Development of parthenium based activated carbon and its utilization for adsorptive removal of p-cresol from aqueous solution

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Abstract

The activated carbon was prepared from carbonaceous agriculture waste *Parthenium hysterophorous* by chemical activation using concentrated H_2SO_4 at $130 \pm 5\,^{\circ}C$. The prepared activated carbon was characterized and was found as an effective adsorbent material. In order to test the efficacy of parthenium based activated carbon (PAC), batch experiments were performed to carryout the adsorption studies on PAC for the removal of highly toxic pollutant p-cresol from aqueous solution. The p-cresol adsorption studies were also carried out on commercial grade activated carbon (AC) to facilitate comparison between the adsorption capabilities of PAC and AC. For PAC and AC, the predictive capabilities of two types of kinetic models and six types of adsorption equilibrium isotherm models were examined. The effect of pH of solution, adsorbent dose and initial p-cresol concentration on adsorption behaviour was investigated, as well. The adsorption on PAC and on AC was found to follow pseudo-first order kinetics with rate constant $0.0016\,min^{-1}$ and $0.0050\,min^{-1}$, respectively. The highest adsorptive capacity of PAC and AC for p-cresol solution was attained at pH 6.0. Further, as an adsorbent PAC was found to be as good as AC for removal of p-cresol upto a concentration of 500 mg/l in aqueous solution. Freundlich, Redlich–Peterson, and Fritz–Schlunder models were found to be appropriate isotherm models for PAC while Toth, Radke–Prausnitz and Fritz–Schlunder were suitable models for AC to remove p-cresol from aqueous solution.
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Keywords: *Parthenium hysterophorous*; Activated carbon; p-Cresol; Adsorption isotherms; Adsorption kinetics

1. Introduction

Organic compounds constitute a very large group of pollutants in the wastewater. Amongst them aromatic compounds mainly phenol and its derivatives such as resorcinol, catechol, and cresols are widely found in the effluent of many industries. These pollutants are recognized as carcinogens and are known to be toxic to the environment. p-Cresol is present in the effluent from many chemical and allied industries, namely petrochemical, oil refinery, metal refining, chemical and glass fiber manufacturing, ceramic plants, steel plants and phenolic resin manufacturing. It is also a naturally occurring metabolic product

that is formed from tyrosin by bacteria under anaerobic conditions [1]. It is highly toxic and even at a very low concentration it may act as a promoter for stomach tumors. It is corrosive to the eyes, the skin and the respiratory track. It may cause adverse effects on the central nervous system, cardiovascular system, lungs, kidney, and liver resulting in CNS depression. Exposure at higher levels may result in lowering in consciousness and death. Further, it is also not readily biodegradable. p-Cresol is listed as a priority pollutant by the US Environmental Protection Agency [2]. Environmental Protection Agency (EPA) has classified p-cresol as pollutant of group C (possible human carcinogens) [2–4]. With ever-increasing concern for public health and environmental quality, therefore, many regulatory agencies have set up a rigid limit for the acceptable level of p-cresol in the environment [5]. The Ministry of Environment and Forest (MOEF), Govt. of India has set a maximum concentration level of 1.0 mg/l of p-cresol in the industrial effluents for the safe discharge into surface waters. The World Health Organization (WHO) recommends the permissible p-cresol concentration of

Nomenclature

a	constant in Toth isotherm $(mg/l)^n$
b	constant in Langmuir isotherm in Eq. (7) (l/mg), and Redlich Peterson isotherm exponent in Eq. (9)
C_e	concentration of adsorbate in solution at equilibrium (mg/l)
C_o	initial concentration of adsorbate in solution (mg/l)
C_t	concentration of adsorbate in solution at any time t (mg/l)
k	constant in Radke–Prausnitz isotherm (mg/g) $(l/mg)^{1/n}$
k_1	adsorption rate constant of pseudo-first order kinetics (min^{-1})
k_2	adsorption rate constant of pseudo-second order kinetics $(g\,mg^{-1}\,min^{-1})$
K	constant in Radke–Prausnitz isotherm (l/g)
K_F	constant in Freundlich isotherm (mg/g) $(l/mg)^{1/n}$
K_1	constant in Redlich–Peterson isotherm (l/g)
K_2	constant in Redlich–Peterson isotherm $(l/mg)^b$
m	weight of adsorbent dose (g)
n	constant in Freundlich, Toth and Radke–Prausnitz isotherms
$q_{e(exp)}$	experimental value of q_e (mg/g)
$q_{e(pred)}$	predicted value of q_e (mg/g)
q_e	amount of adsorbate adsorbed per gram of adsorbent (adsorbate loading) at equilibrium (mg/g)
q_e^∞	constant in Toth isotherm (mg/g)
q_t	amount of adsorbate adsorbed per gram of adsorbent (adsorbate loading) at any time t (mg/g)
Q_0	constant in Langmuir isotherm (mg/g)
t	time (min)
V	volume of adsorbate solution (l)

Greek symbols

α_1	constant in Fritz–Schlunder isotherm $(mg/g)/(mg/l)^{\beta_1}$
α_2	constant in Fritz–Schlunder isotherm $(mg/l)^{-\beta_2}$
β_1, β_2	constants in Fritz–Schlunder isotherm

0.001 mg/l in potable waters [6]. Therefore, to save our aqueous ecosystem, it has been essential to reduce *p*-cresol concentration in wastewater to acceptable level before safe disposal to water bodies.

Various technologies for the removal of phenolic compounds from industrial effluents and so for *p*-cresol, are available in the literature. These include mainly physiochemical treatment processes such as adsorption by using ion-exchange resin and activated carbon, and aerobic and anaerobic biodegradation processes. Amongst these technologies, the adsorptive removal by using granular or powdered activated carbon has gained wide acceptance and popularity [7–12]. Activated carbon is a material with an exceptionally high surface area. Physical adsorption is the primary means by which activated carbon works to remove pollutants from wastewater or industrial liquid effluents. The water pollutants or contaminants get adsorbed on the surface of activated carbon because the attractive forces of the carbon surface for them are stronger than the attractive forces that keep them dissolved in the solution. Besides, the molecules of contaminants generally are smaller than the size of carbon pore opening, so that they can pass into the carbon pores and get adsorbed. The activated carbon is prepared commercially from natural carbonaceous sources such as wood and coal. These materials are expensive and requires high manufacturing cost. Besides, the gradual loss of activated carbon during regeneration increases the treatment cost also. Therefore, in recent years, the research efforts have been intensified to produce low cost, disposable activated carbon. Numerous low cost alternative carbonaceous source materials have been utilized in last decade to prepare activated carbon, which include agricultural wastes (rice husk, toxic grass, etc.), forest wastes (barks, leaves, saw dust, etc.), and industrial wastes (fly ash, sugarcane bagasse, etc.). Our search for a cheap readily available carbonaceous material has identified *Parthenium hysterophorous* weed (an agricultural waste) as a potential attractive material for the preparation of activated carbon.

Parthenium is also known as white top or carrot weed (herbaceous weed—a native of North-East Mexico). It is most noxious weed of mainly uncultured lands, unbuilt or developing residential colonies around the towns, railway tracks, roads, drainage and irrigation canals, etc. This weed is also spreading in established gardens, plantations and in some crops like sugarcane, cotton, fodders, vegetable crops. Due to its high rate of seed germination and production, it has covered large areas. It has now widely spread in India, and few other countries. Parthenium has emerged as a great health hazard to human beings and livestock. Frequent contact with the weed causes allergies, dermatitis, eczema, asthma, bronchitis high fever and gangrene, etc. Even dried plant material is air borne and dust may induce dermatitis in sensitive persons, who do not have direct exposure to the plants. It has also been proved harmful and even fatal to milk cattle grazing in the infested area. Therefore, it is one of the 10 worst weeds in the world [13,14]. Therefore, it is desirable to take proper and efficient control measures to overcome this problem. Now a days, many research activities are going on to wipe out this plant and to treat affected persons, crops and livestock.

From the aforementioned discussion, it is evident that the biomass of parthenium is available round the year at no cost. Recently, in the literature few studies have been reported using parthenium based activated carbon as adsorbent. But these studies are only on the economic removal of metal ions and dyes from wastewater [15–19]. Regarding the removal of phenolic compounds from industrial wastewater, although many studies have been conducted using different types of activated carbon [20–27], the efficacy of parthenium based activated carbon has not yet been explored. Therefore, the present study has been undertaken to prepare activated carbon from parthenium weed, and to study its adsorptive capacity for the removal of *p*-cresol from the aqueous solution.

The activated carbons are classified on the basis of their bahaviour, surface characteristics and preparation methods and thereby characterized by physical properties and activity. Therefore, the present experimental study has been focused on the kinetic and equilibrium behaviour of adsorption of *p*-cresol on two types of activated carbon. First type of the activated carbon has been prepared by using parthenium weed abbreviated as PAC (parthenium based activated carbon) and another type of activated carbon is commercial grade activated carbon abbreviated as AC. The commercial grade activated carbon AC has been used as the standard adsorbent for the comparison of adsorptive capacities of parthenium based activated carbon PAC. The batch experiments have been performed to study adsorption of *p*-cresol on PAC and AC. The experimental adsorption equilibrium data on PAC and AC have been fitted to six isotherm models normally encountered in the studies of adsorption of phenolic compounds on activated carbons to investigate the best isotherm. The kinetics of adsorption of *p*-cresol on PAC has been studied using two different kinetic models and results have been compared with the kinetics on AC. The goodness of the fit of the experimental data to the proposed kinetic and isotherm models was attested by high correlation coefficient R^2 and low percent normalized standard deviation. In addition to this, the effect of adsorbent dose, pH of solution and initial concentration of *p*-cresol in solution on removal of *p*-cresol by AC and PAC has been studied and the removal capacities of AC and PAC have been compared as well.

2. Materials and methods

2.1. Procurement of commercial grade activated carbon (AC)

The commercially available activated carbon was granular LR grade in the size range of 2–5 mm and supplied by s.d. fine chemicals, Boisar, India. It was grinded to make it suitable for present study in the same way as it was converted in our previous studies [24], and sieved through 18 to 44 BS mesh. The average particle size so obtained was 0.536 mm. The sieved carbon was further washed many times with distilled water to remove any attached fines and leachable matter. After washing, it was dried in an oven at 105 °C for 72 h and stored in an air tight bottle.

2.2. Preparation of parthenium based activated carbon (PAC)

The stems of parthenium plants were collected from near by places of Roorkee (India) and washed with water to remove dirt and dust. These stems were cut into small pieces in the size of 5–10 mm and dried in sunlight. The activated carbon was then prepared by chemical activation process. According to this process, the dried parthenium mass was impregnated with concentrated H_2SO_4 in the ratio of 1:2 by weight (weight of parthenium:weight of acid) and was kept at 130 ± 5 °C for 24 h for carbonization. The carbonization was made in an inert atmosphere in a horizontal furnace. The carbonized material was washed several times with distilled water to remove free acid. It was further soaked into 1% sodium bicarbonate solution and kept overnight for the complete removal of acid. The resulting carbon, was again washed many times with distilled water in order to remove fines and leachable matter and it was dried at 110 °C in an oven. Finally, the dried activated carbon was subsequently pulverized and sieved to get the particles of size less then 0.5 mm.

2.3. Characterization of activated carbons

The activated carbons are characterized by their physical and chemical properties. The characterization of PAC and AC has been done by using standard methods. The measured values of the properties are mentioned in Table 1.

It is evident from Table 1 that the surface area of commercial grade activated carbon (AC) is more than the parthenium based activated carbon (PAC). However, PAC particles have pores of larger diameter and have high porosity as compared to AC. This indicates that the fraction of mesopores in PAC particles is more than the fraction of micropores. It is well known that the presence of micropores is essential for the adsorption of small gas molecules on activated carbons. However, when adsorbate is liquid containing organic compound, polymer, and dye, only mesopores allow the adsorption of such giant molecules. The ash content of PAC is higher than AC. The high ash content reduces the overall activity of activated carbon. Thus the adsorption efficiency of PAC is expected to be lower than that of AC. The lower surface area of PAC also supports this conjecture about PAC.

Table 1
Characteristics of activated carbons

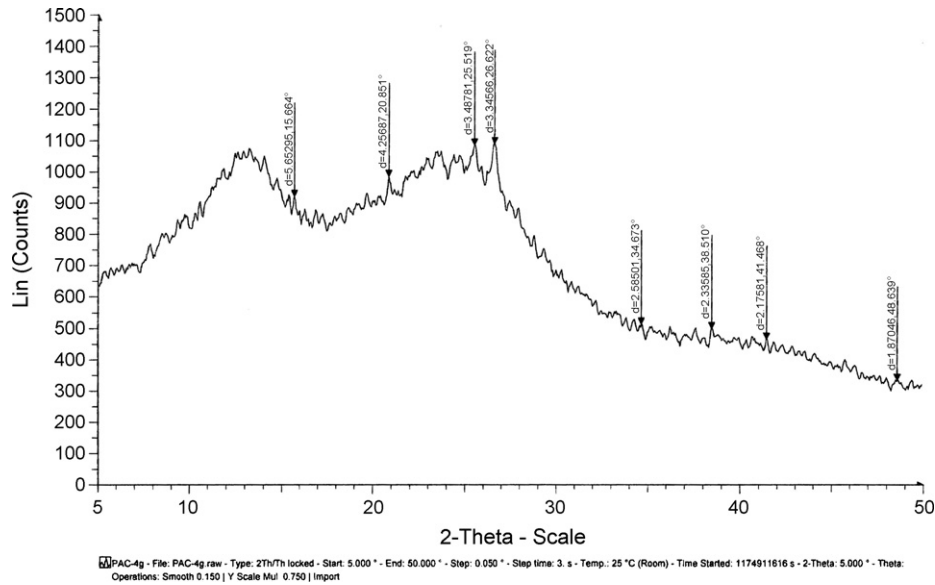| S. no.	Properties	Parthenium based activated carbon PAC	Commercial grade activated carbon AC
1	BET surface area (m^2/g)	260	686
2	pH (1% solution)	6.8	7.2
3	Moisture content (%)	2.1	5.5
4	Ash content (%)	8.2	3.1
5	Bulk density (g/ml)	0.57	0.977
6	Average particle size (mm)	0.512	0.536
7	Average pore diameter (Å)	36.74	18.60
8	Water soluble matter (%)	2.64	2.26
9	Acid soluble matter (%)	4.0	3.23

Fig. 1. X-ray diffraction pattern for parthenium based activated carbon.

Both the activated carbon samples have been analysed by using X-ray diffraction as well. XRD patterns were recorded using Cu Kα radiation (at 40 kV, 30 mA) for phase identification in thin samples. X-ray diffraction patterns for PAC and AC are shown in Figs. 1 and 2, respectively. In XRD pattern of PAC sample, most of the material shows amorphous content along with the X-ray peaks of carbons (major), CaP, and CaO$_2$. While AC sample shows mainly amorphous structure with very broad humps (typical nature of nanoparticles).

2.4. Preparation of adsorbate solution

p-Cresol of analytical reagent grade (purity > 99%) supplied by s.d. fine chemicals limited, Mumbai (India), was used for the preparation of synthetic adsorbate solutions of various con-

centrations in the range of 100–1000 mg/l. The stock solution (1%, w/v) was prepared by dissolving 10 g of *p*-cresol in a small amount of distilled water and making it up to 1 l in a measuring flask. This stock solution was stored in a brown coloured glass bottle, covered with aluminium foil to prevent photo oxidation. The fresh stock solution was prepared every day as per requirement. For the experiment, the solutions of various desired concentrations were prepared by successive dilution of stock solution.

2.5. Determination of concentration of p-cresol in solution

The concentration of *p*-cresol in the solution was determined by estimating the absorbance of the sample solution at maximum wavelength of 277 nm using UV/VIS spectropho-
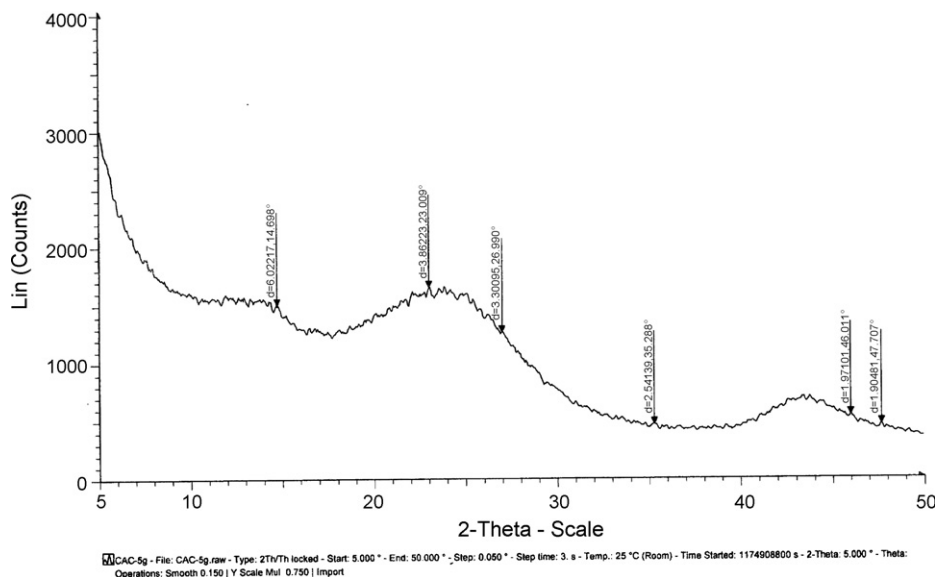

Fig. 2. X-ray diffraction pattern for commercial grade activated carbon.

tometer (model Lambada 35; PerkinElmer, Massachusetts 02451, USA). The calibration plot of absorbance versus concentration for *p*-cresol showed a linear variation in the concentration range of 1–10 mg/l. The concentration of *p*-cresol varied from 100 to 1000 mg/l, while pH of aqueous solution was maintained at 6 by adding NaOH or HCl as required.

2.6. Experimental procedure

The batch experimental studies were conducted for evaluating the adsorption potential of PAC for *p*-cresol. In this regard the rate of adsorption was estimated and equilibrium parameters were determined. Similar experiments were also conducted on AC.

In each adsorption experiment, 100 ml of *p*-cresol aqueous solution sample with known initial concentration and pH was added to known adsorbent dose in a 250 ml stoppered conical flask. This mixture was shaken on a reciprocating type horizontal shaker (S and N Electronics, Kolkata) with temperature control. The temperature was kept constant at 28 °C. The sample flask was taken out from the shaker at appropriate intervals of time and then filtered through a filter paper (Whatman No. 42). The filtrate was kept in a refrigerator prior to its analysis. The absorbance of this solution was determined as mentioned in Section 2.4, and accordingly residual concentration of *p*-cresol and its percent removal were calculated. This procedure was followed in adsorption kinetics, equilibrium and isotherm studies at various operating conditions as discussed below.

In industrial liquid effluents, the concentration of *p*-cresol varies from 100 to 500 mg/l and sometime even more than 500 mg/l [28–30]. Therefore, in the present experimental study, the concentration of *p*-cresol in aqueous solution is chosen to be in the range of 100–1000 mg/l. The experiments for adsorption kinetics and equilibrium studies were conducted at 28 °C by using six initial *p*-cresol concentrations: 100, 200, 300, 400, 500, and 1000 mg/l. In each flask, a fixed adsorbent dose (AC or PAC) of 10 g/l was added. The pH was maintained at 6 by adding HCl or NaOH as required. The samples were withdrawn at pre-specified time intervals (one at a time) and filtered. The filtrates were stored in a refrigerator. The filtrate samples were taken at different time intervals and the concentrations C_t were estimated. This study was carried out on AC as well as on PAC separately. For AC, equilibrium condition was established after 24 h and for PAC, the equilibrium condition was established after 30 h. At equilibrium the samples were taken and the equilibrium concentration C_e was calculated for each run. The amount of adsorption of *p*-cresol per gram adsorbent, q_t (mg/g) at any time *t* was calculated by:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where C_o and C_t are the concentration of *p*-cresol at the initial and time *t*, respectively, *V* is the volume of adsorbate solution, and *m* is the mass of adsorbent dose used in the run. At equilibrium condition, the amount of adsorption per gm of adsorbent,

q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

In the isotherm studies, the experiment was conducted on fixed initial concentration of *p*-cresol of 500 mg/l using AC as well as PAC. On AC the adsorbent dose was varied from 0.5 to 15 g/l with an increment of 0.5 g/l. Thus 30 sample flasks were taken. On PAC, the adsorbent dose was varied from 1 to 24 g/l with an increment of 1 g/l. Thus 24 sample flasks were taken. The equilibrium contact time determined from the kinetics was used for these tests. After shaking for a certain period of time, the samples were filtered and analysed for estimation of residual *p*-cresol concentration.

In order to study the effect of pH on adsorption of *p*-cresol, the experiment was carried out for initial pH (pH$_0$) values in the range of 3–12 at 28 °C upto equilibrium time. The pH of solution was changed from 3–12 by adding NaOH in appropriate amount. The initial concentration of *p*-cresol was kept at 500 mg/l and the adsorbent dose was kept at 10 g/l for both AC and PAC.

3. Results and discussion

3.1. Effect of pH of solution

One of the major factors that controls the adsorption uptake of adsorbate is the distribution of charge on the adsorbent surface, which occurs due to interaction of surface with adsorbate ions. This fact implies that the pH of the solution influences the surface charge of the adsorbent and degree of ionization of the adsorbate which in turn influences the adsorption. Hence in most of the studies available in the literature, initial pH of aqueous solution is considered as one of the most important parameters to be studied [18,19,26,31]. The limiting pH of solution is considered on the basis of pH$_{pzc}$. This is the pH at which the surface of activated carbon has zero charge, i.e. the surface is neutral. At this state, the adsorbate gets adsorbed on the surface of adsorbent by diffusion into micropores and mesopores [32] and not by electrostatic forces. At pH higher than pH$_{pzc}$, the surface of activated carbon becomes negatively charged and the positive ions in the solution are attracted on the surface according to electrostatic attraction. At pH lower than pH$_{pzc}$, the carbon surface becomes positively charged and so negative ions in the solution are attracted on the surface. The experimental value of pH$_{pzc}$ for PAC and AC is found to be 6.8 and 7.2, respectively. It is noteworthy that the functional groups of adsorbate reveal insight into the observed adsorption pattern [7]. The adsorption capacity of the carbon for the adsorbates in their molecular form depends on the electron density of the adsorbate. In *p*-cresol, since methyl and hydroxyl both are electron-donating groups, *p*-cresol is more basic in nature. At the pH value less than pH$_{pzc}$, therefore, carbon surface has more affinity for *p*-cresol which results in high adsorption uptake of *p*-cresol. The lone pair of electron of the OH$^{\bullet}$- groups is available for hydrogen bonding [7]. Therefore in high acidic condition (e.g. pH 3) *p*-cresol molecules become positively charged. The electrostatic repulsion between the surface layer and *p*-cresol molecules
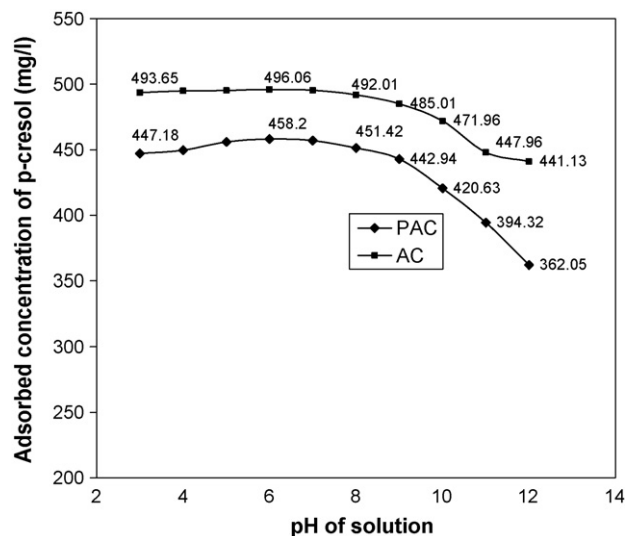
Fig. 3. Effect of variation in pH on adsorption of p-cresol.

Fig. 4. Comparison of effect of adsorbent dose on adsorption of p-cresol.

results in reduced adsorption. At pH greater than pH_{pzc}, repulsion between negatively charged surface and negatively charged p-cresol molecules again reduces the adsorption of p-cresol. The pK_a value of p-cresol is 10.2. Therefore, at pH greater than 10.2 (e.g. pH 12) p-cresol molecules are mainly in ionic form and much less in molecular form. At this state also high electrostatic repulsion between identical charge lowers the adsorption uptake of p-cresol. Thus, it is concluded that the adsorption uptake of p-cresol on carbon surface decreases at both high and low pH. These facts are also revealed through the experimental results.

Fig. 3 represents the effect of pH of solution on adsorption of p-cresol on PAC and AC separately. This figure shows that the adsorption of p-cresol on AC is higher than the adsorption on PAC for all pH values. When pH of solution varies from 3 to 7, the variation in adsorption uptake on both PAC and AC is not significant. However, adsorption increases from pH 3 to 6. For PAC the adsorption is maximum at pH 6. At this value, adsorption on AC also approaches maximum value. At pH > 7, the adsorption decreases. For PAC it decreases continuously whereas for AC, it becomes approximately constant at pH > 11. Hence, the pH value of 6, which is less than pH_{pzc} for both PAC and AC, is considered as the optimum pH value of solution for all further p-cresol adsorption experiments.

3.2. Effect of adsorbent dose

In order to investigate the effect of adsorbent dose on the adsorption of p-cresol and to optimize the dose, series of adsorption experiments were carried out where varying amounts of PAC (1–20 g/l) and AC (0.5–15 g/l) were contacted with p-cresol solution. The initial concentration, temperature and pH of solution were kept constant at 500 mg/l, 28 °C and 6, respectively. Fig. 4 represents the variation in percent removal of p-cresol with the variation in the dose of PAC and AC. From this figure it is clear that AC has more adsorption capacity than PAC. For the initial step change in the dose of PAC and AC, the percent removal of p-cresol is higher. The reason for this is
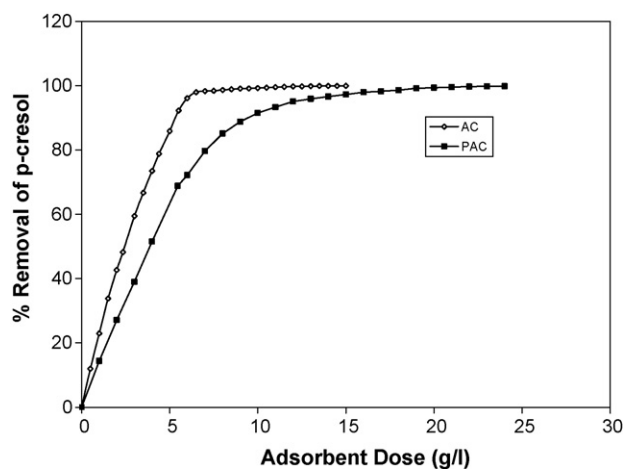
that the higher adsorbent dose provides more active sites for adsorption which results in the overall increase in the removal efficiency. On further increasing the dose the incremental change in percent removal with change in dose of AC and PAC is very low. After achieving 99% removal, adsorbent dose is not much effective and most of the active sites remain unoccupied. Therefore, amount of p-cresol adsorption per unit mass of adsorbent decreases with increase in adsorbent dose. This fact leads to the estimation of the optimum adsorbent dose required for the removal of p-cresol by using two activated carbons at prevailing operating conditions. 10 g/l of PAC dose is required as against 6 g/l of AC dose to achieve the same amount of removal of p-cresol (92%). Afterwards since the removal rate is very low, to treat 500 mg/l of p-cresol solution, the optimum amount of adsorbent dose for PAC is 10 mg/l and for AC is 6 mg/l. The optimum dose varies directly with the initial concentration of p-cresol in the solution. Although the dose of PAC required is more than the dose of AC, yet the high PAC dose can be tolerated to remove p-cresol at the expense of its low cost.

3.3. Effect of initial p-cresol concentration

The adsorption of p-cresol was studied experimentally by varying the initial concentrations of p-cresol from 100 to 1000 mg/l keeping temperature, pH of solution and adsorbent dose constant at 28 °C, 6, and 10 g/l, respectively. Six concentrations were considered (100, 200, 300, 400, 500, and 1000 mg/l). Figs. 5 and 6 show the uptake of p-cresol with time at different p-cresol concentrations for AC and PAC, respectively. The equilibrium was achieved in 24 h in case of AC and in 30 h in case of PAC. The results show that the uptake rate of p-cresol is high at the initial period (approximately 50 min for both AC and PAC). This is due to the existence of sufficient driving force to adsorb the molecules on vacant sites of the surface of PAC and AC. The driving force is the difference in the concentration of p-cresol in solution and on adsorbent surface. As the time passes, the concentration of p-cresol molecules increases on vacant sites, as a result the driving force to adsorb molecules decreases which in turn decreases the adsorption rate. Figs. 5 and 6 also show
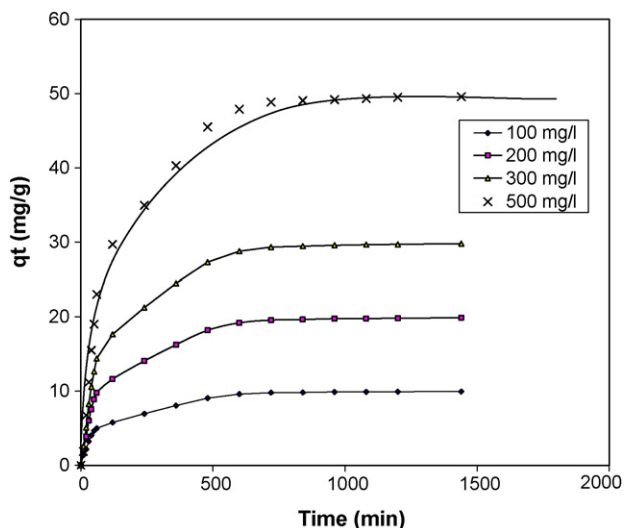
Fig. 5. Typical concentration–time profile for adsorption of *p*-cresol on commercial grade activated carbon (AC).

Fig. 7. Effect of initial concentration on removal of *p*-cresol.

that an increase in initial concentration results in the increased *p*-cresol uptake. The percent removal of *p*-cresol data at different concentrations using AC and PAC are presented in Fig. 7. The results show that the percent removal of *p*-cresol on AC is higher than that on PAC at all concentrations, indicating that the adsorption capacity of AC is higher than that of PAC. The percent removal decreases with increase in concentration in case of both the adsorbents. However, the difference in percent removal by AC and PAC upto a concentration of 500 mg/l is not much. This may be due to availability of sufficient number of vacant sites on adsorbent surface to adsorb *p*-cresol. At fixed amount of adsorbent dose, therefore, the increase in *p*-cresol concentration results in the reduction of percent removal. For concentration greater than 500 mg/l, percent removal in case of
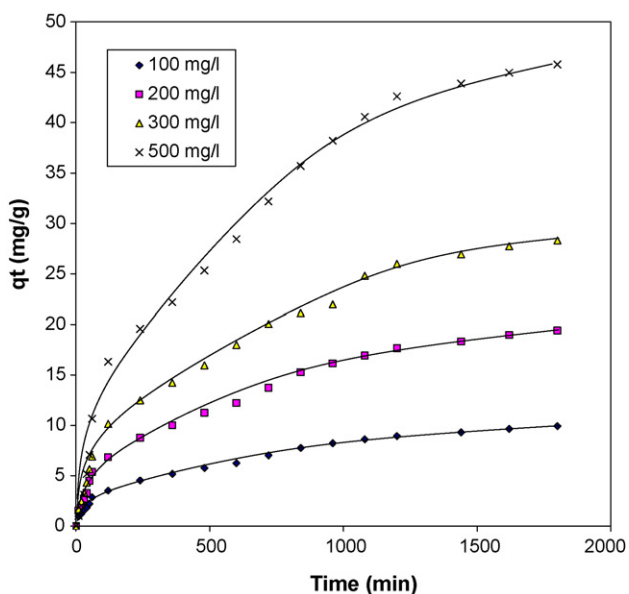
PAC decreases more rapidly than in case of AC. This is because of the fact that most of the surface of PAC becomes saturated whereas the surface of AC still has capacity to adsorb more *p*-cresol molecules. Thus it is suggested that PAC as an adsorbent for *p*-cresol, is as good as AC in the concentration range upto 500 mg/l.

3.4. Adsorption kinetics

Prior to the adsorption equilibrium studies of *p*-cresol it is necessary to analyse the adsorption rate and finally the equilibrium condition after which the variation of the unadsorbed *p*-cresol concentration in the solution is negligible. The most widely applied kinetic models for adsorption of phenolic compounds on activated carbon are pseudo-first order and pseudo-second order kinetic models. In this study, the predictive capabilities of these two types of kinetic models regarding adsorption of *p*-cresol on AC and PAC are examined. The pseudo-first order kinetic model is expressed as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t), \tag{3}$$

where k_1 is pseudo-first order adsorption rate constant (min^{-1}). The pseudo-second order kinetics model is expressed as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is the pseudo-second order adsorption rate constant ($\mathrm{g\,mg^{-1}\,min^{-1}}$). The integrated form of Eqs. (3) and (4) with the boundary conditions, $q_t(t=0)=0$ becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3a}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4a}$$

Fig. 6. Typical concentration–time profile for adsorption of *p*-cresol on parthenium based activated carbon (PAC).

Table 2
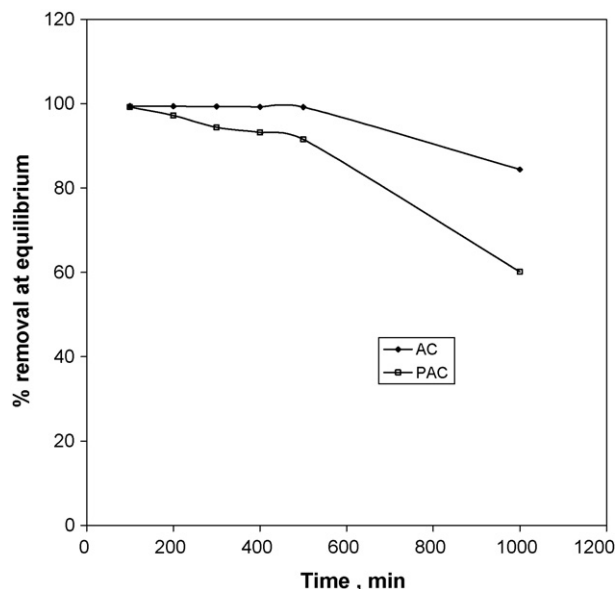Pseudo-first order kinetic constant for adsorption of p-cresol on parthenium based activated carbon (PAC)

S. no.	Concentration of p-cresol (mg/l)	Pseudo-first order kinetics				
		k_1 (min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e (%)
1	100	0.0017	8.7312	9.921	0.9843	
2	200	0.0017	17.348	19.404	0.9839	
3	300	0.0015	25.065	28.308	0.9809	0.9800
4	500	0.0017	42.957	45.770	0.9797	
5	1000	0.0016	55.684	60.150	0.9807	

Table 3
Pseudo-second order kinetics constants for adsorption of p-cresol on parthenium based activated carbon (PAC)

S. no.	Concentration of p-cresol (mg/l)	Pseudo-second order kinetics				
		k_2 (g mg^{-1} min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e (%)
1	100	1.41×10^{-4}	12.87	9.921	0.9910	
2	200	6.94×10^{-5}	25.51	19.404	0.9908	
3	300	5.56×10^{-5}	25.51	28.308	0.9748	4.1776
4	500	2.47×10^{-5}	62.89	45.770	0.9871	
5	1000	7.45×10^{-6}	104.17	60.150	0.9882	

Here, q_e and q_t are the amounts of p-cresol adsorbed per unit mass of adsorbent at equilibrium and at time t, respectively, and can be calculated by using Eqs. (1) and (2).

If the pseudo-first order kinetic Eq. (3a) describes the p-cresol adsorption on activated carbon, the plot of $\ln(q_e - q_t)$ versus t should give a linear relationship with the slope of k_1 and intercept of $(\ln q_e)$. The value of k_1 can be determined from the slope. If the pseudo-second order kinetic Eq. (4a) describes the adsorption, the rate constant k_2 can be determined from the intercept of the linearized plot of t/q_t versus t. In order to determine the kinetic parameters, experiments were conducted at six initial concentrations (100, 200, 300, 400, 500, and 1000 mg/l), keeping pH of solution constant at 6, temperature at 28 °C and adsorbent dose at 10 g/l. For each run the concentration of p-cresol at various time intervals was estimated. The corresponding values of q_t are calculated by using Eq. (1). The values of pseudo-first order and pseudo-second order rate constants k_1 and k_2 have been estimated by linear regression analysis of experimental data using Eqs. (3a) and (4a) for both AC and PAC. The goodness of the fit of the experimental data to the proposed kinetic models is generally attested by

correlation coefficient R^2 and normalized deviations. The percentage deviation between experimental and predicted values for each model has been calculated by following two equations [21,27]:

$$\text{Normalized deviation} = \frac{100}{N} \sum \left| \frac{(q_{e(exp)} - q_{e(pred)})}{q_{e(exp)}} \right| \quad (5)$$

Normalized standard deviation $\Delta q_e \%$

$$= 100 \sqrt{\frac{\sum [(q_{e(exp)} - q_{e(pred)})/q_{e(exp)}]^2}{N}} \quad (6)$$

where $q_{e(exp)}$ is the experimental q_e and $q_{e(pred)}$ is the corresponding predicted q_e according to the equation under study with best fitted parameters, N is the number of measurements. It is clear that lower the values of normalized deviations, the better is the fit of experimental data.

The values of k_1, k_2, q_e, R^2 and $\Delta q_e \%$ for PAC are given in Tables 2 and 3. The results show that k_1 lies between 0.0015 and

Table 4
Pseudo-first order constants for adsorption of p-cresol on commercial grade activated carbon (AC)

S. no.	Concentration of p-cresol (mg/l)	Pseudo-first order kinetics				
		k_1 (min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e (%)
1	100	0.0051	8.2697	9.94	0.9926	
2	200	0.0049	16.1464	19.87	0.9896	
3	300	0.0049	24.4958	29.79	0.9906	1.5385
4	500	0.0052	44.8848	49.51	0.9923	
5	1000	0.0048	74.6120	84.38	0.9917	

Table 5
Pseudo-second order kinetics constants for adsorption of *p*-cresol on commercial grade activated carbon (AC)

S. no.	Concentration of *p*-cresol (mg/l)	Pseudo-second order kinetics				
		k_2 (g mg^{-1} min^{-1})	q_e predicted (mg/g)	q_e experimental (mg/g)	R^2	Normalized standard deviation Δq_e (%)
1	100	1.20×10^{-3}	10.582	9.94	0.9984	
2	200	6.43×10^{-4}	21.052	19.87	0.9972	
3	300	3.37×10^{-4}	32.154	29.79	0.9987	0.8081
4	500	1.16×10^{-4}	54.645	49.51	0.9907	
5	1000	8.15×10^{-5}	76.923	84.38	0.9870	

0.0017 min^{-1} and it can be considered as independent of initial concentration. The variation in the values of k_2 with concentration is large enough. Although correlation coefficient obtained for both the orders are higher than 0.98, the normalized standard deviation Δq_e% is quite low (0.98) in case of pseudo-first order in comparison to Δq_e% in case of pseudo-second order (4.1776). In view of these results it can be concluded that the pseudo-first order kinetic model provides a good correlation for the adsorption of *p*-cresol on PAC. Tables 4 and 5 provide the kinetic results for AC. It looks evident that the values of k_1 are very close while the values of k_2 are not close at different initial concentrations. The values of R^2 for both orders are greater than 0.99, while Δq_e% is very much lower in case of pseudo-second order (0.8081) than in case of pseudo-first order (1.5385). This indicates that the adsorption of *p*-cresol on AC follows the pseudo-second order kinetics for a given initial concentration range (100–1000 mg/l). Further, from Table 5 it is noteworthy that the ratio of maximum to minimum values of k_2 is approximately 15, i.e. k_2 varies widely with concentration. From these results, therefore, it is evident that even on getting low value of Δq_e%, pseudo-second order kinetic model cannot be considered to predict a good correlation for adsorption kinetics on AC in entire concentration range (100–1000 mg/l) because of dependence of k_2 on initial concentration. As the values of k_1 ($\approx$0.0050 min^{-1}) are quite close, for entire concentration range

pseudo-first order kinetic model is only applicable for adsorption of *p*-cresol on AC.

3.5. Adsorption equilibrium isotherms

In adsorption, a dynamic phase equilibrium is established between the adsorbate in liquid and on the solid surface. This equilibrium is usually expressed in terms of concentration of the adsorbate in the liquid and adsorbate loading on the adsorbent. An adsorption equilibrium isotherm relates the adsorbate loading on the adsorbent (q_e) and liquid phase concentration of adsorbate (C_e) at equilibrium condition keeping temperature constant. Thus, adsorption isotherm describes the interaction between adsorbate and adsorbent which is critical in optimizing the use of adsorbents [12]. The models used to describe the experimental isotherm data are either theoretical or empirical equations based on the shape of the isotherm curve. The isotherm curve q_e versus C_e, predicting the behaviour of the experimental data of *p*-cresol adsorption on activated carbon, is concave downwards. The slope is always positive and it decreases steadily as concentration of *p*-cresol increases. In order to correlate the isotherm data of this type, six isotherm models are selected from the literature as given in Table 6. Langmuir, and Freundlich are two parameter models, Redlich–Peterson, Toth and Radke–Prausnitz are three parameter models, and

Table 6
Adsorption equilibrium isotherm constants of *p*-cresol on activated carbons at 28 °C

Adsorbent	Isotherm model									
	Freundlich			Langmuir			Redlich–Peterson			
	$q_e = K_F C_e^{1/n}$			$q_e = \dfrac{Q_0 b C_e}{1 + b C_e}$			$q_e = \dfrac{K_1 C_e}{1 + K_2 C_e^b}$			
	K_F	$1/n$	R^2	Q_0	b	R^2	K_1	K_2	b	R^2
PAC	19.7	0.216	0.9858	62.91	0.110	0.7914	19700	999.2	0.784	0.9858
AC	42.37	0.166	0.969	98.93	0.381	0.8352	255.7	5.348	0.857	0.9752

Adsorbent	Isotherm model											
	Toth				Radke–Prausnitz				Fritz–Schlunder			
	$q_e = \dfrac{q_e^\infty C_e}{[a + C_e^n]^{1/n}}$				$\dfrac{1}{q_e} = \dfrac{1}{KC_e} + \dfrac{1}{kC_e^{1/n}}$				$q_e = \dfrac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}}$			
	q_e^∞	a	n	R^2	K	k	$1/n$	R^2	α_1	α_2	β_1	β_2	R^2
PAC	3557	0.338	0.05549	0.986	998.9	20.74	0.197	0.975	18.85	0.0001	0.233	1.12	0.989
AC	246.3	0.318	0.1519	0.977	480.9	43.96	0.162	0.977	136.6	2.431	0.609	0.4908	0.978

Fritz–Schlunder model is four parameter model. Out of these isotherms, two parameter models of Langmuir and Freundlich are still dominant in adsorption of phenolic compounds on activated carbon. The Langmuir model equation is expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{7}$$

where b is the adsorption equilibrium constant. It is related to the free energy of adsorption and is the measure of adsorption affinity or heterogeneity. Q_0 is the maximum amount of p-cresol per gram of activated carbon to form a complete monolayer on the surface, indicating monolayer adsorption capacity. This model relies on that all the surface of the activated carbon has the same activity, adsorption is monolayer adsorption, and there is no interaction between molecules. It is also limited to a restricted range of low concentration [9].

The Freundlich model is an empirical model and is described by the equation

$$q_e = K_F C_e^{1/n} \tag{8}$$

K_F is the measure of the adsorption capacity and n is a measure of the adsorption intensity [33]. This model is applicable to the system involving heterogeneous surface and organic compound (e.g. activated carbon—phenolic compound). Model assumes logarithmic decrease in heat of adsorption in the surface coverage. This model is very much acceptable over a wide range of concentration [9]. The disadvantage is that it does not follow Henry's law at concentration approaching zero.

Redlich–Peterson model is three parameter model which combines elements of the Langmuir and Freundlich isotherm in a single equation as given below.

$$q_e = \frac{K_1 C_e}{1 + K_2 C_e^b} \tag{9}$$

where K_1 and K_2 are Redlich–Peterson isotherm constants and b is Redlich–Peterson isotherm exponent which lies between 0 and 1 [33]. This model is also valid for wide range of concentration. For $b = 1$, the equation is converted to the Langmuir isotherm, for $K_2 C_e^b \gg 1.0$, it reduces to Freundlich model and for $K_2 C_e^b \ll 1.0$, it reduces to Henry's law.

The Radke–Prausnitz, Toth, and Fritz–Schlunder models are not common in use to describe adsorption of phenolic compounds on activated carbon. In order to determine p-cresol adsorption isotherm, experiments were conducted at 28 °C and initial concentration of 500 mg/l. Adsorbent dose was varied from 0.5 to 15 g/l for AC and from 1 to 24 g/l for PAC. For each run the value C_e was different. These experimental data are fitted to six isotherm models given in Table 6. The parameters of two parameter models are easily obtained using the linear least square method. However, for models with more than two parameters, model parameters are estimated by a non-linear least square method. For this purpose, curve fitting tool of MAT-LAB 6.5 on Windows XP has been used. Model parameters are estimated for both AC and PAC. The values of correlation coefficient (R^2) are tabulated with the values of isotherm parameters in Table 6. The normalized deviation and normalized standard deviation between experimental and predicted values for each
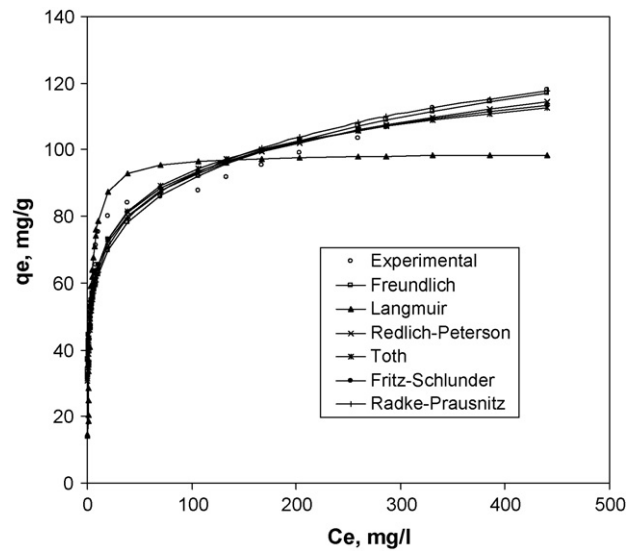

Fig. 8. Comparison of different isotherm models for p-cresol on AC.

isotherm model are calculated by Eqs. (5) and (6). Figs. 8 and 9 provide the comparison of different isotherm models vis-a-vis experimental results of AC and PAC, respectively. It is clear that Langmuir model could fit the data for both adsorbents only at very low concentration range while at high concentration, it could not fit the data at all. One way to assess the goodness of fit of experimental data to isotherm model equations, is to check the correlation coefficients. It is observed that the value of correlation coefficient R^2 for five models is greater than 0.97 while it is less than 0.85 for Langmuir in case of PAC as well as AC. However, the R^2 values are very close to each other in five isotherm models except Langmuir model. Thus it is very difficult to decide best model to represent the
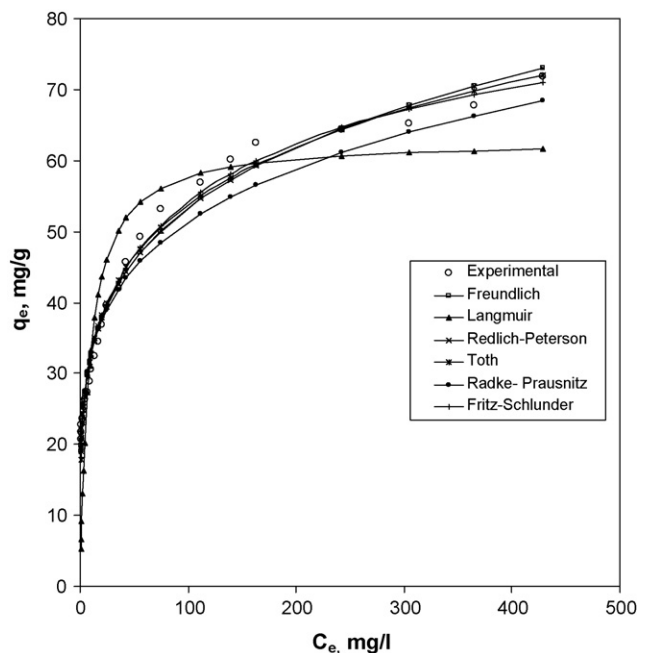

Fig. 9. Comparison of different isotherm models for p-cresol on PAC.

Table 7
Comparison of normalized deviation and normalized standard deviation for various isotherm models for both AC and PAC

S. no.	Adsorption isotherm model	AC		PAC	
		Normalized deviation	Normalized standard deviation	Normalized deviation	Normalized standard deviation
1	Langmuir	17.81	23.46	20.24	28.98
2	Freundlich	6.31	7.57	4.40	5.17
3	Redlich–Peterson	5.40	6.52	4.41	5.19
4	Toth	4.75	5.79	4.80	6.09
5	Radke–Prausnitz	4.78	6.20	5.32	6.05
6	Fritz–Schlunder	5.04	6.01	4.33	5.52

Table 8
Comparison of adsorption isotherm (Freundlich) for adsorption of *p*-cresol on activated carbon

S. no.	Author(s)	Freundlich adsorption isotherm $q_e = K_F C_e^{1/n}$		Surface area (m^2/g)	Adsorbate concentration (mg/l)	Temperature (°C)
		K_F (mg/g) (l/mg)$^{1/n}$	$1/n$			
1	Tanada et al. [8]	46.50	0.243	674.11	10–1000	25
2	Maurao et al. [9]	90.28	0.122	647.00	Upto 1000	30
3	Ayranci and Duman [21]	115.916	0.25	1464	10–40	30
4	Li et al. [22]	33.456	0.34	880	100–600	10–50
5	Li et al. [23]	13.462	0.395	880.2	100–500	10–30

experimental data on the basis of correlation coefficient R^2. A better criterion to test the goodness of fit of isotherm data is by normalized deviation and normalized standard deviation. Table 7 reports the normalized deviation and normalized standard deviation for all six models. In case of AC, the normalized deviation and normalized standard deviation are minimum for Toth model. In case of PAC, the minimum value of normalized deviation and normalized standard deviation are found for Fritz–Schlunder model and Freundlich model, respectively. On the other hand it is noteworthy that normalized deviation and normalized standard deviation both are quite high for Langmuir model. The aforementioned results show the poor agreement for Langmuir isotherm with experimental data on AC and PAC. Although the remarkable similarity is observed in the results of all five adsorption models, Freundlich, Redlich–Peterson and Fritz–Schlunder represent data more closely for adsorption on PAC, while Toth, Radke–Prausnitz and Fritz–Schlunder are more appropriate isotherm models for AC. These results support the fact that three parameter and four parameter models further minimize the error observed in two parameter models and hence give better representation of data. The slight difference in the values may be due to the nonlinear fitting procedure.

The magnitude of the Freundlich exponent $1/n$ is an indicator of the favourability of adsorption. For beneficial adsorption, n should lie between 1 and 10 [33]. Table 8 shows the value of $1/n$ obtained in various *p*-cresol adsorption studies on activated carbon in the literature. In all these studies the values of $1/n$ is greater than 0.1 and less than 1, giving the value of n less than 10. In the present study, the value of $1/n$ also lies between 1 and 0.1 for PAC as well as for AC (Table 6), indicating that adsorption of *p*-cresol is favourable on PAC as well as on AC. In the Langmuir isotherm, the constant b can also be used as an indicator of the favourablity of adsorption (or efficiency of adsorption process) through the determination of the dimensionless separation factor or equilibrium parameter R_L which is defined as $R_L = 1/(1 + bC_o)$ [16,34]. Here C_o is initial concentration of adsorbate (g/l), and b is Langmuir constant (l/g). This indicates the nature of adsorption as $R_L > 1$ (unfavourable), $0 < R_L < 1$ (favourable), $R_L = 0$ (irreversible), and $R_L = 1$ (linear). The values of R_L for all studies mentioned in literature regarding adsorption of *p*-cresol on AC are in favourable range (Table 9). In the present investigation, the values of R_L have been found to be below 1.0 for PAC and AC, showing that the adsorption of *p*-cresol on PAC and on AC is very much favourable under prevailing operating conditions.

Table 9
Comparison of adsorption isotherm (Langmuir) for adsorption of *p*-cresol on activated carbon

S. no.	Author(s)	Langmuir adsorption isotherm $q_e = \frac{Q_o b C_e}{1 + b C_e}$		Surface area (m^2/g)	Adsorbate concentration (mg/l)	Temperature (°C)
		Q_o (mg/g)	b (l/mg)			
1	Nouri et al. [7]	174.96	0.13	–	Upto 200	28
2	Maurao et al. [9]	196.56	0.147	647	Upto 1000	30
3	Moreno-Castilla et al. [11]	172	0.19	633	150	25
4	Wu and Tseng [12]	253.8	0.0106	1371	200	30
5	Ayranci and Duman [21]	207.36	1.722	1464	10–40	30
6	Haghseresht et al. [26]	174.96	0.957	–	35–100	28

4. Conclusion

In the present research work, the activated carbon was prepared by using the inexpensive and easily available noxious parthenium weed. The characterization of the activated carbon, prepared from parthenium, was done by standard methods. The characterization results suggest that parthenium based activated carbon (PAC) is an activated carbon with comparable characteristics. The batch removal of *p*-cresol from aqueous solution was investigated on parthenium based activated carbon (PAC) at different operating conditions and the results were compared with those obtained by using commercial grade activated carbon (AC). The adsorption of *p*-cresol was dependent on adsorbent surface characteristics, adsorbent dose, and *p*-cresol concentration in the aqueous solution. On conducting the experiments it was found that at lower concentrations of *p*-cresol (upto 500 mg/l), the difference in the percent removal of *p*-cresol by PAC and AC was not significant for same operating conditions of pH (6) and temperature (28 °C). The percent removal of *p*-cresol was observed maximum at pH of 6 for both PAC and AC. Therefore, further adsorption studies were carried out at pH of 6. The dose of PAC required for 92% removal of *p*-cresol was 10 g/l, while it was 6 g/l in case of AC at the same operating conditions ($C_o = 500$ mg/l, pH 6, temperature = 28 °C). Since the manufacturing cost of PAC is much lower than that of AC, the high PAC dose can be tolerated to remove *p*-cresol at the expense of its low cost. The kinetic studies revealed that the adsorption of *p*-cresol on PAC as well as on AC followed pseudo-first order kinetics, and the first order kinetic constant k_1 was 0.0017 min^{-1} for PAC and is 0.0050 min^{-1} for AC. Adsorption isotherm studies suggested that the Freundlich, Redlich–Peterson and Fritz–Schlunder models were appropriate isotherm models for *p*-cresol–PAC system. It was noteworthy that under certain numerical approximations, Redlich–Peterson and Fritz–Schlunder reduced to Frendlich isotherm within acceptable accuracy. Therefore, it was stated that the Freundlich isotherm may be used for *p*-cresol–PAC system.

AC is an expensive activated carbon and so regeneration is essential. In contrast to this, PAC is inexpensive activated carbon so regeneration is not necessary. Parthenium is a common weed in India and is easily available in the countryside at zero or negligible price. In view of aforementioned results, it is concluded that the PAC has excellent adsorptive characteristic and can be successfully utilized for the removal of *p*-cresol from industrial wastewater. Therefore, parthenium weed which is one of the major environmental concerns can be commercially converted into an adsorbent PAC for successful and economic removal of *p*-cresol from industrial wastewaters. The adsorption data may be useful for designing an economically cheap treatment process for the removal of *p*-cresol from industrial wastewater.

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