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Adsorption studies on treatment of cooking oil mill effluent using crab shell chitosan

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ABSTRACT

In this research, the removal of pollution load from cooking oil mill effluent (sun flower oil, ground nut oil) was done using a naturally available biological adsorbent-crab shell chitosan of low molecular weight. The parameters which affect the pollutant load in the effluent are COD, TSS, TDS, TS and Turbidity. In these parameters, COD is having the major effect in the pollution load of the cooking oil mill effluent. Batch adsorption studies were done for the reduction of COD from the effluent by varying the chitosan dosage(2g-15g), pH (2-9), contact time (0.5hr-3hr), agitation speed (500rpm-1000rpm), adsorbent size (0.4mm-5mm). All the parameters were optimized graphically by conducting batch experimental runs. Studies on the kinetics of batch adsorption were done for the determination of equilibrium constants for predicting the best kinetic model among pseudo first order equation, pseudo second order equation, Elovich equation and fractional power model. Adsorption isotherms were also done for analyzing the process using equilibrium data to better understanding the system. Based on the experimental results, it was found that the maximum COD reduction of 86% were obtained using the crab shell chitosan as an adsorbent at optimized values of above parameters. From the research, it was found that the kinetics of adsorption in the reduction of COD was evidently fitting to pseudo first order kinetics.

INTRODUCTION

For many decades, the treatment of cooking oil effluent like palm oil, sunflower oil, groundnut oil, mustered oil, corn oil etc. is a major issue of environmental concern in developing countries like India, China, and Srilanka etc.

The waste water stream coming out from the processing plant of refineries make serious environmental effects which become great threats to aquatic and terrestrial life. It is due to the high organic and inorganic content present in the effluent. Hence its treatment is essential prior to its disposal .The choice of method used for the treatment of this effluent is based on the amount of organic and inorganic substance present in it and its discharge conditions [3, 4, 5].

There are many methods used for the treatment of the cooking oil mill effluent successfully. Great deals of literatures are also available on this research aspect. Studies tell that physiochemical and biological methods of treatment of cooking oil mill effluent is efficient. But still there is a chance of waste generation in it. So that it is a major challenge to be overcome by cooking oil process industries. The presence of fatty acids, aldehydes, alcohols, other organic materials and suspended impurities in the cooking oil effluent creates the toxicity and low pH in it [1, 3, 5, 7]. This serious environmental problem can be solved by adsorption using low cost biological adsorbents such as chitin and chitosan [8, 9].

The use of low cost chitin by many researchers had given successful results in the removal of metals, dyes and organic compounds from waste water [11, 12]. Recent research on the removal of anionic dyes with organic chitosan has been recorded a great achievement [9, 10]. The metal adsorption capacity of chitosan affects the distribution of acetyl groups present in the waste water. Another research illustrates the coagulation efficiency of chitosan with respect to the molecular weight of the main organic pollutant present in it [4, 7].

Considering all these applications of the biological adsorbents, the crab shell chitosan is newly recommended as a good adsorbent because of its excellent properties like biodegradability, biocompatibility, adsorption antibacterial property and non toxicity. It can be also used as a coagulant, bactericide and pollutant reducing agent for the removal of organics pathogens, suspended solids, turbidity, biological oxygen demand, chemical oxygen demand etc from the waste water. The main advantages of the use of crab shell chitosan for the treatment of cooking oil mill effluent as an adsorbent are its local availability, eco friendly nature and cost effectiveness [15]. We can make a meaning full change in the operating cost, efficiency and portability by selecting a suitable biological treatment method. Hence by this study, we are proposing a special attention on the comparison on the effluent treatment by batch process and continuous process (packed bed adsorption column) as future work.

Many researches are working on the reduction of pollution load in the waste water by using low cost, high efficient adsorbents. But no major studies are going for the removal pollution load in the cooking oil mill effluent. Therefore in this project we are carried out a multiple analysis of the treatment of cooking oil mill effluent by the usage of low cost crab shell adsorbent. The optimum values of pH, adsorbent dosage, adsorbent size, speed of agitation, mixing time to the best performance of crab shell chitosan were determined and the kinetic data are analyzed using various models and isotherms for better exploration.

EXPERIMENTAL SECTION

Crab shell of low molecular weight was obtained from the sea or market. It was dried and pulverized by using secondary crusher. Ex: Ball mill. For the pH adjustment of the adsorbent, it was treated by using 1M HCL and activated chemically by using $ZnCl_3$. The molecular structure of the crab shell chitosan is shown below.

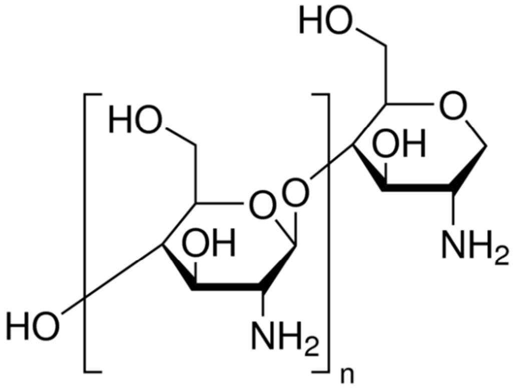

Figure 1: Structure of crab shell chitosan of low molecular weight

The waste water sample collected from the cooking oil refinery was stored at low temperature to avoid the bacterial action. The main parameters studied are COD, TDS, TSS, TS, and Turbidity. Chemical oxygen demand (COD) is defined as the amount of oxygen required to oxidize or degrade the organic and inorganic pollutants present in the given sample completely chemically. COD is measured by the oxidation of organic matters by a strong chemical oxidation which is equal to the amount of organic matters in the sample, and it was measured volumetrically in the analysis laboratory.

2.1 Adsorption Process and Experimental Condition

In the present work, the adsorption of the organic pollutants from the raw effluent sample was conducted by batch mode experiments for reducing COD. The process was performed by agitating 100ml of cooking oil mill effluent sample solution having an initial value of COD of 5504mg/l with the known amount of crab shell adsorbent.

Experiments were conducted to study the effect of various parameters in different ranges such as pH (2-12), Adsorbent dosage (5g/l-30g.l), Size of the adsorbent (0.4mm- 5mm), Agitation speed (0rpm-1200rpm), and Time (0.5hr-3hr). All the experiments were repeated after varying the temperature of the system by 30ºC, 40ºC and 50ºC. The influence of these parameters on the removal of COD from the cooking oil mill effluent were determined and optimized.

The amount of adsorption at time t, qt (mg/g) was calculated by

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

- C_0 = initial COD of the waste water sample (mg/l).
- C_t =final COD of the waste water sample at time 't'(mg/l).
- V = volume of the sample (ml).
- m = mass of the dry adsorbent used (g).

The percentage removal of COD from the effluent can be calculated by the formula

$$\text{Percentage of COD reduction} = \frac{C_0 - c}{c_0} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

3.1 Effect of pH removal of Organic matter

The pH of the cooking oil mill effluent is one of the most important factors controlling the adsorption process to remove the toxic pollutants [17, 18]. In this work we studied the effect of pH on the adsorption process by varying the pH level of the waste water sample from 2-12. From the experimental results, it was observed that the increase in the pH value enhance the removal of COD, Turbidity etc. This may be due to that number of positive charge on the adsorbent surfaces increases the attraction of negative charged molecules present in the effluent. The experimental results and graph shown in the figure 2gives that the optimum pH was 9 for this study.

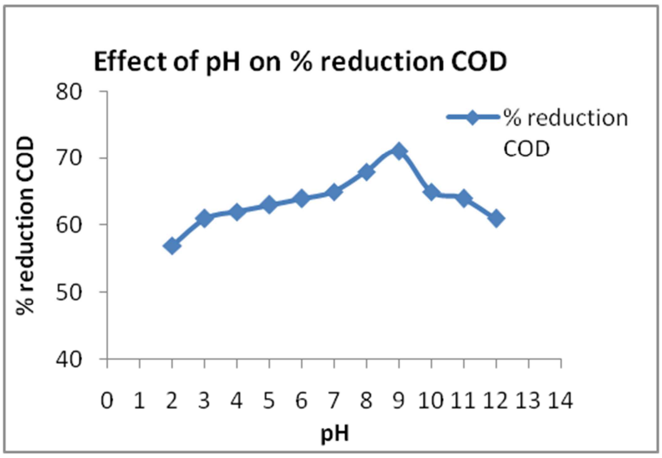

Figure 2: Effect of pH removal of Organic matter:

3.2 Effect of adsorbent dosage on removal of organic matter

In order to study the effect of adsorbent dosage on percentage reduction of COD from cooking oil mill effluent, the adsorbent dosage of the waste water sample was varied from 5 g/l – 30 g/l. The pH was maintained at its optimum value throughout the experiment. It was observed that the percentage reduction of COD increases with increase in adsorbent dosage for a given contact time. This is due to the fact that the increase in adsorbent dosage enhances the surface area and availability of more adsorption sites [21, 22]. The optimum adsorbent dosage was found to be 20 g/l.

3.3 Effect of agitation speed on removal of organic matter

Agitation is an important parameter in batch adsorption process. It increases the distribution of the solute in the bulk solution and the formation of the external boundary layer [19 20]. The experiments were performed to investigate the effect of agitation speed on the removal of various parameters by varying the speed of the agitator from 500 rpm to 1000 rpm. The experiments were conducted at constant pH and adsorbent dosage. From the result, it was observed that the agitation speed is directly proportional to the removal percentage and the optimum value is found to be 800 rpm.

3.4 Effect of particle size on removal of organic compounds

In adsorption process the size of the adsorbent is an important factor. The magnitude of adsorption is directly proportional to the surface area of the adsorbent, therefore we have got the good results by decreasing the effective diameter of the chitosan while performing the experiment [16, 19, 20]. The experiment was conducted at size range of the adsorbent from 5mm to 0.4mm (powder).At the end of the investigation, it was obtained that, fine powdered form of crab shell chitosan is suitable for the process.

3.5 Effect of contact time on the removal of organic compounds

In this investigation, it was concluded that the more time reacted the more organic compounds were removed. This experiment is conducted by varying the time from 30min to 4 hours. After further increase in time from 3 hours, there is no distinguishable change in the reduction of COD. As the result given in the figure 3, the optimum value of time for the batch reaction is 3 hours.

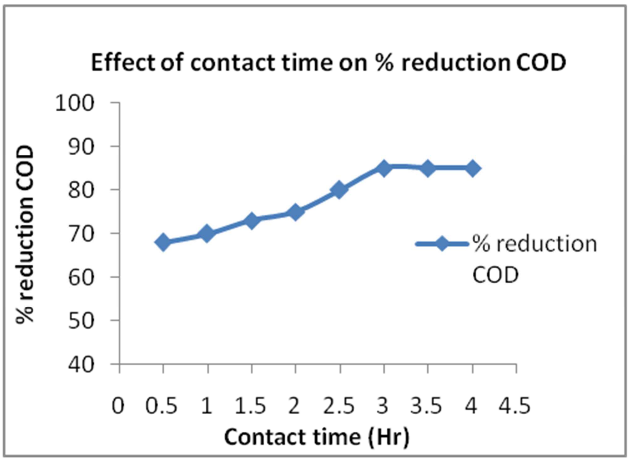

Figure 3: Effect of contact time on the removal of organic compounds

KINETICS OF ADSORPTION

4.1 Pseudo First Order Equation

The adsorption kinetics may be described by a pseudo first order equation. The linear first order equation is

$$\log(q_e - q_t) = \log\, q_e - \frac{k_1 t}{2.303} \qquad (3)$$

- q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t (hr) respectively.
- k_1- equilibrium rate constant of pseudo first order equation. (hr^{-1})

The slopes and intercepts of the plot of log (q_e-q_t) Vs time were used to determine the first order rate constant $k_1$and the equilibrium adsorption capacity. The results are presented in the **Table 1**. Since the theoretical q_e values found from the first order kinetic model has given reasonable values, the kinetics of adsorption of is taken as a pseudo first order mechanism.

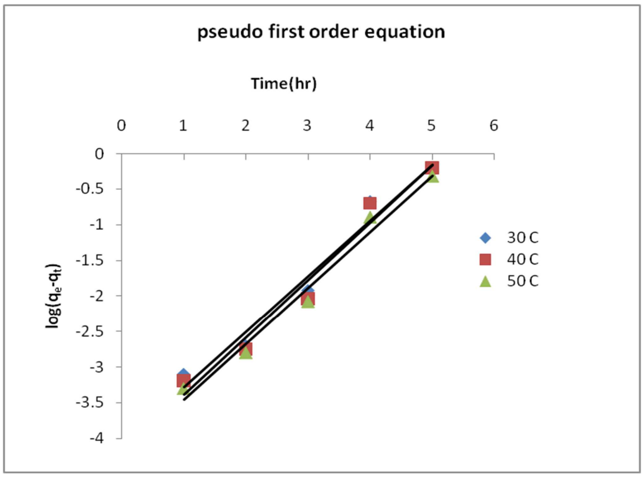

Figure 4: Determination of constants in pseudo first order equation

4.2 Pseudo Second Order Equation

The adsorption kinetics may be also described by pseudo second order equation. The linear pseudo second order equation is

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (4)$$

- q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t (hr) respectively.
- k_2 - equilibrium rate constant of pseudo second order equation (g/mg hr).

The slopes and intercepts of plot t/q_t Vs t were used to calculate the second order rate constant k_2 and q_e. The correlation coefficients R^2 for the second order kinetic model obtained were found to be 0.9 for all the adsorbents. The calculated q_e values also agree with the experimental data as exposed in the **Figure 5**. The regression coefficient $R^2$for this model is lesser than the pseudo first order kinetics. Hence it may not be used to explain the kinetics of this adsorption experiment.

4.3 Fractional Power Model

The adsorption kinetics can also be described by the power fraction equation. The linear fractional power equation is

$$\ln q_t = \ln k + \gamma \ln t \qquad (5)$$

- γ- power fuction constant
- k - constant
- t - time taken(hr)
- q_t - Adsorption capacity (mg/g) at time t (hr)

The plot $\ln q_t$ Vs ln t should give linear relationship from which γ and k can be calculated from the slope and intercept of the plot respectively [19-25]. This is shown in the **Figure 6**. Since the values of the rate constant for power function is high and the regression coefficient R^2 for the temperature 30 ° C is very low, then it was taken that the fractional power model does not correlate the experimental kinetic data.

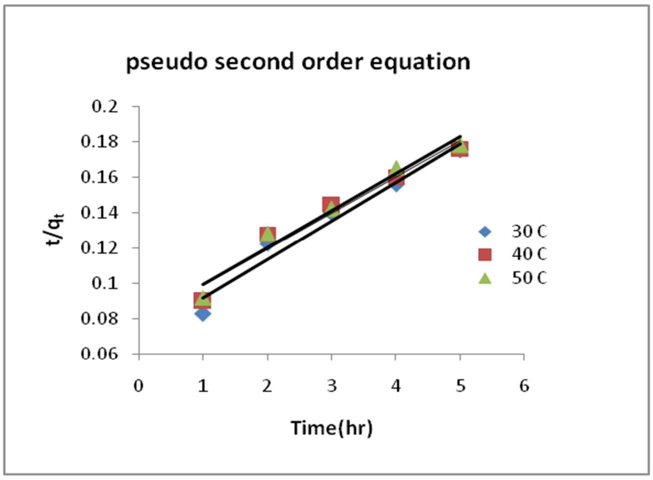

Figure 5: Determination of constants in pseudo second order equation

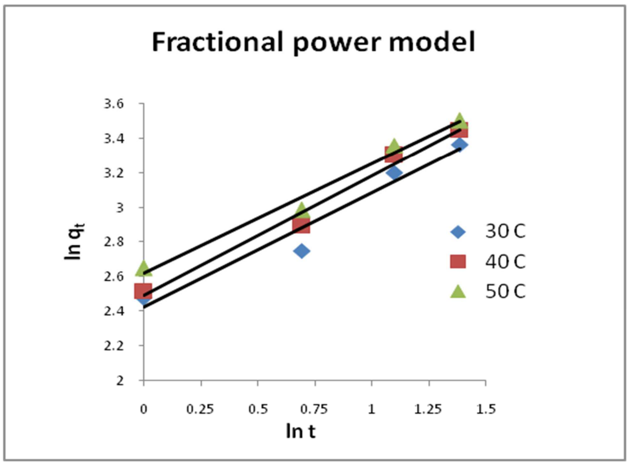

Figure 6: Determination of constants in Fractional power model

4.4 The Elovich Equation

The linear form of Elovich equation is used to describe the adsorption kinetics

$$q_t = \frac{1}{\beta} ln\alpha\beta + \frac{1}{\beta} \ln t \quad (6)$$

- q_t - Adsorption capacity (mg/g) at time t (hr)
- α - initial adsorption rate (mg/g).
- β is related to the extent of surface coverage and the activation energy for chemical adsorption (g/mg).

The linear relationship obtained between q_t and ln t [21, 22, 23] over the whole adsorption study is given in the **Figure 7**. The regression coefficient $R^2$for this model is lesser than the pseudo first order equation. Hence it may not be used to explain the kinetics of this adsorption experiment.

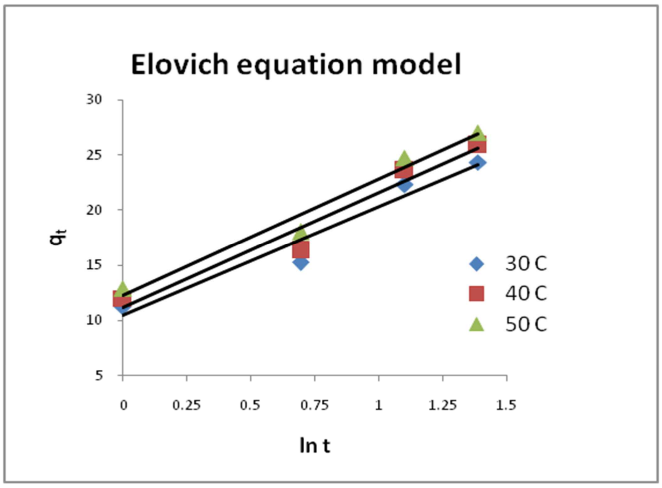

Figure 7: Determination of constants in Elovich model

When the calculated constants and parameters of various models were compared, it was observed that the pseudo first order equation proved the best correlation for all the batch adsorption experiments for the reduction of COD from cooking oil mill effluent, where the pseudo second order, fractional power model and Elovich equation did not give the best fit to correlate the kinetic data.

Table 1: Details of calculated constants and parameters for various models

Models	Parameters	At 30°C	At 40°C	At 50°C
Pseudo first order reaction	R^2	0.988	0.964	0.987
	K_1(g/mgmin)	0.182	1.890	1.823
	q_e(mg/g)	0.0301	0.0146	0.0142
	RMSE	9.133	6.722	6.722
Pseudo second order reaction	R^2	0.960	0.954	0.967
	K_2(g/mgmin)	5.79×10^{-3}	5.71×10^{-3}	5.71×10^{-3}
	q_e(mg/g)	50	50	50
	RMSE	4.213	3.352	2.739
Fractional power model	R^2	0.952	0.982	0.981
	K	1.15×10^{-3}	1.15×10^{-3}	1.15×10^{-3}
	N	0.602	0.601	0.600
	RMSE	3.743	4.792	5.526
Elovich model	R^2	0.946	0.952	0.970
	α	2.9×10^{-3}	2.98×10^{-3}	3.0×10^{-3}
	β	938	935	910
	RMSE	6.826	5.429	5.336

5. ADSORPTION ISOTHERMS

The analysis and design of adsorption process requires equilibrium data to understand the process. In the present investigation, the equilibrium data has been analyzed for various adsorbents using Freundlich and Langmuir isotherms.

5.1 Freundlich Adsorption Isotherm

The linear expression for the Freundlich adsorption isotherm is

$$q_e = k_f C_e^{1/n} \tag{7}$$

- q_e - adsorption capacity (mg/g) at equilibrium.
- k_f and n are Freundlich constants.
- C_e – COD of the solution at equilibrium.(mg/l).

The above equation can be linearized to a logarithmic form to determine the Freundlich constants. The values are given in the **Table 2**. From the values of k_f and 1/n, it is found that the isotherm is linear. The k_f parameter is a measure of adsorption capacity, which increases with increase in the efficiency of the adsorbent [14, 25, 26]. The Freundlich plot is given in the **Figure 8.**

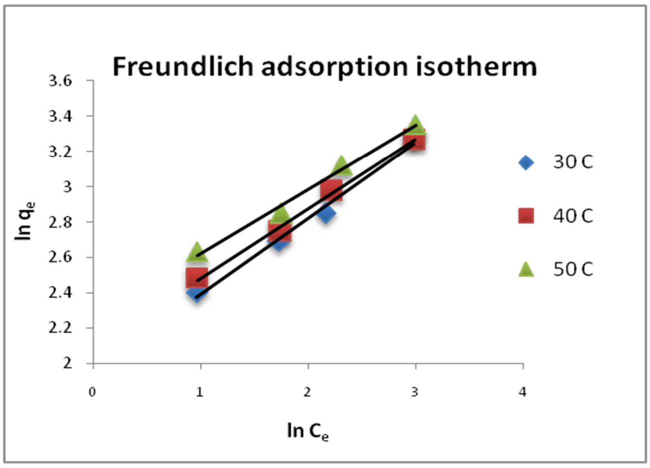

Figure 8: Determination of constants in Freundlich isotherm

From the table 2, it is clear that the determined Freundlich constants 1/n and k_f did not show linear variation with temperature. Hence it was concluded that the kinetic data did not relates to the freundlich adsorption isotherm.

5.2 Langmuir Adsorption Isotherm

The linear expression for the Langmuir adsorption isotherm is

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (8)$$

- q_e - adsorption capacity (mg/g) at equilibrium.
- C_e COD of the solution at equilibrium (mg/l).
- q_{max} - maximum adsorption capacity (mg/g).
- b - Langmuir constant.

The linear plot of Langmuir isotherm is given in the **Figure 9**. By using the constants, various parameters were calculated and tabulated. From those parameters, it is found that the Langmuir adsorption isotherm fits best to the kinetic data.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor or equilibrium parameter R_L [27, 28, 29, 30] which is defined as

$$R_L = \frac{1}{1+bC_0} \qquad (9)$$

Where, b is the Langmuir constant and C_0 is the initial COD of the waste water. The value R_L indicates the type of isotherm. To be reversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) or unfavorable (R_L>1). In our kinetic studies, the value of R_L was found to be less than 1 and greater than 0, representing favorable adsorption.

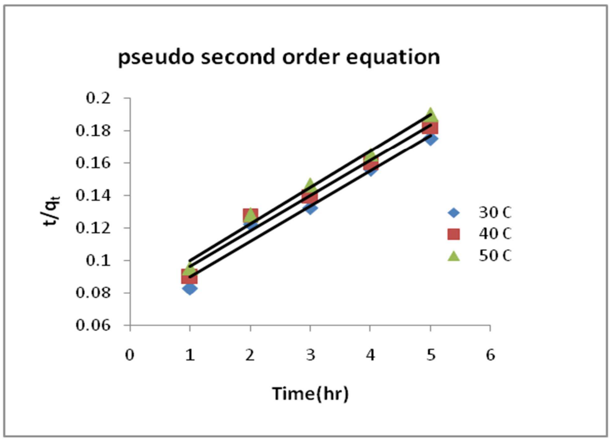

Figure 9: Determination of constants in Langmuir isotherm

Table 2: Details of calculated isotherms parameters and corresponding RMSE values

Parameters	**Adsorption Isotherms**					
	Langmuir			**Freundlich**		
	30°C	40°C	50°C	30°C	40°C	50°C
RMSE	4.396	4.323	4.318	6.198	6.199	7.210
R^2	0.998	0.983	0.938	0.992	0.966	0.990
q_{max}(mg/g)	33.33	33.33	32.25			
b(l/mg)	0.204	0.205	0.146			
k_f(mg/g)				8.27	8.149	8.50
1/n				0.415	0.419	0.395
Equilibrium parameter(R_L)	0.03	0.027	0.021			

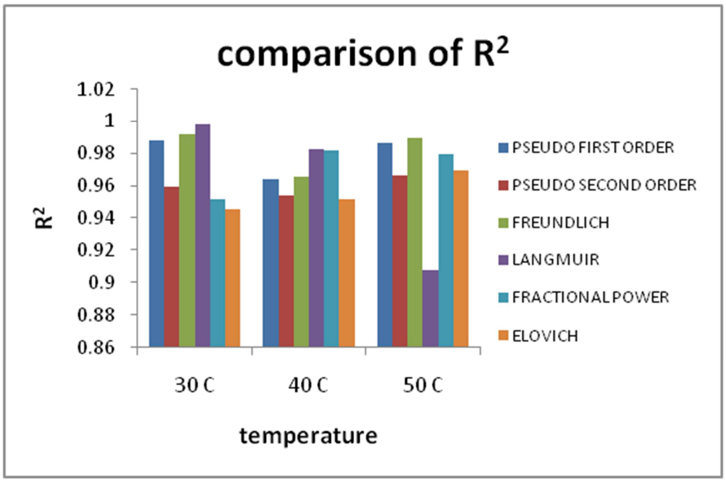

Figure 10: Comparison of R^2 for various kinetic models

CONCLUSION

Adsorption experiments were carried out using the low molecular weight crab shell chitosan for the removal of organic and inorganic pollutants from the cooking oil mill effluent. Experiments were done in batch mode of operations. In batch studies, the influence of various important parameters such as adsorbent dosage, adsorbent size, contact time, agitation speed and pH of the sample were studied. The experimental results show that the percentage reduction of COD increases with contact time, adsorbent dosage and agitation speed. And it was found that the optimum values for contact time, adsorbent dosage and agitation speed were 3 hours, 20 g/l and 800 rpm respectively. The percentage removal of COD decreases with the increase in adsorbent size. The percentage reduction of COD increases with pH of the system and the optimum pH value was found to be 9. This may be due to the counter ionic nature of adsorbent surface and the pollutant molecules and get increased when the pH is augmented. The maximum COD reduction percentage of 86% was obtained in this batch studies at the optimum conditions of the experimental parameters. The kinetics of adsorption of the effluent was studied using pseudo-first and second order kinetics, Fractional power model and Elovich equations. From the experimental results, it was observed that the kinetics of adsorption was appropriate to pseudo-first order kinetics. The equilibrium data was analyzed using Freundlich and Langmuir adsorption isotherms. And it was concluded that the equilibrium adsorption data was most appropriate to Langmuir adsorption model than Freundlich adsorption model.

Acknowledgements
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Symbols Used
b – Langmuir adsorption isotherm constant
C_0– Initial COD of the waste water sample (mg/l).
C_t– final COD of the waste water sample at time t (mg/l).
R_L- Separation factor or equilibrium parameter
q_e - Adsorption capacity at equilibrium (mg/g)
q_t - Adsorption capacity at time t (mg/g)
C_e - COD of the waste water sample at equilibrium.(mg/l)
$k_f$and n – Freundlich constants.
α - Initial adsorption rate (mg/g).
β - Extent of surface coverage and the activation energy for chemical adsorption (g/mg).
R^2- Regression coefficient
γ- Power fuction constant
R – Removal % of COD.
m – Mass of the dry adsorbent(g).
v – Volume of the waste water sample(l)

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