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Kinetic and Isotherm Studies on Biodegradation of Sugar Mill Waste Water Using *Mangifera Indica* Leaf Powder

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ABSTRACT

Waste water samples from sugar industry were collected and analyzed for biological oxygen demand (BOD) and chemical oxygen demand (COD). In the present study, *Mangifera indica* leaf powder was used for the treatment of sugar mill effluent. The kinetics of COD and BOD degradation were measured and fitted to several equations (zero-, first-, second-, diffusion, parabolic diffusion, simple Elovich and exponential equations). Two initial COD and BOD concentrations were 21216 mg/l and 9333 mg/l respectively and the observations were carried out for 8 hours. Even though zero-, second-, parabolic diffusion and exponential kinetics adequately describe the data, diffusion kinetics indicated the best model for describing the degradation of organic matter with high coefficient of determination (R^2 = 0.928 and 0.937 respectively for COD and BOD reduction). The data indicate that the prepared adsorbent surface sites are heterogeneous in nature and that fits into a heterogeneous site-binding model. Commonly used isotherms namely Freundlich and Temkin models were studied. The present system followed the Temkin isotherm model. The results supported that the *Mangifera indica* based bioadsorbent can be used to remove the excess organic waste from its contaminant sources.

Key words: parabolic diffusion model, simple Elovich model, exponential equation, Freundlich isotherm, Temkin isotherm.

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INTRODUCTION

Industrial revolution has generated unprecedented disturbances in the environment due to the introduction of anthropogenic pollutants such as organic, inorganic and xenobiotic chemicals in the form of untreated industrial waste water. With increasing population and industrial expansion, the need for the treatment and disposal of the waste has grown [1].

Studies of Nomulwar et al (2005) on the sugar factory effluents revealed that most of the parameters such as colour, odour, total dissolved solids, chemical oxygen demand, total alkalinity, pH, temperature, phosphate and sulphate have exceeded ISI limits. The effluents contain high amount of total hardness, total dissolved solids, biological oxygen demand (BOD) and chemical oxygen demand (COD). The effluent not only affects the plant growth but also deteriorate the soil properties when used for irrigation [2].

Adsorption is one of the most widely applied techniques for pollutant removal from contaminated media. The common adsorbents include activated carbon, molecular sieves, polymeric adsorbents, and some other low-cost materials. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems.

Adsorption as a primary treatment process offers effective and economical alternative, however adsorption of organic matter is slow and seldom reaches equilibrium [3]. The adsorbent that is used in practice remains activated carbon. However because of high cost of activated carbon, its use is sometimes restricted on economic considerations. Natural biodegradable waste materials from industrial and agricultural operations may have potential as inexpensive adsorbents. A range of products has been examined. These include Coir Pith [4], Bagasse Pith [5], Cassava Waste [6], Soya Cake [7] and Eucalyptus bark [8] just to mention a few.

In the past decades, several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature. Adsorption diffusion models are always constructed on the basis of three consecutive steps [9]: (1) diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion; (2) diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and (3) adsorption and desorption between the adsorbate and active sites, i.e., mass action. However, adsorption reaction models originating from chemical reaction

kinetics are based on the whole process of adsorption without considering these steps mentioned above.

At present, adsorption reaction models have been widely developed or employed to describe the kinetic process of adsorption [10-24]; however, there still exist some problems. For example, pseudo second order rate equation based on chemical adsorption was unsuitably employed to describe organic pollutants adsorption onto several non-polar polymeric adsorbents. This is essentially a process of physical adsorption [25]. In addition, Lagergren's [26] models were still widely applied to data modeling, though no adsorption mechanisms could be reasonably available.

The objectives of this study were to treat the sugar mill effluent using *Mangifera indica* leaf powder and to compare the suitability of different kinetic equations and to investigate the relationships between the parameters of the various equations.

MATERIALS AND METHODS

Adsorbate

The effluent samples for this study was collected every month from October 2010 to March 2011 from the effluent discharge stream of sugar mill. On the day of sampling, the samples were collected in 2 litre polythene can, once in 4 hour for 24 hour and mixed in equal proportions to get uniform homogeneous samples [27].

The bottles for sample preservation were thoroughly cleaned by rinsing with 8M Nitric acid solution followed by washing it with distilled water and finally with double distilled water. Then, the bottles were rinsed thrice with the effluent samples and the effluent samples were stored in a refrigerator at temperature approximately 4ºC, after adding the necessary preservatives. This is essential for retarding biological action, hydrolysis of chemical compounds and complexes and reduction of volatility of constituents. For COD, Sulphuric acid was added to bring pH to 2 and refrigerated. The mixed, homogeneous effluents were taken out from the refrigerator only at the time of analysis. These samples were used for analysis of BOD and COD using the methods of USEPA [28] and Young et al [29].

Adsorbent

The *Mangifera indica* tree leaves were collected from Periyakulam, Tamilnadu, India. They were gathered from twigs into clean plastic bags. Washed with triple distilled water and laid flat on clean table to dry. Dry leaves were grounded with grinder. After grounded, the leaf particles were sieved and stored into plastic bag by size, and ready to use. 40 mesh size of *Mangifera indica* leaf particles were used as adsorbent for these studies.

Adsorption Experiment

Adsorption experiments were conducted by varying contact time. The experiments were carried out in 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the required time period in a water bath shaker. The kinetics study was carried out by agitating 250 mL flasks containing 2 g of *Mangifera indica* leaf powder and 100 mL lead solutions in water bath shaker. The mixture was agitated at 120 rpm at room temperature. The contact time was varied from 0 to eight hours. At predetermined time, the flasks were withdrawn from the shaker and the reaction mixtures were filtered through Whatman filter paper No. 40. The isotherm study was performed. All the experiments were performed in duplicates. The filtrate samples were analyzed for COD and BOD. The percentage removal of organic matter from the waste water was calculated according to the following equation:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_f} \quad X\ 100$$

where C_i and C_f are initial and final COD and BOD.

Kinetics and Modeling

Zero Order Model

The zero order model is given by

$$C_s = C_{so} - k_0 t$$

Where

C_{so} - Initial substrate concentration, mg COD or BOD/L

C_s – Substrate concentration, mg COD or BOD /L

t - Degradation time, h

k_0 - Zero-order rate constant, h^{-1}

First Order Model

The first order model is given by [30]

$$- \frac{dC_s}{dt} = k_1 C_s$$

On integration between known limits, the model can be written as

$$\ln \left[\frac{C_s}{C_{so}} \right] = - k_1 t$$

where k_1 – first order rate constant, h^{-1}

Second Order Model

The typical second-order rate equation in solution systems is [31]

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$$-\frac{dC_s}{dt} = k_2 C_s^2$$

Equation was integrated with the boundary conditions of Cs = 0 at t = 0 and Cs = Cs at t = t to yield

$$\frac{1}{C_s} = k_2 t + \frac{1}{C_{so}}$$

where k_2 – second order rate constant, L $mg^{-1}h^{-1}$

Simple Elovich's Equation

A kinetic equation of chemisorption was established by Zeldowitsch [32] and was used given by

$$C_s = 1/\beta s \ln (\alpha_s \beta_s) + 1/\beta_s \ln t$$

where α_s – initial COD or BOD reduction constant, β_s – COD or BOD reduction rate constant

Exponential Model

The exponential model is presented as follows

$$C_s = at^b$$

where a - COD or BOD reduction magnitude constant ($L(mg^{-1}h^{-1})^b$), b – COD or BOD reduction rate constant

Adsorption Diffusion Models

It is generally known that a typical liquid/solid adsorption involves film diffusion, intraparticle diffusion, and mass action. For physical adsorption, mass action is a very rapid process and can be negligible for kinetic study. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or intraparticle diffusion, i.e., one of the processes should be the rate limiting step. Therefore, adsorption diffusion models are mainly constructed to describe the process of film diffusion and/or intraparticle diffusion.

Diffusional Model

The Diffusional model is given by

$$-\frac{dC_s}{dt} = k_D C_s^{0.5}$$

When integrated between the known limits, the above equation becomes

$$(C_s)^{½} - (C_{so})^{½} = -\frac{k_D t}{2}$$

where k_D = Rate constant for Diffusional model ($mgCOD^{0.5}/L^{0.5}\,h$)

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Parabolic Diffusion Model

The typical parabolic diffusion equation is given by

$$C_s = C_{so} + kpt^{0.5}$$

where k_p = Rate constant for parabolic diffusion model

Adsorption Equilibrium Study

It is important to evaluate the most appropriate correlations for equilibrium curves, to optimize the design of a sorption system. Freundlich and Tempkin isotherm models were used to describe the adsorption equilibrium.

Freundlich Isotherm

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of Freundlich isotherm may be represented as follows [33, 34]:

$$\log C_a = \log K_f + \frac{1}{n_f} \log C_e$$

where K_f (L/g) and $1/n_f$ are the Freundlich constants, indicating the sorption capacity and sorption intensity, respectively.

Tempkin Isotherm

Tempkin isotherm, assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent-adsorbate interaction [35]. The Tempkin isotherm has generally been applied in the following linear form [36]:

$$C_a = B \ln A + B \ln C_e$$

$$B = \frac{RT}{b}$$

where A (L/g) is Tempkin isotherm constant, b (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 J/mol K) and T the absolute temperature (K). A plot of C_a versus ln Ce enables the determination of the isotherm constants A, b from the slope and intercept.

Linear Regression Method

The coefficient of determination, R^2, was used to test the best-fitting kinetics and isotherm to the experimental data. The determination coefficient (R^2) is defined as the ratio of explained variance to the total variance.

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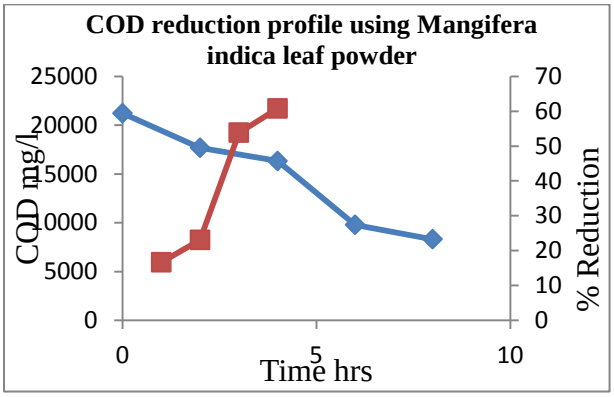
RESULTS AND DISCUSSION

The initial substrate concentration was 21216 mg/l for COD and 9333 mg/l for BOD. When the soaking time was 2 hours, the percentage reduction of COD and BOD were 16.67% and 24.99% respectively. There were increase in percentage reduction of COD and BOD (23.08% and 35.71%), when the soaking time was raised to 4 hours. 53.85 % of COD and 71.42 % of BOD were reduced after 6 hours. Maximum decrease of 60.78 % (COD) and 78.57 % (BOD) were observed after 8 hours. The percentage reduction of COD and BOD were tabulated in table 1 and depicted in figures 1 and 2.

Table 1 COD and BOD reduction profile using *Mangifera indica* powder

S.No.	Time hours	Percentage of reduction (%)	
		COD	BOD
1	2	16.67	24.99
2	4	23.08	35.71
3	6	53.85	71.42
4	8	60.78	78.57



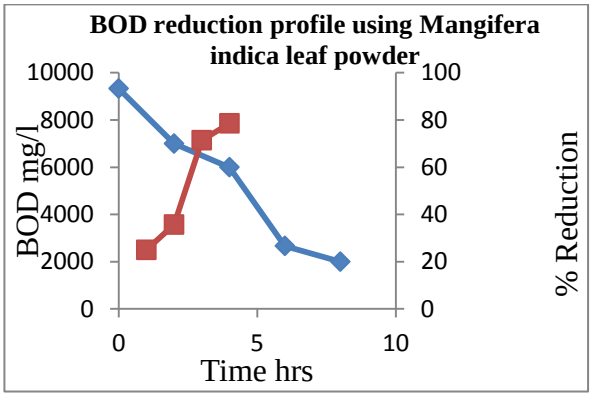
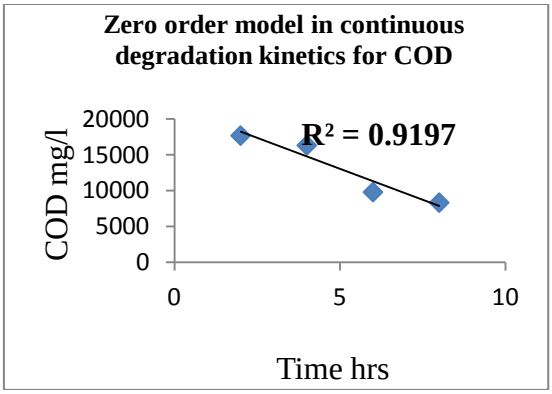


Figure 1 and 2 COD and BOD reduction profile using *Mangifera indica* powder



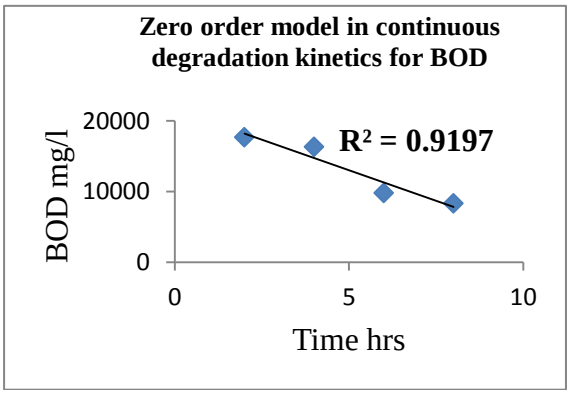


Figure 3 and 4 Zero order model in continuous degradation kinetics for COD and BOD

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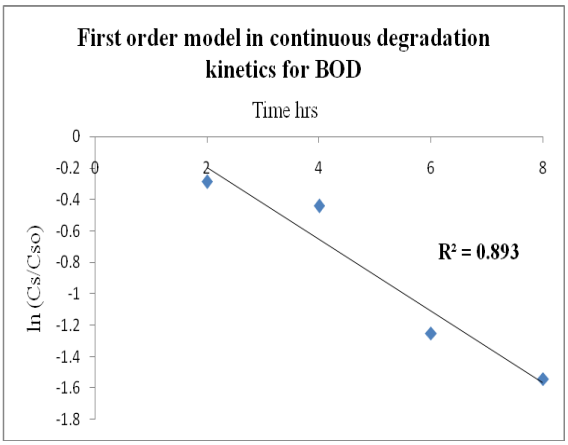


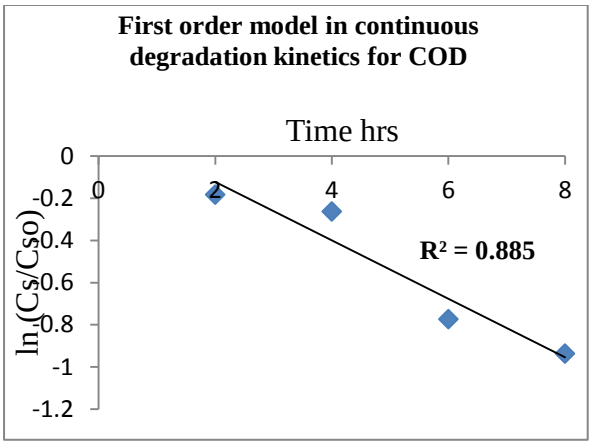
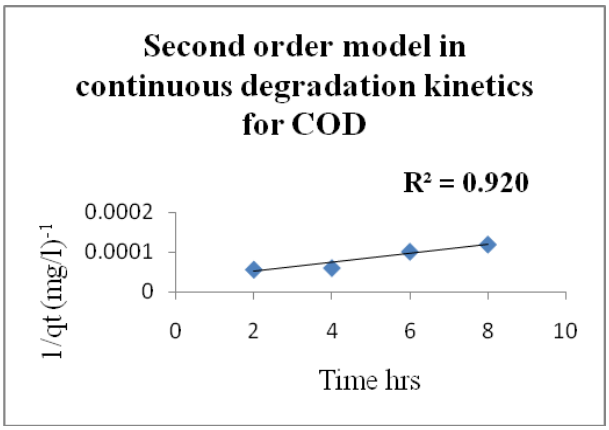


Figure 5 and 6 First order model in continuous degradation kinetics for COD and BOD



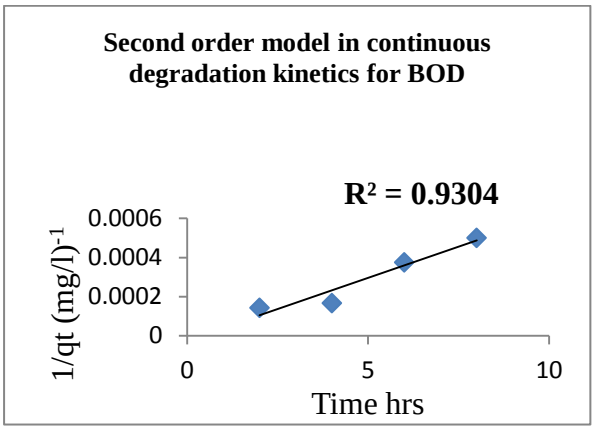
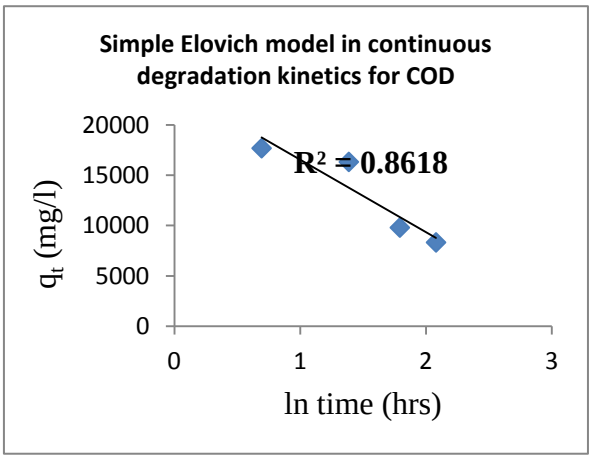


Figure 7 and 8 Second order model in continuous degradation kinetics for COD and BOD



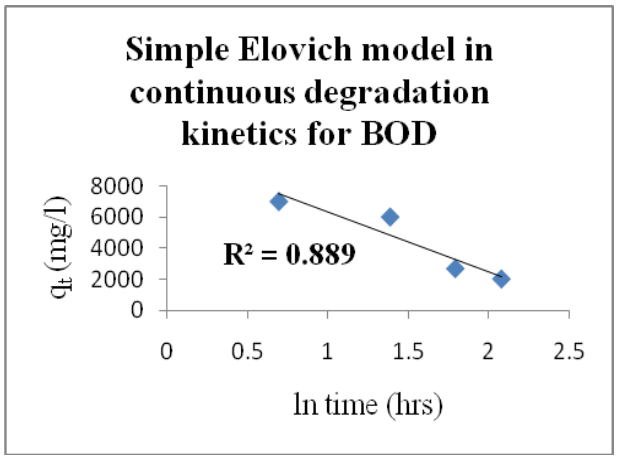


Figure 9 and 10 Simple Elovich model in continuous degradation kinetics for COD and BOD

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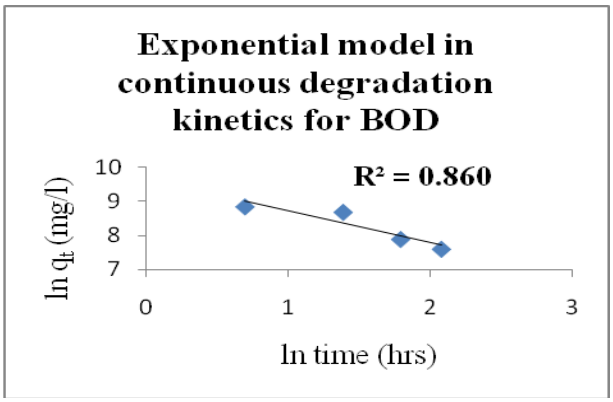


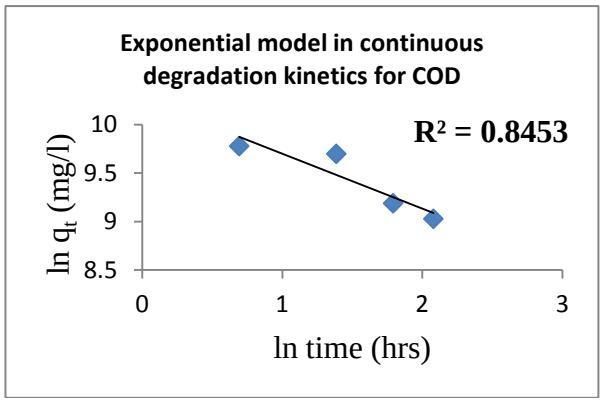
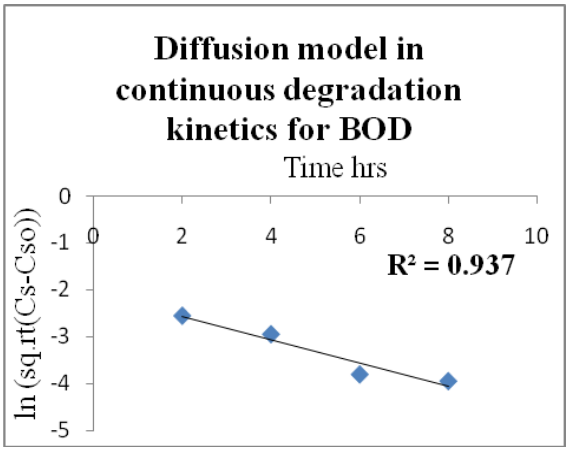


Figure 11 and 12 Exponential model in continuous degradation kinetics for COD and BOD



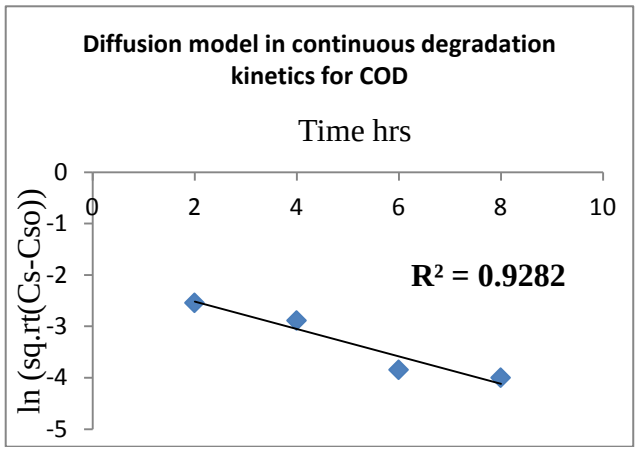
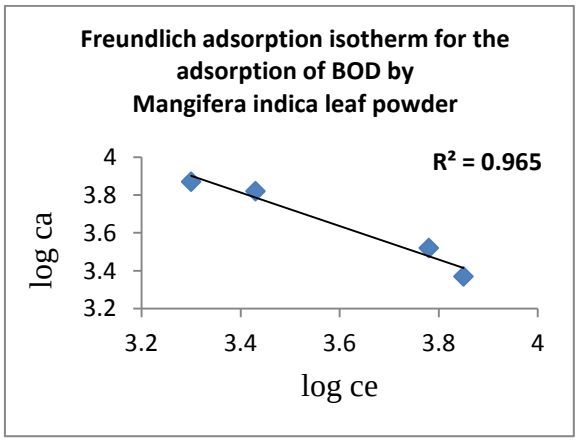


Figure 13 and 14 Diffusion model in continuous degradation kinetics for COD and BOD



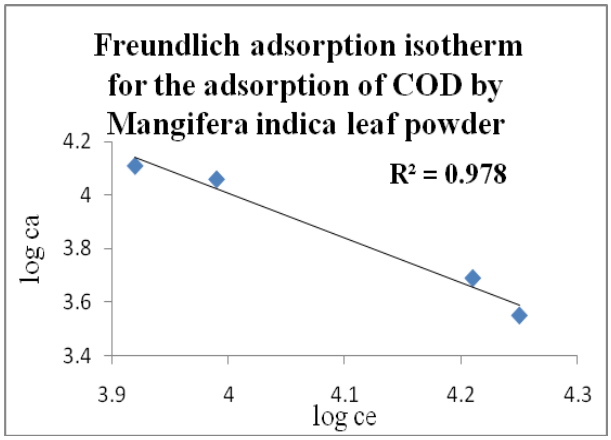


Figure 15 and 16 Freundlich adsorption isotherm for the adsorption of COD and BOD by *Mangifera indica* leaf powder

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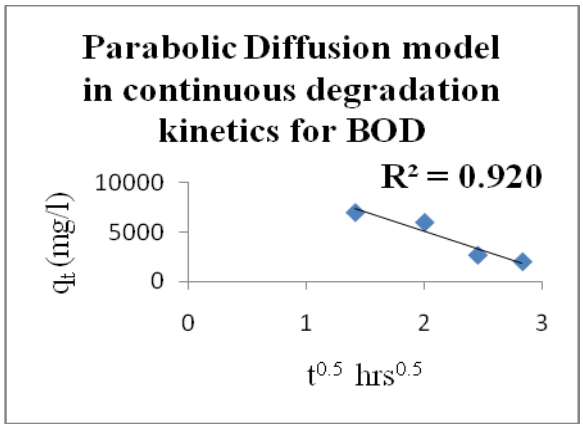


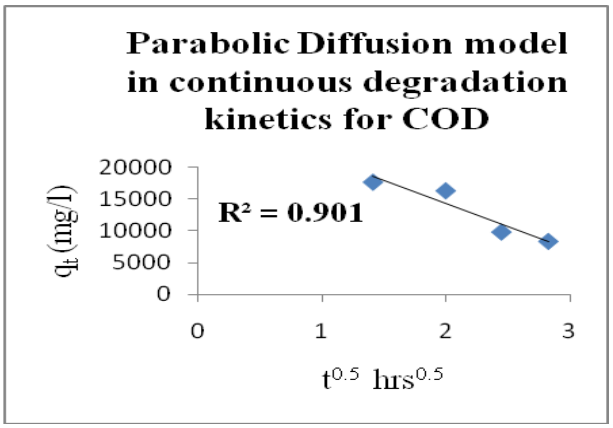
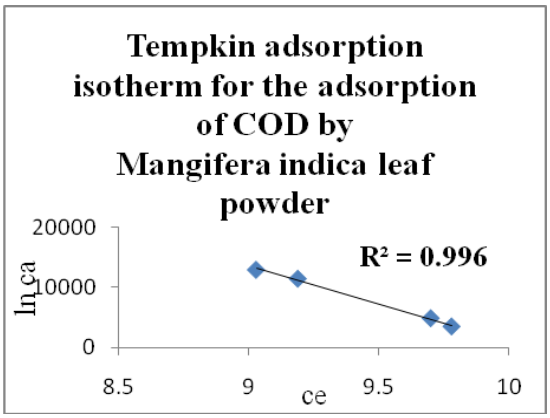


Figure 15 and 16 Parabolic diffusion model in continuous degradation kinetics for COD and BOD



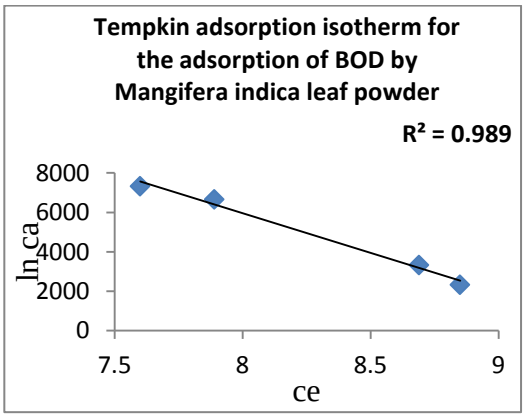


Figure 17 and 18 Temkin adsorption isotherm for the adsorption of COD and BOD by *Mangifera indica* leaf powder

Kinetic Studies

The rate constants and the determination coefficient (R^2) for zero-, first- and second-order equations, simple Elovich, exponential, diffusion and parabolic diffusion were presented in tables 2,3 and 4.

Sorption kinetics were poorly described by the zero-, first-, second-, simple Elovich, exponential and parabolic equations as indicated by low values of R^2 for COD and BOD compared to diffusional model (figures 3 to 16). The diffusional model best fits to represent the experimental data. This is clearly depicted in figure 11 and 12.

Several equations that provided a poor description of the data exhibited a systematic departure of data points from the fitted curves. High values for the coefficient of determination (R^2 = 0.928 and 0.937 for COD and BOD respectively) for diffusional model indicated that the best model for describing the data. The results obtained by Durai et al was in controversial to the present study where the best fit model was first order and not diffusional.

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Table 2 Rate constants obtained using different kinetic models

S.No.	Kinetic Models	Rate constant (K)	Parameters (COD and BOD)	Hours			
				2	4	6	8
1	Zero order	K L mg h^{-1} x 10^{3}	COD	1.77	1.22	1.90	1.61
			BOD	1.17	8.33	1.11	0.92
2	First order	K_1 L mg h^{-1}	COD	0.09	0.07	0.13	0.12
			BOD	0.14	0.11	0.21	0.19
3	Second order	K L $mg^{-1}h^{-1}$ x 10^{-6}	COD	-9.66	14.86	-26.33	-10.12
			BOD	-5.79	-20.26	14.22	11.80
4	Diffusion	K mg (COD or BOD)$^{0.5}$/$L^{0.5}$ h	COD	12.69	8.96	15.57	13.61
			BOD	12.94	9.57	14.99	12.97
5	Parabolic	K L mg h^{-1} x 10^{3}	COD	2.50	2.45	4.66	4.56
			BOD	1.65	1.67	2.72	2.59

Table 3 Reduction and rate constant for simple Elovich and exponential models

S.No.	Parameters (COD and BOD)	Hours	Simple Elovich model		Exponential model	
			ln α_s	β_s x10^{-3}	a	b
1	COD	2	14.39	0.09	12.27 x 10^{3}	0.46
		4	9.63	0.12	50.74 x 10^{9}	-10.80
		6	-12.11	-0.16	8.52	3.93
		8	8.84	0.36	78.43 x 10^{3}	-1.08
2	BOD	2	11.38	0.02	98.46 x 10^{3}	-7.10
		4	-11.31	0.08	4.00 x 10^{-5}	15.19
		6	-10.72	-0.49	4.71 x10^{2}	0.96
		8	12.68	0.69	8.09 x10^{2}	0.43

Table 4 Coefficient of determination for various kinetic models

S.No.	Kinetic models	COD	BOD
		R^2	R^2
1	Zero order	0.919	0.919
2	First order	0.885	0.893
3	Second order	0.920	0.930
4	Simple Elovich	0.861	0.889
5	Exponential	0.845	0.860
6	Diffusion	0.928	0.937
7	Parabolic	0.901	0.920

Table 6 Types of isotherm depending on the values of R_L

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

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Adsorption Isotherms

The equilibrium data has been analyzed by linear regression of isotherm model equations, such as Freundlich (figure 15 and 16) and Temkin (figure 17 and 18). The related parameters obtained by calculation from the values of slopes and intercepts of the respective linear plots are shown in table 5.

Table 5 Isotherm parameters obtained using the linear method for the reduction of COD and BOD using *Mangifera indica* powder

S.No.	Isotherms	Parameters	COD	BOD
1	Freundlich	K_f (mg/L)$^{1/n}$	5.25 x 10^{10}	6.55 x 10^{6}
		n	0.59	1.13
		R^2	0.978	0.965
2	Temkin	A (mg/L)	0.365	7.60
		b	0.209	0.651
		R^2	0.996	0.989

The present data fit Temkin isotherm model for which R^2 value for COD and BOD were 0.996 and 0.989 respectively. The Freundlich adsorption constants (K_f) obtained for COD and BOD from the linear plot was 5.25 x 10^{10} and 6.55 x 10^{6} respectively. The Freundlich coefficient (n), which should have values ranging from 1 to 10, is low (0.53 and 1.13), and that lowers the adsorption of organic matter onto the adsorbent. The linear plot for Temkin adsorption isotherm, which contains the features of chemisorptions, relatively described the present isotherm adsorption data. This indicated that the adsorption of organic matter onto the adsorbent might be happened by chemisorptions which were in controversial to the findings of Veeraputhiran et al [37].

The effect of isotherm shape can be used to predict whether an adsorption system is 'favorable' or 'unfavorable' using the following equation

$$R_L = 1/\ 1 + K_a C_o$$

Where R_L is a dimensionless separation factor, C_0 the initial COD and BOD concentration (mg/L) and K_a constant (L/mg). The parameter R_L indicates the isotherm shape accordingly as given in the table 6.

Table 6 Types of isotherm depending on the values of R_L

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present work, R_L values calculated for Temkin isotherm was found to be 129 x 10^{-6} and 14 x 10^{-6} for COD and BOD respectively which suggests the favorable adsorption of organic matter onto the studied adsorbent, under the conditions used for the experiments.

CONCLUSION

A simple and cost effective treatment procedure was proposed for the removal of organic matter through the adsorption on tree leaves. Adsorption is a strong choice for removal of organic waste from the wastewater. Maximum reduction of COD and BOD were 60.78% and 78.57% respectively. The kinetic and equilibrium data fitted well with Diffusion model and Temkin isotherm respectively indicating that the sorption system involved here is chemisorption. *Mangifera indica* leaf powder has showed high adsorption capacities and can be successfully be used for treatment of organic matter containing wastewater. Since this method involves less capital cost and is highly efficient it is practicably feasible for developing countries. The regeneration of leaves is not essential because, it is easily available material and also cost value is zero. The results of investigation will be useful for the removal of organic waste from industrial effluents.

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