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Kinetics of COD and Dye Removal for Waste Water from Textile Industry

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Abstract: Water pollution poses serious threats to both the environment and the organisms that depend on their environment for survival. Due to the toxicity from dyes in textile wastewater, there is a dire need for the development of innovative and efficient treatment technologies. In this study treatability studies, using a electrochemical treatment (ECT) method followed by activated carbon (AC) based adsorption. ECT method was studied extensively for the treatment of reactive black dye. Moreover, to understand the practical applicability of ECTs, the findings were optimized for treatment of synthetic textile wastewater (STW).

I. INTRODUCTION

Industrial development has introduced a large amount of waste materials into the water bodies. This activity has been going on since a long and continuous discharge of wastewater of industries has drastically affected the ecosystem. In the race of development, countries are lenient in setting the permissible limits and permitted discharge limits of the wastewater. Among the various industries, textile industries have been growing at a higher rate and the discharge of dyes from these industries highly alters the chemical composition of the water and water becomes unsuitable for drinking purposes. Therefore, removal of toxicants from the wastewaters of the textile industries has become a crucial issue in various nations. Among the various types of industries, dye and textile industries have a huge impact on human health. These industries comparatively generate a larger amount of wastewater. Dyeing and finishing operations in this industry uses a large amount of organic compounds which are not easily degraded and are dumped into the water bodies. Among the numerous organic dyes, azo dyes and its pigments are most used as they are easily bound to synthetic as well as natural textile fibers. For an instance, the major problem with these azo dyes is their complex chemical structure due to which they are not easily degraded by microorganisms and they get accumulated in different food chains (Pagga and Brown, 1986). Therefore, they finally enter into bodies of living beings and affect their body. These complex compounds if enter in human body could cause carcinogenic effects. Moreover, there are several other organic dyes such as: benzidine and other aromatic compounds, which have been reported to cause carcinogenic effects (Calrke and Anliker, 1980). In intestine of living beings these complex compounds are degraded into their monomers i.e. amines, which could cause serious health issues. Therefore, it is required to develop some new innovative technologies so as to the treat the wastewater containing dyes. Since last few decades, legislations have been made stricter for the pollution control and investments have been made, in research and development, to design some novel techniques for the treatment of effluent of textile industries. However, further research is still required to provide efficient solution for the emanating issues of treatment of effluent originating from textile industries.

II. EXPERIMENTAL DESIGN

To develop a model emphasizing the relation between various factors was generated using a statistical approach. The operational parameters used for this analysis include, electric current passing through the electrodes, reaction time and initial pH of the reaction mixture.

There impacts on the response parameters were estimated. The response parameters chosen in the present study were percentage removal of COD and dye and amount of energy consumption.

The statistical approach adopted for this objective was a combination of a five-level central composite (CC) design and response surface methodology (RSM). Stat–Ease Design Expert (version 8.0.7.1) regression software was used for performing the statistical analysis.

This approach is comparatively better than a time consuming and labor demanding one variable at a time (OVAT) approach. Also, this approach was used to design experiments and generate models based on linear or quadratic relations between the operating and response parameters (Banerji and Chaudhari, 2016).

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III. ANALYSIS AND DISCUSSION

A. Kinetics of COD and Dye removal

The optimized conditions derived in this study, were further used for understanding the kinetics of the treatment process. For this objective, the kinetics of COD and dye removal were observed at optimized conditions of the operating parameters i.e., current = 14.17 mA/cm^2; t = 102 min and pH = 6.25. These experiments were conducted in two conditions i.e., at 30 ºC and 50 °C.

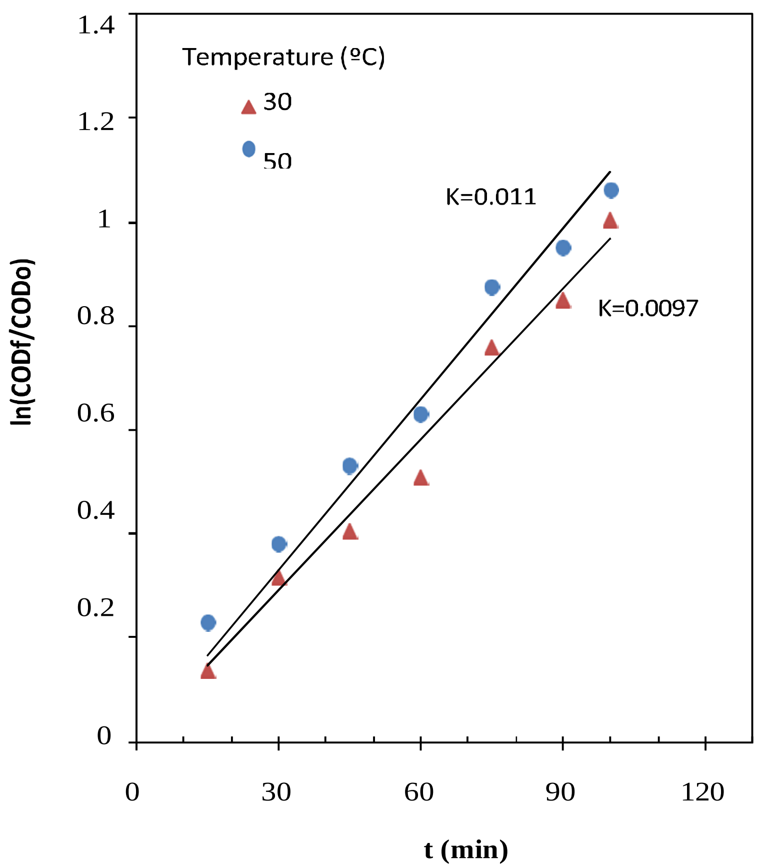
The findings of this analysis were assessed as per the first order kinetic equation, which can be defined using Eq. (1).

$$\frac{dC_At}{dt} = kC_A \qquad (1)$$

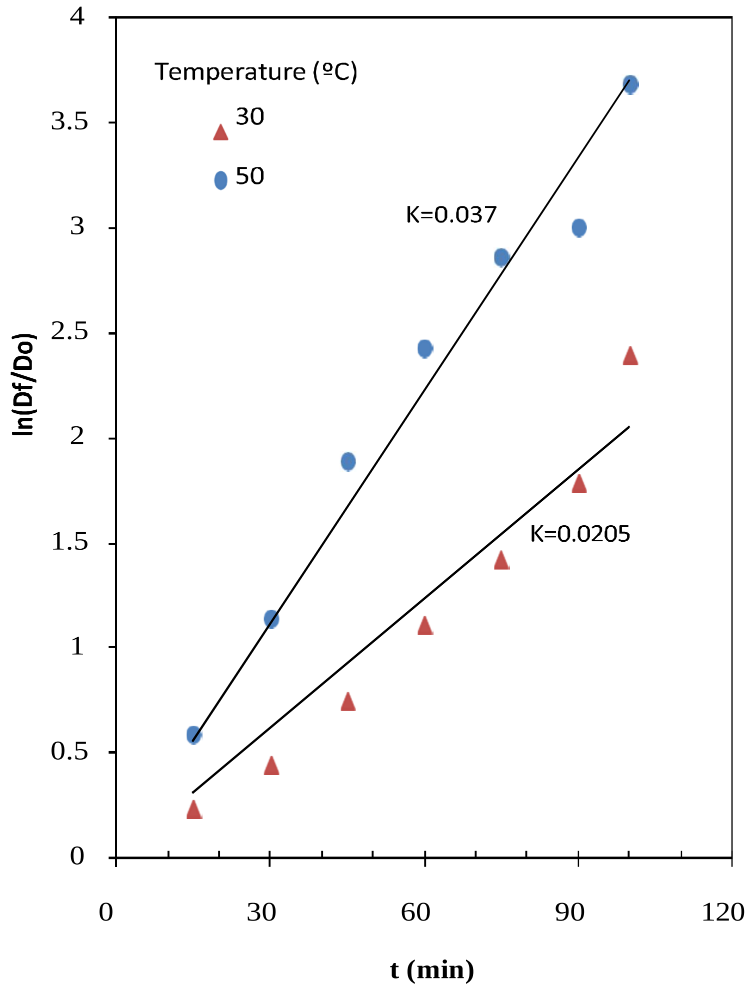
Where, C_A depicts the COD of the reaction mixture and concentration of dye and hence, dC_A will define the change in COD of the reaction mixture and change in the concentration of dye. Similarly, *dt* shows the change in the time i.e., time of the reaction; *k* is the kinetic constant.

The results of the kinetic studies are shown in Figure -1. From Figure - 1, it can be seen that kinetic plots for both the COD removal and dye removal were straight line graphs. Following these graphs the rate constant/kinetic constant i.e., value of k, was estimated for each type of parameter.

The plots showed that value of k for removal of dye and removal of COD was at 30°C was 0.0205 min^{-1} and 0.0097 min^{-1}, respectively. However, at 50°C the value of k for removal of dye and removal of COD was 0.037 min^{-1} and 0.011 min^{-1}, respectively. Thus, it can also be derived that reactions also depend on the temperature of the reaction mixture, as higher removal of COD and dye were reported at higher temperature.



(a)



(b)

Fig. 1 Findings of kinetic studies: a) for COD removal; b) for dye removal

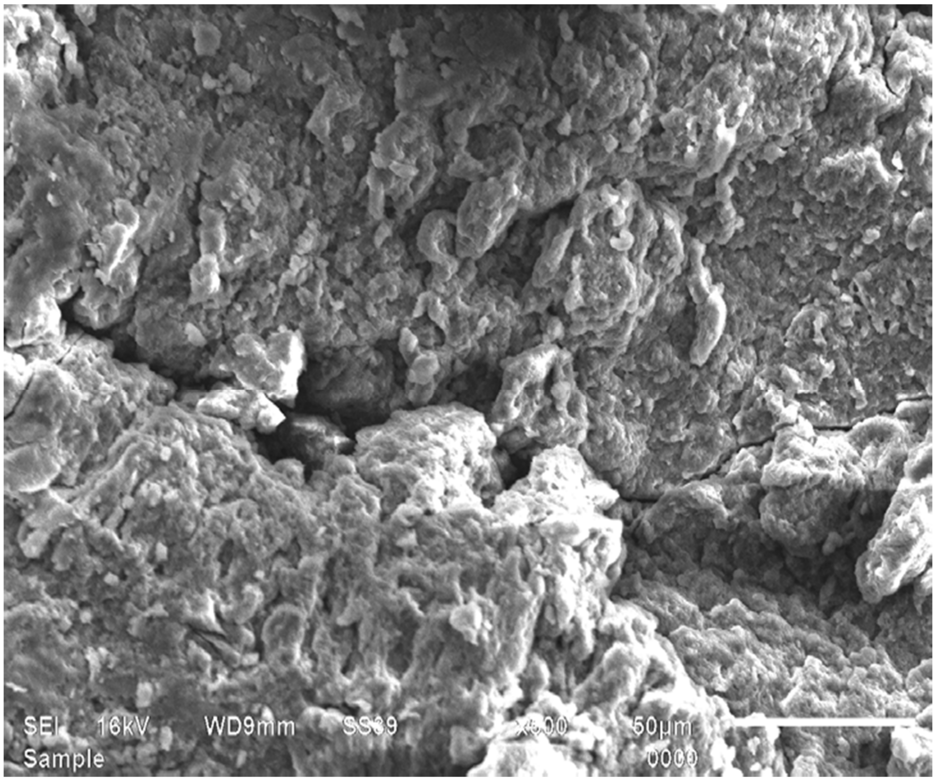
B. Physico-chemical Analysis of Residues

Two types of residues were generated during the ECT-based treatment of STW and these were scum and sludge. These two residues were examined using the SEM and EDX analysis. The images obtained from SEM analysis of the residues are shown in Figure 2.

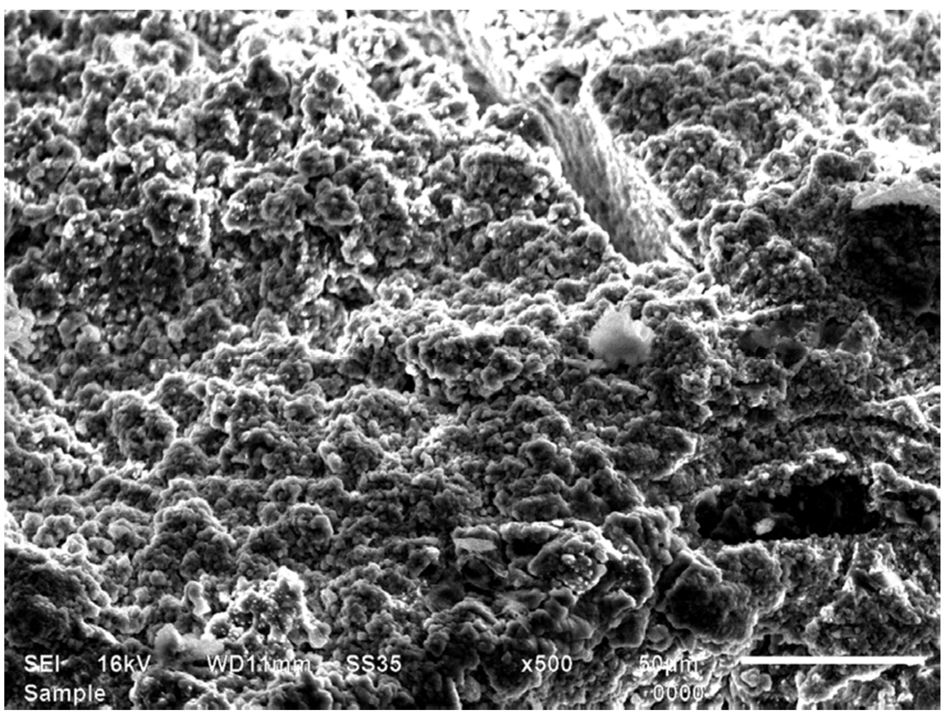
From Figure 2, it can be seen that the texture of both the residues is different. The sludge was observed to have harder texture as compared to scum. However, scum was observed to be puffy, as passing of hydrogen gas from cathode, could have produced bubbles on its surface. Further, both the types of residues were examined using EDX machine.

The findings of EDX revealed that the order of concentration of different elements in the sludge was in the order of: C (45.47%) > Cu (23.66%) > Zn (21.39%) > Al (5.46%) > Fe (2.12%) > Cl (1.89%). Similarly, the concentration of different elements in case of scum was in the order of: Na (36.51%) > C (23.02%) > Cl (20.06%) > O (14.95%) > Al (0.46%). Therefore, it can also be implied that the concentration of carbon was more in sludge as compared to scum. Further, aluminum mass balance was estimated for the processes during which residues i.e., sludge and scum were generated and its results are shown in Table 1

After the treatment process, the STW was observed to have 25.12 mg/l of aluminum and as per EPA 0.2 mg/L of aluminum is prescribed for drinking purposes. The COD of treated STW was observed to be 1152 mg/L and as per Indian standards this treated STW still couldn't directly be disposed into the water bodies. Therefore, further treatment of the STW using activated carbon-based adsorption is advised.



(a)



(b)

Fig. 2 SEM images: (a) sludge; (b) scum.

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Table 1 Findings of Al mass balance calculation

Total AL (input)	
Al in STW (mg/l)	2.03
Total AL in STW (g)	0.339
Al introduce by erosion of electrodes (g)	2.6925
Total Al in reaction mixture (g)	3.0115
Total Al remained in reaction systeme	
Sludge (g)	9.3
Total Al (sludge) (g)	0.50778
Scum (g)	1.1
Total Al (scum) (g)	0.06006
Al (treated STW) (mg/l)	25.12
Total Al (treated STW) (g)	2.512
Total Al (residues + treated STW) (g)	3.07984
% Error	-2.43

C. *Adsorption of Electrochemically Treated STW*

The STW treated using ETC was further treated using adsorption process. Activated carbon was used as an adsorbent and 250 ml conical glass flask was used as a reaction chamber. 100 ml treat STW was poured into the reaction chamber and initial pH of the STW was set. Afterwards, 5-40 g/l of the activated carbon (AC) was added in the reaction chamber. The reaction chamber was then kept on a temperature controlled shaker at 150 rpm and 30 ºC for 22 h. pH of the reaction chamber was adjusted between 2 to 10. After the completion of reaction time, the samples were collected from the STW and analyzed for estimating the COD. The % removal of COD was also assessed as per the Eq. (2).

$$\% \, COD \ removal = \frac{(COD_i - COD_f)}{w} \times V \qquad (2)$$

Where, $COD_{i/f}$ depicts the initial and final COD of the reaction chamber. V is the volume of the STW and *w* is the mass of the adsorbent used during the process.

Isotherms were also plotted for the treatment process. Initial COD of the reaction mixture was adjusted from 300 to 1152 mg/L. During these reactions, pH and concentration of AC were optimum. Langmuir isotherm was adopted to represent the adsorption equilibrium.

After completion of each reaction, the STW was collected and analyzed for estimating the equilibrium COD_e. The equilibrium adsorption uptake, q_e, was calculated using the Eq. (3).

$$q_e = \frac{(COD_i - COD_f)}{w} \times V \qquad (3)$$

The best fit of the isotherms were estimated on the basis of the Chi-square error analysis. This analysis compares the experimental and calculated values

D. Effect of Initial pH and Dosage of AC

Initial pH of the reaction mixture and dosage of AC are two of the parameters that significantly impact the adsorption based treatment of STW. The impacts of initial pH and dosage of the AC are shown in Figure 3

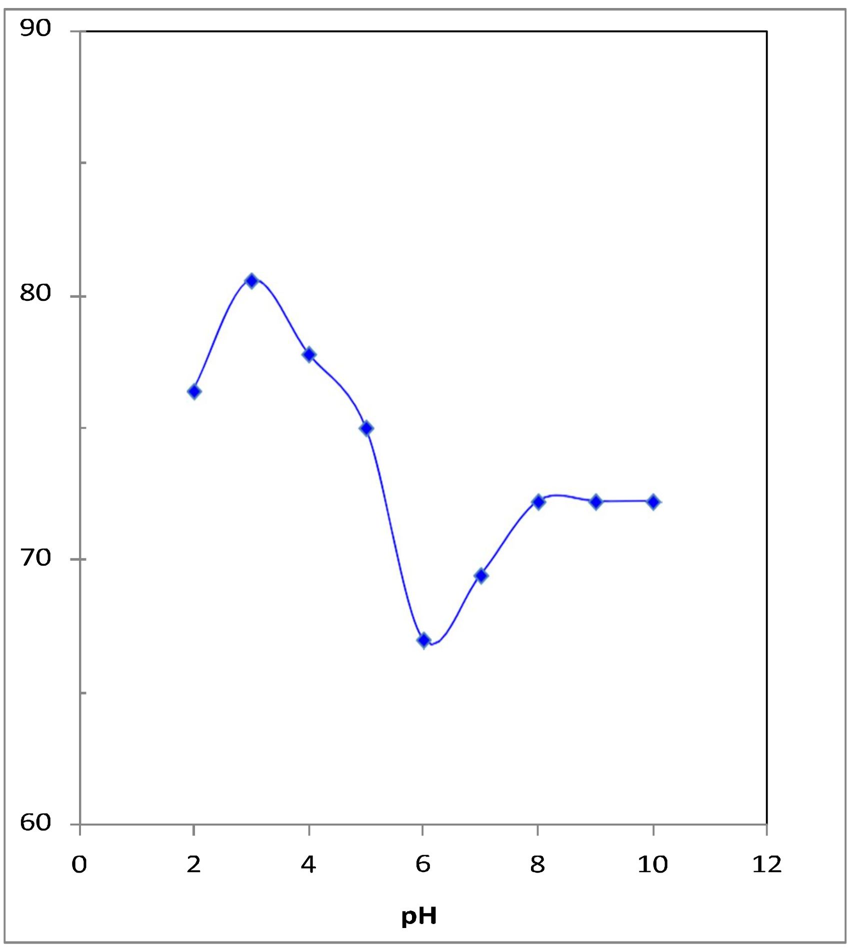
From Figure 3a, it can be implied that the initial pH had distorted impact on the COD removal of the STW. At pH = 3, the maximum removal of COD was observed i.e., 80.56%. After it, the removal started decreasing and lowest removal of COD was observed at pH =6. After pH = 6, the removal of COD increased upto 72.22% at pH = 8. Afterwards, the removal of COD was constant and didn't show much change.

The impacts of dosage of AC on the adsorption based treatment of STW are shown in Figure 3b. From Figure 3b, it is evident that with the increase in dosage of AC, the removal of COD increased up to certain dosage i.e., 35 g/l, after which the curve was almost stagnant.

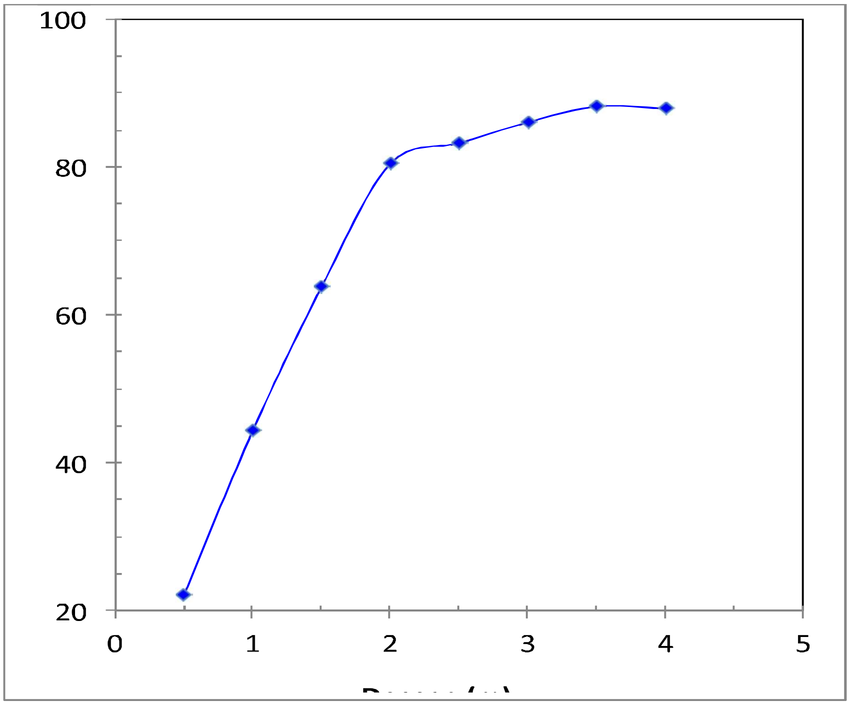
With the increase in dosage of AC, more surface area was available for the contaminants to adsorb to. However, after a certain dosage this surface area was completely filled and it had no more efficiency to adsorb the contaminants. Therefore, ≥ 35 g/l, dosage of AC was identified as the most appropriate for the decontamination of the STW.

E. Isotherm Modeling

The findings of the isotherm analysis depicted that its results fits the Langmuir isotherm the most. Moreover, the predicted and experimental values of the Langmuir isotherm were also observed to be significantly related with each other. It is also evident from the findings of the R^2 and Chi^2, i.e., 0.95 and 1.43, also showed that the results are substantially correlated and adequate for use. The Langmuir isotherm plotted in this way, showed that the parameters K_L and q_m were found to be 0.00004 l/mg and 4509.02 mg/g, respectively. The value of q_m was observed to be very high which denotes the high affinity of the adsorbent and adsorbate.



a. Effect of initial pH



b. Effect of AC dosage

Fig. 3. Effects of (a) initial pH; (b) AC dosage, on adsorption

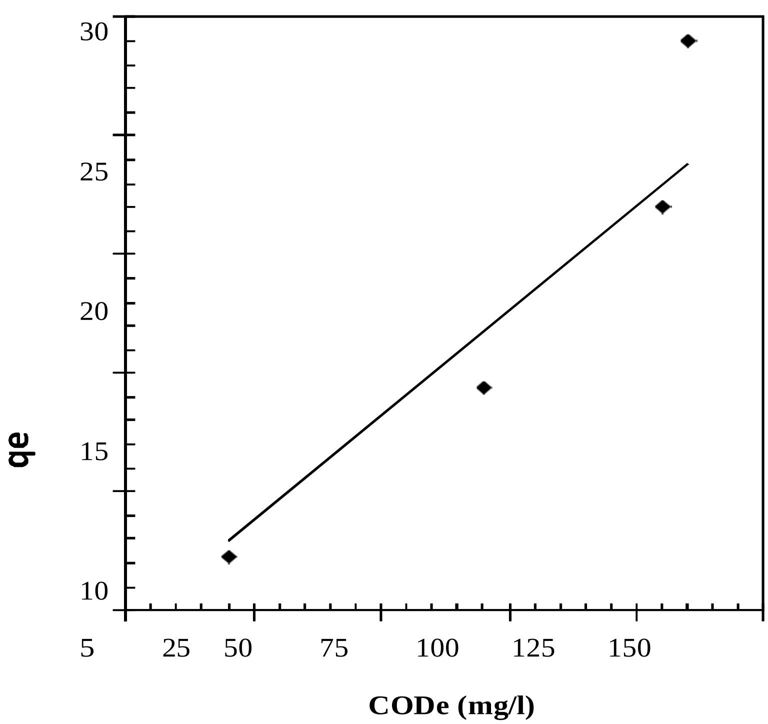


Fig. 4. Equilibrium adsorption isotherms at 30 °C

IV. CONCLUSION

A. Kinetic studies showed that EC based treatment of STW followed first order kinetics and the kinetic constants at 30°C for each response parameter i.e., % COD removal and % dye removal were 0.0205 min^{-1} and 0.0097 min^{-1}, respectively. Similarly, at 50°C the kinetic constants for % COD removal and % dye removal were 0.037 min^{-1} and 0.011 min^{-1}, respectively.

B. Amount of Al in the treated STW, sludge and scum was observed to be 25.16 mg/l, 0.50778g and 0.06006 g, respectively.

C. At optimum conditions the values of the operating parameters i.e., pH, adsorbent dose and time, were observed to be 3, 35 g/L and 22 h.

D. At the optimum conditions of the operating parameters 88.28% COD removal was observed.

E. Isotherm analysis showed the Langmuir isotherm fits the best to the adsorption process, with $R^2 \sim 1$.

F. For Langmuir isotherm, the values of K_L and q_m were observed to be 0.00004 l/mg and 4509.02 mg/g, respectively. Moreover, high value of q_m depicted that the adsorbate had higher affinity for adsorbent.

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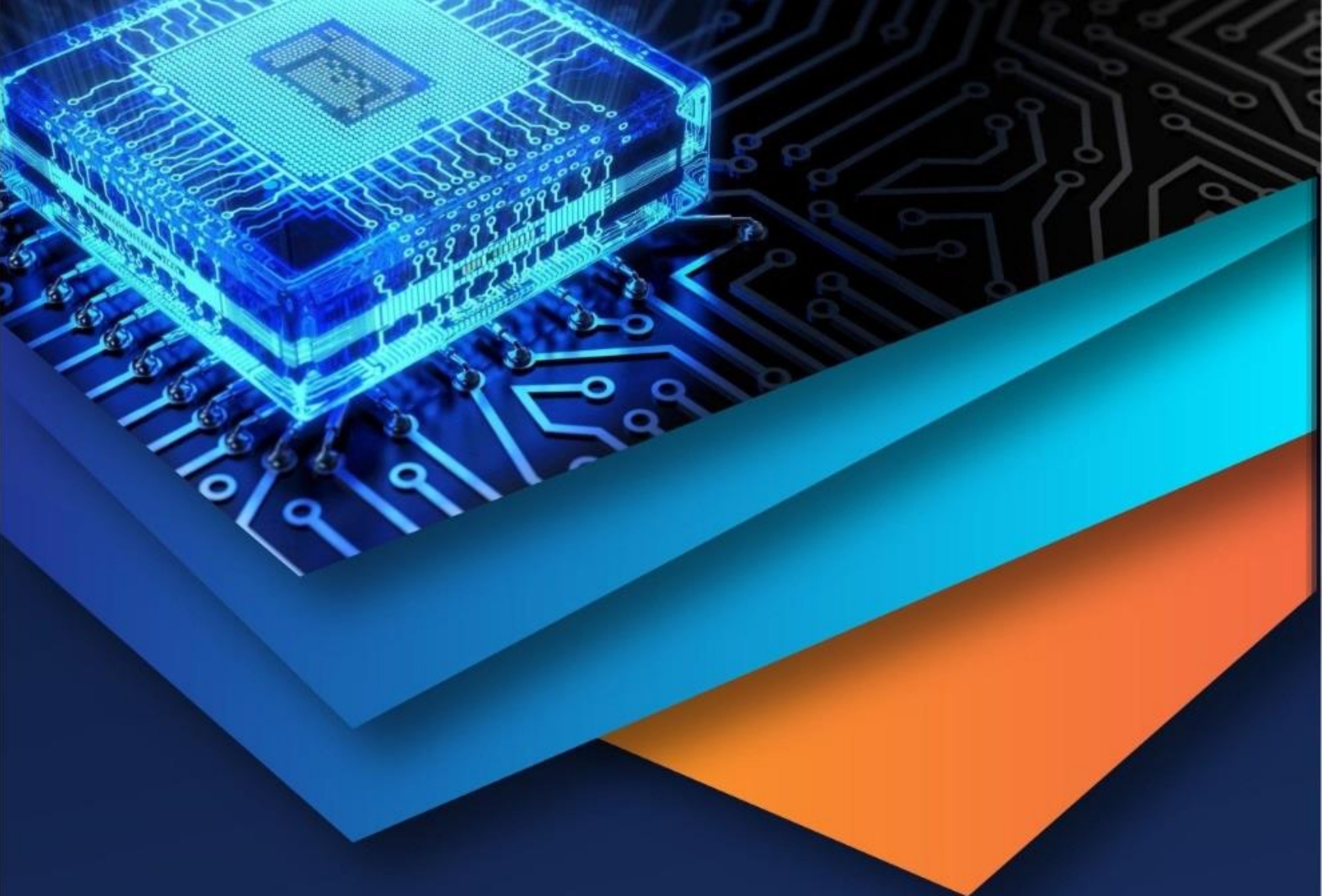

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