favorable isotherm; $R_s < 0$: irreversible isotherm [52]. The processed data in Eq. (7) showed R_s value as 1.7×10^{-3} and indicated that the E3-activated charcoal adsorption system under study was irreversible in nature.

Freundlich's sorption isotherm model was used to study the non-ideal sorption involving heterogeneous sorption phenomena by using linearized form of Eq. (8)

$$\log q_e = \frac{1}{n} \times [\log C_{eq} + \log k_f] \quad (8)$$

Transformation of experimental data to Freundlich's sorption isotherm plot showed comparatively less linearization ($R^2 = 0.8855$) than the Langmuir's isotherm model indicating its non-acceptability (Fig. 4b). From the linearization plot of Freundlich's isotherm model respective empirical constants, viz., sorption capacity (k_f) of $2.921/\mu\text{g}$ and intensity ($1/n$) of 3.171 were estimated for E3-activated carbon system under study.

3.1.5. Effect of pH

Aqueous phase pH and ionic state (at particular pH) along with the functional groups on the sorbent contribute significantly to the sorption capacity of an adsorbent. The ionic form of E3 in solution and the activity and function of electrical charge on the activated carbon (functional groups) mostly depend on the solution pH. Batch sorption experiments were performed at various aqueous phase pH values (3.0, 6.0, 7.0, 8.0, 11.0) by keeping all other experimental conditions constant ($5 \mu\text{g}$ estriol/l; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; adsorbent, 5 g/l; contact time,

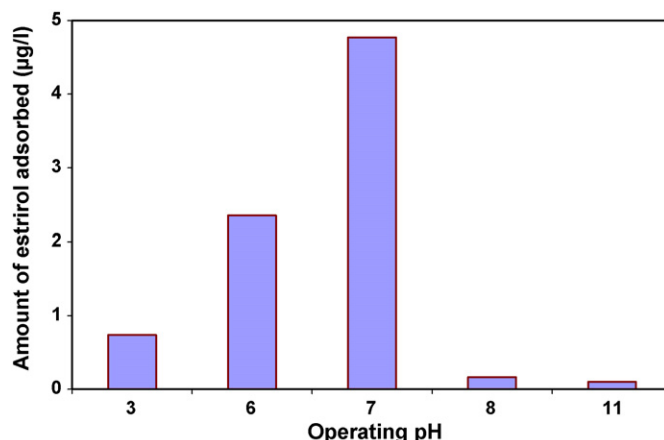


Fig. 5. Influence of aqueous phase pH on E3 adsorption [E3 concentration, $5 \mu\text{g/l}$; temperature, $30 \pm 1^\circ\text{C}$; agitation, 200 rpm; adsorbent mass, 5 g/l; contact time, 300 min].

300 min). The effect of aqueous phase pH on the adsorptive removal of E3 is depicted in Fig. 5. Aqueous phase pH showed significant influence on E3 sorption on to AC. Neutral conditions depicted the highest E3 sorption capacity (95.40%). Relatively less sorption was observed in basic condition compared to acidic conditions. Lower E3 sorption efficiency 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 [34,44]. For all practical purposes and up-scaling of the process, aqueous phase pH 7.0 might be used for sorption of E3 onto activated charcoal.

3.1.6. Influence of temperature and thermodynamic parameters

The effect of temperature on the sorption of E3 from aqueous phase was evaluated at different temperatures (0 – 50°C) by keeping all other experimental conditions constant ($5 \mu\text{g}$ estriol/l; pH 7.0; agitation, 200 rpm; adsorbent, 5 g/l; contact time; 300 min). With increase in temperature a marked increase in E3 sorption was observed as depicted in Fig. 6a. Rapid improvement in E3 sorption was noticed with increase in temperature from 0 to 10°C . The thermodynamic parameters associated with the sorption process such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using Eqs. (9)–(11) [53]

$$K_C = \frac{C_{eq}}{C_s} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_C \quad (10)$$

$$\ln K_C = \frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

The plot of $\ln K_C$ as a function of $1/T$ yielded a straight line ($R^2 = 0.9236$) from which ΔH° and ΔS° were calculated from the slope and intercept, respectively (Fig. 6b). The negative value of ΔH° (-9.189 kJ/mol) and ΔS° (0.492 J/mol K) suggested the exothermic nature of E3 adsorption process. The magnitude of free energy change (ΔG°) increased from 2.51 to 2.97 kJ/mol when the temperature was increased from 0 to 50°C . If sorption is governed only by physical phenomena, an increase in temperature is followed by a decrease in sorption capacity. Temperature can also influence the desorption and consequently the reversibility of the sorption equilibrium [54].

3.1.7. Adsorption–desorption studies

Adsorption–desorption experiments are useful to understand the sorption mechanism of particular system with respect to regeneration capacity of the sorbent for reuse in a more economic

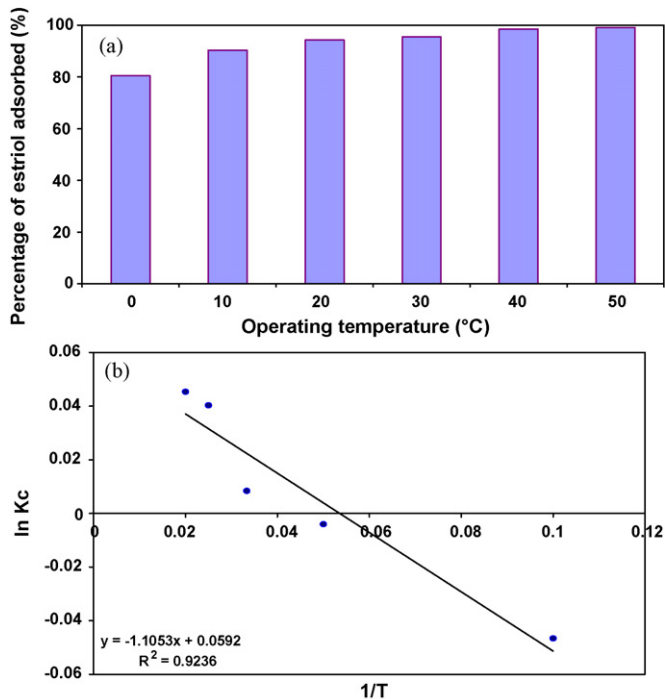


Fig. 6. (a) Effect of operating temperature on E3 adsorption; (b) plot of K_c versus $1/T$ for estimation of thermodynamic parameters for sorption of E3 onto activated carbon in the temperatures range from 0 to 50 °C [pH 7.0; agitation, 200 rpm; adsorbent, 5 g/l; E3 concentration, 5 µg/l; contact time; 300 min].

manner. The amount of desorption also provides an insight into the nature of adsorbent–adsorbate bonding and also on the ion exchange property of the sorbent. Adsorption–desorption experiments [5 µg estriol/l; temperature, 30 °C; agitation, 200 rpm; adsorbent mass, 0.1 g; contact (adsorption) time, 300 min; desorption time, 30 min] were carried out separately with three different desorption solvents [0.1 N HCl, 0.1 N NaOH and distilled water (pH 7)]. Relatively less desorption of E3 from activated charcoal was observed in all the cases of experimental variations studied. Highest desorption of E3 was observed in alkaline solution (2.86%; 0.1432 µg/l) followed by distilled water (0.75%; 0.0373 µg/l) and acid solution (0.06%; 0.0029 µg/l) from activated charcoal. Last desorption of E3 was observed particularly in distilled water and inorganic solvents which might be attributed to the chemical type of interaction rather than physical type.

3.1.8. FT-IR spectral analysis

FT-IR spectra of activated charcoal prior (virgin) to sorption and after E3 sorption are depicted in Fig. 7. Interpretations of the spectra were based on the information acquired from literature [55–57]. Visible changes in the FT-IR spectra after the E3 sorption were observed. The peaks appeared in the region of 1540 cm^{-1} might be attributed to the presence of quinone and OH groups. The bonds observed in the virgin sorbent disappeared after E3 sorption. Carboxylic/phenolic stretching bands in the region of 3000 cm^{-1} and $\equiv\text{C}-\text{N}<$ and $-\text{C}-\text{F}$ stretch groups in the region 1040 cm^{-1} were observed. Peak belonging to OH stretch was observed around 3600 cm^{-1} .

3.2. Fixed bed column studies

Bulk removal of the adsorbate by column studies proved to be more advantageous and practical over the batch studies [58–60]. An attempt was made in this study to evaluate the sorption potential

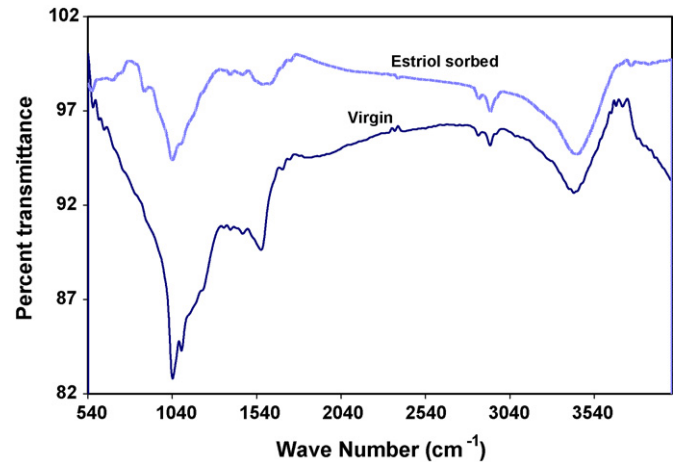


Fig. 7. FT-IR spectra of virgin and E3 loaded activated charcoal.

of E3 in fixed bed column (down-flow) by spiking in distilled water as well as from untreated and treated domestic sewage under similar operating conditions (temperature, 30 °C; depth of activated charcoal bed, 12.5 cm; pH 7.0). Three columns were operated separately employing distilled water (C_0 , 5 µg/l; Q_w , 1.8 l/h), untreated domestic sewage (C_0 , 5.11 µg/l (back ground E3 concentration in domestic sewage); 340 mg COD/l; Q_w , 1.68 l/h) and treated sewage (C_0 , 5 µg/l; 180 mg COD/l; Q_w , 1.68 l/h) to enumerate the potential of adsorptive removal of E3 from various types of aqueous bases. The breakthrough curves obtained from column operations are depicted separately for E3 and COD, respectively (Fig. 8). The time required for the exchange zone to move along the length on its own height up/down (t_z) the column once it has become established could be calculated using Eq. (12) [58]

$$t_z = \frac{(V_E - V_B)}{Q_w} \quad (12)$$

The time required for the exchange zone to become established and move completely out of the bed (t_E) and the rate at which the exchange zone is moving up or down through the bed can be represented by Eqs. (13) and (14), respectively

$$t_E = \frac{V_E}{Q_w} \quad (13)$$

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \quad (14)$$

Rearranging Eq. (14) provides an expression for the height of the exchange zone as given below

$$h_z = \frac{h(t_z)}{t_E - t_f} \quad (15)$$

The value of t_f can be calculated as follows:

$$t_f = (1 - F)t_z \quad (16)$$

At breakthrough point, the fraction of activated charcoal present in the sorption zone still poses capacity to adsorb E3 which can be represented by Eq. (17)

$$F = \frac{S_z}{S_{\max}} = \left\{ \int_{V_B}^{V_E} \frac{(C_0 - C)}{C_0(V_E - V_B)} dV \right\} \quad (17)$$

The percentage of the total column saturated at breakthrough point can be calculated by the following Eq. (18)

$$\text{Saturation (\%)} = \left[\frac{h + (F - 1)h_z}{h} \right] \times 100 \quad (18)$$

Table 2
Evaluation of parameters for fixed bed column studies

E3 spiked	C_0	Q_w (l/h)	t_z (h)	U_z (cm/h)	Bed saturation (%)
Distilled water	5 μ g estriol/l	1.80	24.12	0.536	96.46
Untreated domestic sewage	5.11 μ g estriol/l	1.68	23.32	0.559	95.85
	340 mg COD/l	1.68	3.63	3.47	97.48
Treated domestic sewage	5 μ g estriol/l	1.68	19.15	0.736	88.52
	180 mg COD/l	1.68	11.95	3.24	72.72

D: 12.5 cm; down-flow mode.

The details of breakthrough curve analysis in concurrence with the experimental variations studies are summarized in Table 2. Exhaustion of sorption bed took 1450 min with distilled water spiked E3, while with treated and untreated domestic sewage it took 1400 and 1150 min, respectively. In the case of treated domestic sewage, the sorption took 720 min of bed exhaustion compared to 220 min with untreated domestic sewage. The data obtained revealed that the time required for the exchange zone to move down (t_z) the column was higher with distilled water compared to sewage. Moreover, t_z was relatively higher when E3 was considered as parameter especially with sewage as spiked solute than COD. For all the systems the fractional capacity at breakpoint was calculated and found to be around 0.9. The percentage saturation was observed to be higher with distilled water [96.46% (E3)] than

untreated sewage [95.85% (E3); 97.48% (COD)] and treated sewage [88.52% (E3); 72.72% (COD)].

4. Conclusions

Experimental studies documented efficacy of sorption process in removing estriol (E3), an important endocrine disruptive aquatic toxicant from aqueous phase using activated charcoal as adsorbent. Agitated batch sorption studies performed on E3-activated carbon sorption system showed good fit with pseudo-first-order rate equation. The intra-particle diffusion plot showed boundary layer diffusion effect and also observed that intra-particle diffusion was not the only rate-controlling step. Isothermal data showed good fit with Langmuir's sorption isotherm model. Experimental data showed that the E3 sorption on activated charcoal was controlled by film diffusion process. Neutral pH conditions depicted highest E3 sorption capacity. Increase in operating temperature showed improvement in E3 sorption. The plot of $\ln K_C$ as a function of $1/T$ yielded a straight line and the resulting negative value of ΔH° (-9.189 kJ/mol) and ΔS° (0.492 J/mol K) suggested the exothermic nature of E3 sorption process. Effective desorption of E3 from AC was observed in alkaline solution. Fixed bed column studies operated with E3 spiked distilled water, untreated domestic sewage and treated domestic sewage showed the potential of sorption process as tertiary unit operation in the ETP system

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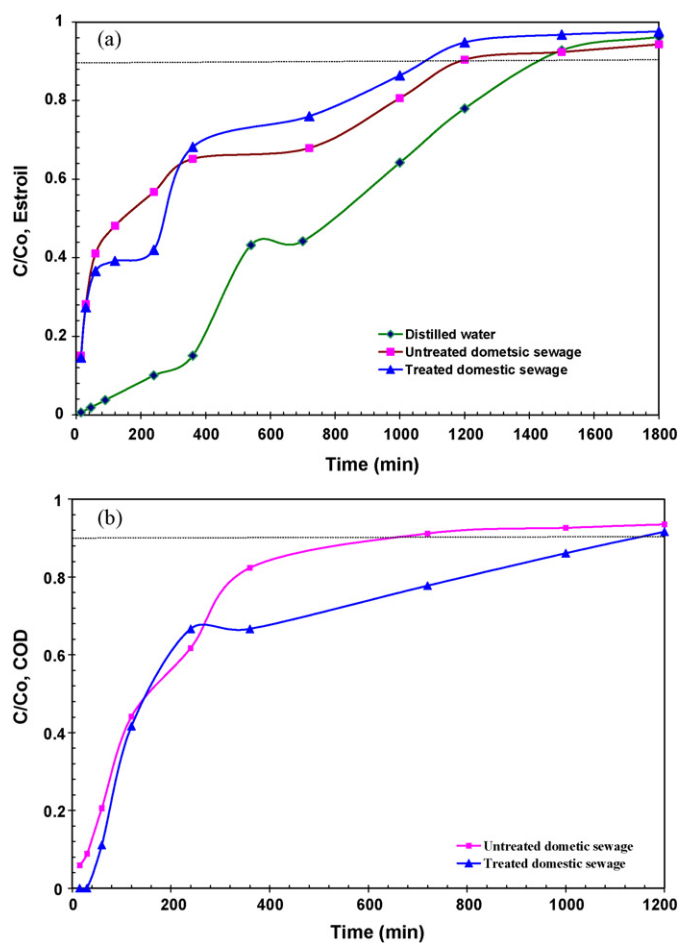


Fig. 8. Breakthrough curve (a) E3; (b) COD [temperature, 30 ± 1 °C; depth of activated charcoal bed, 12.5 cm; pH 7.0; distilled water (C_0 5 μ g E3/l; flow rate (Q_w); 1.8 l/h), untreated domestic sewage (C_0 5.11 μ g E3/l; 340 mg COD/l; Q_w , 1.68 l/h) and treated sewage (C_0 , 5 μ g E3/l and 180 mg COD/l; Q_w , 1.68 l/h)].

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