



Adsorption of para chloro meta xylenol (PCMX) in composite adsorbent beds: Parameter estimation using nonlinear least square technique

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ABSTRACT

Phenols and phenolics are considered to be potentially hazardous water pollutants. Para chloro meta xylenol (PCMX) is the major component of several disinfectants, produced commercially by internationally well-known pharmaceutical companies. Adsorption of PCMX in various combinations of adsorbents, both natural and artificial, has been studied. Specially, water hyacinth (*Eichhornia crassipes* [Mart] Solms-Laubach) was used as an adsorbent in combination with powdered activated carbon (PAC) and granular activated carbon (GAC). Prediction of PCMX adsorption capacities is important in design considerations. Various equilibrium adsorption isotherms have been studied using experimental data. Equilibrium was achieved after approximately 24 h. Five isotherm models, namely, Tempkin isotherm, Freundlich isotherm, Langmuir isotherm, Redlich–Peterson isotherm and Toth isotherm were studied and parameterized. Respective parameters for each of the models were estimated by the nonlinear *Levenburg–Marquardt* parameter estimation method, based on the χ^2 minimization. Model performance was ascertained using uncertainty analysis on both the parameters, k_1 and k_2 , for each of the five models. The models were simultaneously ranked. The Tempkin isotherm was ranked 1 in case of all the 3 samples with extremely low uncertainties on both parameters k_1 and k_2 . Depending on the nature of the sample and its range of concentration levels, isotherm model by Langmuir scored 2 in the ranking scale on 2 occasions out of 3 with low uncertainties on both k_1 and k_2 .

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1. Introduction

Water pollution by organic and inorganic chemicals is of great public concern. A typical group of organic chemicals that are considered as both unwanted by-products as well as raw materials in several industries is the phenols. Phenol and its corresponding substituted compounds are important environmental pollutants because of their toxic effects towards life in the aquatic environment even when present in small concentrations as demonstrated by Mbui et al. [1] and Polaert et al. [2]. Several potential sources of phenolic compounds have been widely used in industry and agriculture and this has led to the classification of phenol itself and 10 other substituted phenols by the United States Environmental Protection Agency (USEPA) as priority pollutants. Phenol is classified as a 'Class B' poison by the interstate commission, reported by Mbui et al. [1]. Phenolics are key components of the effluents from coke production, coal gasification, pharmaceuticals, pesticides, fertilizers, dye manufacturing, synthetic chemicals, pulp and paper

industries. According to the USEPA [3] maximum concentration level of total phenolic compounds in the treated industrial effluent and water supplies should be less than 1 $\mu\text{g}/\text{ml}$. The permissible limit of phenol and phenolics for the treated industrial effluents is 1 mg/l as mentioned by Central Pollution Control Board (CPCB), India [4]. Therefore it seems to be extremely important to remove the PCMX from water and wastewater before its transport and cycling into the natural environment. This in turn poses real challenges for the developing countries to evolve efficient techniques for their removal.

The specific objective of the work was to develop a relationship between the amount of PCMX adsorbed per unit amount of adsorbent and equilibrium concentration by using various concentrations of PCMX solutions. The adsorption behaviors were evaluated using some adsorption isotherm models. A number of well-known isotherm models (e.g. Tempkin isotherm, Freundlich isotherm, Langmuir isotherm, Redlich–Peterson isotherm and Toth isotherm) have been discussed that can successfully relate the experimental data. The parameters of five different adsorption isotherms were estimated using a robust nonlinear least square scheme, based on chi-squared minimization, established by *Levenberg* and *Marquardt*. The uncertainties on the estimated parameters were computed, along with the range of confidence limits. Later,

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Table 1
Details of the experiments for the batch study.

Expt #	Adsorbent used	Equilibrium time	Experimental result (Y = amount adsorbed (mg/100 ml of solution)/amount of adsorbent used (g); X = equilibrium PCMX concentration (mg/100 ml of solution))										
1	Powder activated carbon	23 h	X	0.025	0.033	0.037	0.077	0.141	0.228	0.252	0.351	0.451	0.686
			Y	0.121	0.281	0.393	0.565	0.702	0.756	1.009	1.093	1.230	1.345
2	Powder activated carbon	24 h	X	0.526	0.179	0.099	0.093	0.089	0.083	0.079	0.067	–	–
			Y	1.292	1.142	0.946	0.790	0.678	0.595	0.530	0.479	–	–
3	Water hyacinth:granular activated carbon = 4:3	24 h	X	0.178	0.291	0.409	0.407	0.445	0.524	0.728	0.75	0.916	1.05
			Y	0.049	0.084	0.14	0.168	0.21	0.294	0.277	0.282	0.368	0.381

these models were ranked according to their performance, based on minimum 2 . The overall performance of the models is tested statistically against sets of data from the analysis of PCMX concentration in the wastewater.

Batch experiments were conducted to characterize the PCMX (para chloro meta xylene) removal capacity of various combinations of commercial and natural adsorbents. Specially, water hyacinth (*Eichhornia crassipes* [Mart] Solms-Laubach) was used as an adsorbent in combination with powdered activated carbon (PAC) and granular activated carbon (GAC). The ensuing modified fibers appeared to be efficient adsorbent for different dissolved organic molecules in water. The main advantage of this natural adsorbent lies in its relative facile regeneration without a significant loss of its adsorption capacity, even after repeated use of up to three cycles. This has been reported by Sun and Wang [5] and Aloulou et al. [6].

2. Materials and methods

2.1. Experimental procedure

Water hyacinths were collected from a pond near Kolkata, India. Then it was thoroughly washed to remove mud and any other dirt particle. Then it was kept under the sun for 3–4 days till it became fully dry. It was cut into small cylindrical pieces by a pair of Teflon scissors.

Pretreatment of the adsorbents, including drying and chopping affected the adsorptive potential of the biomass. Experiments showed that dilute PCMX solutions reached equilibrium within 24 h. In the current study, we attempted to find an adsorbent material based on water hyacinth. So a series of adsorbent combinations (a mixture of water hyacinth, powdered activated carbon [PAC] and granular activated carbon [GAC]) with different compositions were prepared. Then the adsorption properties of these were examined.

The feed solutions of various strengths were prepared by mixing a known volume of PCMX solution with ultra-pure water. The experiments were carried out in 250 ml glass beaker. Adsorbents of known ratio and weight were taken into those glass beakers. The feed solutions of 100 ml volume were then added. All the equilibriums were obtained at the same and constant condition. The experiments were carried out in an incubator, keeping a constant temperature of 25 °C. After reaching the equilibrium in 23–24 h (approximately 12 experiments with 10 samples each of various feed concentration and adsorbent combination and quantity have been carried out to optimize the equilibrium time) those mixtures were filtered by Whatman 589² (125 mm) filter paper. The standard 4-amino-antipyrene method was chosen as the specific analytical technique to determine PCMX. 5 ml of this filtrate was taken to a 100 ml volumetric flask and volume was made up with ultra-pure water. These 100 ml solutions were transferred into a beaker. Then 2 ml NH₄Cl solution was added and then pH was

adjusted to 10 ± 0.2. After that, 2 ml each of 4-amino-antipyrene and potassium-ferricyanide solution was added. Then the intensity of the colour of the solution was measured by absorption spectra at 510 nm. A 330–900 nm wavelength spectrophotometer (Make: PERKIN ELMER, Model: PRECISELY LAMDA 25 UV/Visible) equipped with a standard 10 nm path length sample cell was used for absorption measurement. From the absorption intensity data, concentration of the solution was calculated using the standard curve. Table 1 shows the details of the experiments for the batch study for finding out the amount of adsorption for various dilutions of PCMX solution samples, along with the weight ratio of various adsorbents.

3. Theory and calculation

3.1. Adsorption isotherms

Much of the earlier work on the nature of adsorbents sought to explain the equilibrium capacity and the molecular forces involved. Adsorption equilibrium is a dynamic concept, which is achieved when the rate at which molecules get adsorbed on to a surface is equal to the rate at which they desorb. The physical chemistry involved may be complex and no single theory of adsorption has been put forward which satisfactorily explains all the systems. The capacity of an adsorbent for a particular adsorbate involves the interaction of three properties: the concentration C of the adsorbate in the fluid phase; the concentration C_s of the adsorbate in the solid phase and the temperature of the system [7–10].

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature [7].

3.2. Adsorption isotherm models

3.2.1. The Tempkin isotherm (Model 1)

Tempkin and Pyzhev [11] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions. The Tempkin isotherm has been used in the following form:

$$q = k_2 \log C + k_1 \quad (1)$$

Here q is the equilibrium solid phase concentration in mg per 100 ml per g of adsorbent and C is the equilibrium liquid phase concentration in mg per 100 ml. The constant k_1 is related to the heat of adsorption.

3.2.2. The Freundlich isotherm (Model 2)

The Freundlich expression assumes that the adsorbate concentration increases along with the concentration of adsorbate on the

adsorbent surface:

$$q = k_1(C)^{k_2} \quad (2)$$

In this equation k_1 and k_2 are the Freundlich constants. This expression is characterized by the heterogeneity factor, k_2 and so this isotherm may be used to describe various heterogeneous systems [12,13]. The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constant.

3.2.3. The Langmuir isotherm (Model 3)

The theory for Langmuir isotherms assumes a monolayer coverage of adsorbate over a homogenous adsorbent surface. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur and adsorption takes place at specific homogeneous sites within the adsorbent. In the following equation, k_1 and k_2 are the Langmuir constants:

$$q = \frac{k_1 C}{k_2 + C} \quad (3)$$

3.2.4. The Redlich–Peterson isotherm (Model 4)

Redlich and Peterson [14] have proposed an empirical equation, designated as the “three parameter equation”. This may be used to represent adsorption equilibria over a wide concentration range:

$$q = \frac{k_1 C}{1 + k_2 C^M} \quad (4)$$

Here $M \leq 1.0$. This equation reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration, and to the Langmuir isotherm when $M = 1$. Eq. (4) was used with $M = 0.2$.

3.2.5. The Toth isotherm (Model 5)

The Toth isotherm [15] is derived from potential theory and is applicable to heterogeneous adsorption. It assumes a quasi-Gaussian energy distribution. The equation is given as follows:

$$q = \frac{k_1 C}{(k_2 + C^t)^{1/t}} \quad (5)$$

where k_1 , k_2 and t are constants. Eq. (5) was used with $t = 0.9$.

3.3. Parameter estimation method

The nonlinear *Levenburg–Marquardt* parameter estimation method as described in Beck and Arnold [16] and Press et al. [17] was used to obtain the parameters in each of the five models described in Eqs. (1)–(5). In this method, we usually define a merit function chi-squared (χ^2), and determine the best-fit parameters by its minimization. The parameters are iteratively adjusted, due to nonlinear dependences, to minimize chi-squared in order to achieve a global minimum. We start with a set of trial values for the parameters to be estimated, which are gradually improved and the procedure is then repeated until χ^2 effectively stops decreasing. A sensitivity matrix was derived for the five models for the adsorption function (amount adsorbed/unit amount of adsorbent used versus equilibrium PCMX concentration) with respect to the parameters k_1 and k_2 .

The *sensitivity matrix* can be written as:

- For Model 1:

$$\frac{\partial q}{\partial k_1} = 1.0 \quad (1a)$$

$$\frac{\partial q}{\partial k_2} = \log C \quad (1b)$$

- For Model 2:

$$\frac{\partial q}{\partial k_1} = C^{k_2} \quad (2a)$$

$$\frac{\partial q}{\partial k_2} = k_1 C^{k_2} \log C \quad (2b)$$

- For Model 3:

$$\frac{\partial q}{\partial k_1} = \frac{C}{(k_2 + C)} \quad (3a)$$

$$\frac{\partial q}{\partial k_2} = -\frac{k_1 C}{(k_2 + C)^2} \quad (3b)$$

- For Model 4:

$$\frac{\partial q}{\partial k_1} = \left(\frac{C}{1 + k_2 C^M} \right) \quad (4a)$$

$$\frac{\partial q}{\partial k_2} = -k_1 \cdot \left(\frac{C^{(1+M)}}{1 + k_2 C^M} \right) \cdot \left(\frac{1}{1 + k_2 C^M} \right) \quad (4b)$$

- For Model 5:

$$\frac{\partial q}{\partial k_1} = \frac{C}{(k_2 + C^t)^{1/t}} \quad (5a)$$

$$\frac{\partial q}{\partial k_2} = -\frac{1}{t} \frac{k_1 C}{[k_2 + C^t]^{(1+(1/t))}} \quad (5b)$$

3.4. Evaluation of the five models

Inference about the nonlinear regression parameters require the evaluation of the following statistical parameters [18]:

1. The minimized chi-squared function, (χ^2), which is the least-squares measure of fit (the smallest χ^2 gives the best model). The χ^2 minimization is a useful means for estimating parameters even if the measurement errors are not normally distributed.
2. The uncertainties associated with the estimate of each parameter, formally termed as the standard error (σ). These are the square root of the error term covariance matrix C_{ij} of the fit. The closer this value is to zero, the better the fit.

When the method used to estimate the parameters is χ^2 minimization, there is a natural choice for the shape of the confidence intervals. If the confidence level and the degrees of freedom are known, the confidence interval ∂a for each of the fitted parameters can be computed as:

$$\partial a_1 \cong \pm \sqrt{\Delta \chi_v^2} \sqrt{C_{11}} \quad (6)$$

where $\Delta \chi_v^2$ are given in tables as functions of confidence levels and degrees of freedom (v). This relation is approximate and holds good when

- The fit is good.
- The error terms (*noise*) in the nonlinear regression model are normally distributed.
- The sample size is large.

Table 2
Parameter estimation and uncertainty analysis.

Sample	Model	k_1	k_2	d.f.	χ^2	$((\chi^2))$	Uncertainties on		Rank	95% confidence limits (k_1)		95% confidence limit (k_2)	
							k_1	k_2		Lower	Upper	Lower	Upper
ADRB1	1	1.4412	0.3460	8	6.3635	0.3934	0.0037	0.0014	1	1.4296	1.4528	0.3414	0.3506
	2	1.6300	1.0442	8	217.8541	1.000	0.0399	0.0274	4	1.5056	1.7543	0.9587	1.1297
	3	1.6769	0.1851	8	7.0906	0.4731	0.0248	0.0065	3	1.5995	1.7543	0.1647	0.2055
	4	0.3629	0.2007	8	690.5615	1.000	219.9534	654.3190	5	-684.6781	685.4038	-2037.6644	2038.0657
	5	1.7838	0.2129	8	6.7481	0.4359	0.0324	0.0083	2	1.6827	1.8849	0.1869	0.2389
ADRB2	1	1.6531	0.3941	6	11.5901	0.9282	0.0178	0.0077	1	1.5976	1.7087	0.3699	0.4182
	2	1.7294	0.8670	6	199.9912	1.000	0.0779	0.0305	2	1.4865	1.9723	0.7719	0.9621
	3	0.3629	0.2007	6	388.8946	1.000	0.0856	0.0892	4	0.0961	0.6296	-0.0771	0.4785
	4	0.3629	0.2007	6	489.3833	1.000	540.6232	2118.0153	5	-1683.3985	1684.1242	-6596.3203	6596.7216
	5	0.3629	0.2007	6	385.7939	1.000	0.0892	0.0883	3	0.0849	0.6408	-0.0743	0.4757
ADRB3	1	0.3629	0.2006	8	1.1468	0.0028	0.0031	0.0037	1	0.3531	0.3726	0.1889	0.2123
	2	0.3850	0.9240	8	1.4034	0.0058	0.0121	0.0981	3	0.3472	0.4228	0.6183	1.2297
	3	2.3721	5.2417	8	1.3384	0.0049	126.0131	318.9120	2	-390.0936	394.8380	-988.0041	998.4876
	4	0.4104	-0.1281	8	4.0930	0.1513	71.8360	267.3928	5	-223.3217	224.1425	-832.9183	832.6620
	5	1.2026	1.9784	8	1.5882	0.0088	5.9189	12.0456	4	-17.2318	19.6372	-35.5374	39.4943

3.5. Estimation of the noise

We know that,

$$\chi^2 = \frac{\sum (y - \bar{y})^2}{\sigma^2} \quad (7)$$

$$\Rightarrow \chi^2 \propto \frac{1}{\sigma^2}$$

Hence estimate of σ^2 is important in all model fitting technique that use χ^2 estimates.

In order to estimate the standard deviation of PCMX concentration data, we assume:

$$E(\sigma^2) = \frac{\int \rho(x) \cdot (x - \bar{x})^2 \cdot dx}{\int \rho(x) \cdot dx}$$

$$\Rightarrow E(\sigma^2) = \int_{\bar{x}-(1/2)}^{\bar{x}+(1/2)} (x - \bar{x})^2 \cdot dx$$

$$\Rightarrow E(\sigma^2) = \frac{x^3}{3} \Big|_{-1/2}^{1/2} = \frac{1}{12}$$

When the sample size is large, the Gaussian distribution can be approximated as a Poisson's and the mean is approximately equal to the variance. Thus,

$$E(\sigma^2) \approx \sigma^2$$

Thus, the value of σ is $1/\sqrt{12} = 0.288$. Now, each reported concentration level was an arithmetic mean of n number of reported data, each of which was an integer. The actual noise (population) was:

$$\text{noise} = \frac{\sigma}{\sqrt{n}}$$

Table 3
Residual concentrations (residual concentration = predicted concentration – measured concentration) corresponding to various isotherms.

Samples	Range of residuals				
	Model 1	Model 2	Model 3	Model 4	Model 5
ADRB1	+0.04 to +0.767	-0.622 to -0.086	-0.114 to +0.17	-1.135 to -0.112	-0.104 to +0.169
ADRB2	+0.217 to +0.711	-0.753 to -0.301	-1.029 to -0.388	-1.129 to -0.457	-1.033 to -0.382
ADRB3	-0.014 to +0.171	-0.082 to +0.039	-0.079 to +0.041	-0.052 to +0.114	-0.070 to +0.054

4. Results and discussion

Removal of chlorophenols from wastewater by biofilm and biofilm components has been reported in many literatures (Wang et al. [19]; Armenante et al. [20]).

Removal of PCMX by dried and dead water hyacinth is appealing. Wolverton and McKown [21] reports that the water hyacinth (*E. crassipes* [Mart] Solms-Laubach) is a large, free-floating, tropical aquatic plant. Water hyacinths grow most rapidly in water temperatures ranging from 28 to 30 °C and at a pH in the range of 4.0–8.0. They cease to grow when water temperature is above 40 °C or below 10 °C, and the pH range for growth is below 4.0. With these characteristics, the water hyacinth has become a major ecological and economic problem in this century in the tropics and subtropics. On many occasions it has been demonstrated that this weed is excellent for the removal of pollution for domestic wastewater. Abdel-Halim et al. [22] reports that the percent removal of lead was 100% by bone powder, 90% by active carbon, 80% by plant powder from water hyacinth and 50% by commercial carbon. A study by Kruatrachue and co-workers [23] demonstrates the phytoremediation potential of water hyacinth *E. crassipes*, for the removal of cadmium (Cd) and zinc (Zn). The accumulation of Cd and Zn in shoots and roots increased with the initial concentration and also with the passage of time. Plants treated with 4 mg/l of Cd accumulated the highest concentration of metal in roots (2044 mg/kg) and shoots (113.2 mg/kg) after 8 days; while those treated with 40 mg/l of Zn accumulated the highest concentration of metal in roots (9652.1 mg/kg) and shoots (1926.7 mg/kg) after 4 days.

PCMX is a major component of the very popular antiseptic called Dettol. The untreated effluent of the Dettol Plant may contain very high levels of PCMX. We have tried to make an attempt to remove this PCMX by physical adsorption using various combinations of natural adsorbents. Experiments have been carried out to obtain the adsorption equilibrium data to parameterize five popular isotherms. Table 1 shows the details of the experiments for the batch study for finding out the amount of adsorption for various dilutions of PCMX solution samples. Parameter estimation results

Table 4

Overall model performance.

Rank	Model 1	Model 2	Model 3	Model 4	Model 5
1	3	0	0	0	0
2	0	1	1	0	1
3	0	1	1	0	1
4	0	1	1	0	1
5	0	0	0	3	0

are given in Table 2 where the uncertainties and confidence intervals of each parameter are presented for each of the models for various samples. Models are ranked according to their performance in the nonlinear least squares fit and rated with their respective values of χ^2 (see Table 2). Table 3 gives the ranges of residual concentrations (defined as: *residual concentration = predicted concentration – measured concentration*) with respect to the five models tested. Table 4 gives the details of overall performance all five models.

Fig. 1a shows how the amount of PCMX adsorbed (per unit amount of adsorbent) varies with the equilibrium PCMX concentration from the sample ADRB1 with respect to each of the five models. The performance of Model 1 was best with a rank of 1 out of 5 based on the estimate of minimum χ^2 and quite low values of uncertainties on k_1 ($=0.0037$) and k_2 ($=0.0014$). The corresponding 95% confidence intervals were worked out with a χ^2 estimate for each of the parameters. The widths of the interval with regard to both model parameters look quite narrow. The confidence interval for k_1 ranged from 1.4296 to 1.4528, while that on k_2 varied from 0.3414 to 0.3506. In Fig. 1b residual concentrations are plotted against the equilibrium PCMX concentration. It did not show any serious departures from the model assumptions with the residuals ranging from +0.04 to +0.767. Models 2 and 3 had a similar regression trend with the residuals ranging from -0.622 to -0.086 (Model 2) and -0.114 to $+0.17$ (Model 3). However both of them showed higher values of χ^2 than Model 1. Models 4 and 5 had larger values of χ^2 and was preferentially discarded. Thus it could be concluded that Model 1 (based on the Tempkin isotherm) and the corresponding regres-

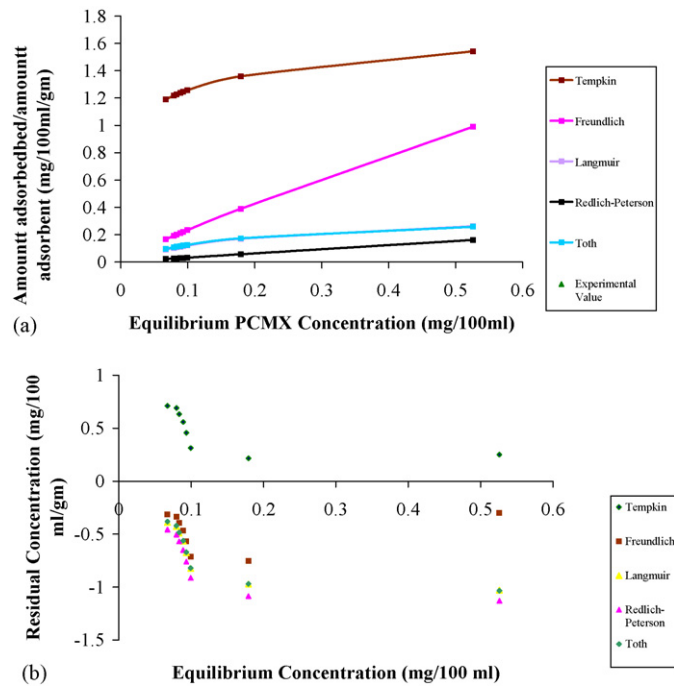


Fig. 2. (a) Comparison of different isotherm models for the sample ADRB2. (b) Plot of residual concentrations for different isotherm models for ADRB2.

sion function could be accepted for the concentration analysis of the PCMX sample ADRB1.

Similarly, Fig. 2a shows how the amount of PCMX adsorbed (per unit amount of adsorbent) varies with the equilibrium PCMX con-

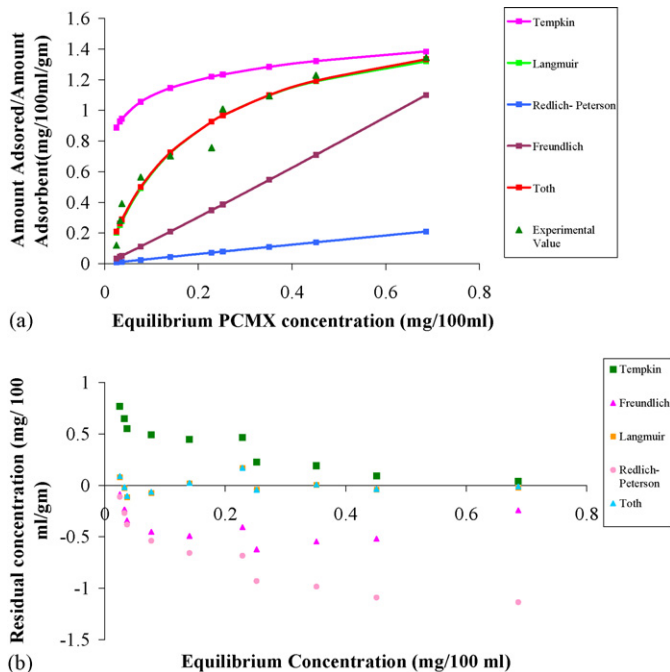


Fig. 1. (a) Comparison of different isotherm models for the sample ADRB1. (b) Plot of residual concentrations for the different isotherm models for ADRB1.

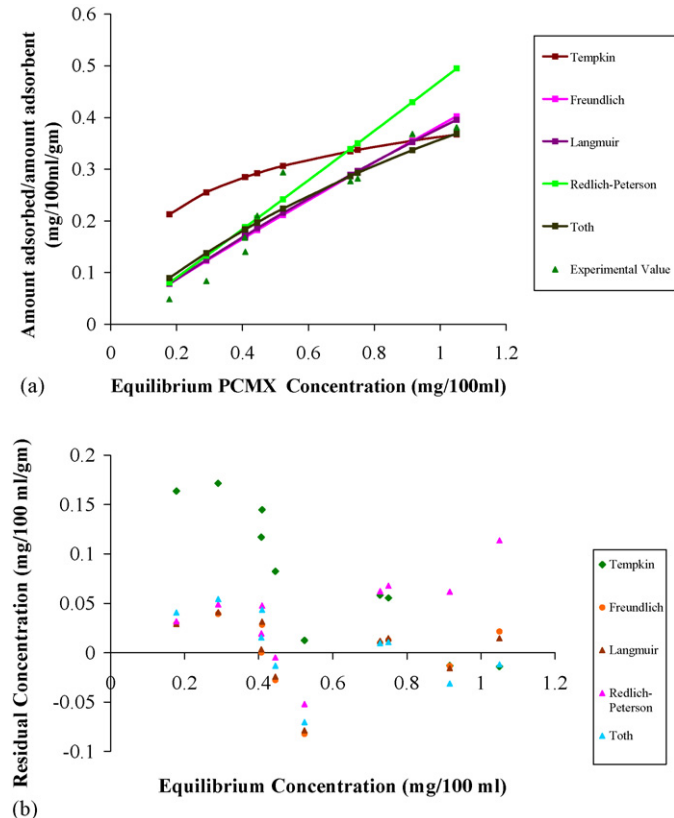


Fig. 3. (a) Comparison of different isotherm models for sample ADRB3. (b) Plot of residual concentrations for the different isotherm models for ADRB3.

centration from the sample ADRB2 with respect to each of the five models. Model 1 performed best, while Model 2 was ranked second. Fig. 2b did not show any serious departures from the model assumptions with the residuals ranging from +0.217 to +0.711. Fig. 3a gives the example of how the amount of PCMX adsorbed (per unit amount of adsorbent) varies with the equilibrium PCMX concentration from the sample ADRB3 with respect to each of the five models. For ADRB3 again Model 1 did best while Model 2 was ranked 3. Fig. 3b did not show any serious departures from the model assumptions with the residuals ranging from -0.014 to $+0.171$.

Thus from the analysis it could be concluded that for different strengths of PCMX samples Model 1 represents the best fitted isotherm. Now from the analysis it can be clearly seen that among the five models, almost in all the samples Models 1–3 have performed better, while the other models based on Redlich–Peterson isotherm and the Toth isotherm due to much larger values of χ^2 have been discarded. Depending on the nature of the sample and its range of concentration levels isotherm model by Langmuir did fit the data well on certain occasions. Model 3 (based on Langmuir isotherm) scored 2 in the ranking scale on 2 occasions out of 3 occasions with extremely low uncertainties on both k_1 and k_2 .

5. Conclusion

The equilibrium adsorption of PCMX by various combinations of adsorbents has been reported. Various well-known isotherm models and their respective parameters were estimated using nonlinear least square technique and the overall performance of the models was tested against sets of data from the experimental analysis. The water hyacinth appears to be very effective at removing the PCMX from the effluent. Equilibrium results have been modeled and evaluated using five different isotherms and the well-known *Levenburg–Marquardt* parameter estimation method, based on the χ^2 minimization. The Tempkin isotherm yields the best fit for all the samples, having performed better than Freundlich isotherm. Model 1 (based on Tempkin isotherm) was ranked 1 in case of all the 3 samples. Some agreement was observed between predicted Langmuir output and experimental data for the system considered. The basic assumptions of the extended Langmuir model, namely constant energy of adsorption, no interaction, and equal independent competition between species, appear not to hold perfectly true in this application. For all the samples, the models based on the Redlich–Peterson as well as Toth isotherms got the highest ranks

with much larger values of χ^2 as well as much higher ranges of uncertainties, hence they are discarded.

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