International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.1, pp 427-435, Jan-Mar 2010

REMOVAL OF HAZARDIOUS TEXTILE DYES FROM AQUEOUS SOLUTION BY USING COMMERCIAL ACTIVATED CARBON WITH TiO_2 AND ZnO AS PHOTOCATALYST

K.M.JOSHI* and V.S. SHRIVASTAVA

**Department of P.G. Studies and Research in Chemistry,
G.T.P. College, Nandurbar 425412,India.**

Email:kmjoshi35@gmail.com, Tel. +919423497945

Abstract: The objective of this study was to investigate the ability of semiconductors like TiO2 and ZnO with Commercial activated Carbon used to remove a Hazardous textile dye from aqueous solution. The adsorption of the Acid blue29 and Congo red were selected as a reference molecule for the adsorption studies. The experiment results shows that TiO2 and activated Carbon (AC) can totally remove the Acid blue 29 dye and Congo Red dye removed by ZnO with activated Carbon from waste water. The factor affecting rate process involved in the removal of dye for initial dye concentration, effect of various process parameters like initial dye concentration, contact time, dose of catalyst and pH. The adsorption rate data were analyzed using the pseudo I order of kinetics of Lagergren and Pseudo II order model to determine adsorption rate constant. The optimum contact time is fixed at 210 minutes for both TiO2 and ZnO .The well known Freundlich and Langmuir isotherm equation were applied for the equilibrium adsorption data were evaluated.

Key words: Adsorption, Acid blue29, Congo red, Photocatalysis, TiO2, ZnO

Introduction

Textile dye produces huge amount of polluted effluents that are normally discharged to surface water bodies and ground water aquifers. These wastewater causes damages to the ecological system of the receiving surface water capacity and certain a lot of disturbance to the ground water resources. Most of the dyes are used in the textiles industries are stable to light and are not biodegradable. In order to reduce the risk of environmental pollution from such waste (1). It is necessary to treat them to before discharging it receiving in the environment. Today more than 10,000 dyes have been incorporated in colour index (2). In order to remove hazardous materials like dyes, adsorption is a method which has gain considerable attention in the recent few years adsorption is such a useful and simple technique (3).

Physical and chemical processes have been usually used to treat the wastewater. However these processes are costly and can not be used effectively to treat the wide range of dye wastewater (4). Here we used two dyes as Acid Blue29 is cationic dye Congo Red is an anionic dye which are widely used in Textiles, Paper, Rubber and Plastic industries The purpose of the work was to study the removal of dyes by using TiO2 and ZnO as Photocatalyst with Commercial activated Carbon (CAC) to degrade the dye (5).

In recent years a greate efforts have been made using widely called advance oxidation technologies (AOT) for treatment of these recalcitrant pollutant to more biodegradable molecule or miniaturization. The AOT, materials with photocatalytic function could be used (6). The semiconductors like TiO2, ZnO CdS are effective with UV light, easily available relatively inexpensive and chemically stable photocatslyst. Among the various oxide semiconductor photocatalyst, TiO2 is an important photocatalyst due to its strong oxidizing power, non toxicity and long term photostablilityTiO2 exists in three different crystalline phases. Rutile, anatase, and brookite, among which rutile is thermodynamically stable state, and other two state are metastable (7). Zinc oxide is n-type semiconductor with many attractive features. Zinc oxide with the wide band gap of 3.17 eV as compared to TiO2 (anatase) =3.2 ev is capable to generate hydroxyl radicals. ZnO was also shown to absorb more UV light than any other powder. This means that the high UV absorption efficiency leads to generation of more electron and holes. The electrons and holes are considered the main species involved in the photodegradation process.

$ZnO/ TiO2 \longrightarrow ZnO/TiO2\ (h^+ + e^-)$

$h^+ + H2O \longrightarrow °OH + H^+$

$h^+ + OH^- \longrightarrow °OH$

$E + O2 \longrightarrow °O2^-$

In the present study, TiO2 has been used as an adsorbent for the removal of Acid Blue29 and ZnO used to remove Congo Red dye from textile waste water (8). The efficiency of colour removal was tasted. The adsorption study was carried out involving various parameters as initial concentration, adsorbent dosage, agitation time and pH. The data has been tabulated and discussed (9).

Materials and Methods

Adsorbent Materials :

Commercial activated Carbon was used as Adsorbent supplied by BDH, India. The commercial activated Carbon with the size of 150μm to 250μm was used. This was to reduce the time needed to achieve equilibrium. (10). Some adsorbate in the liquid phase to adsorb on to the impurities surface may affects the accuracy of the experimental result.

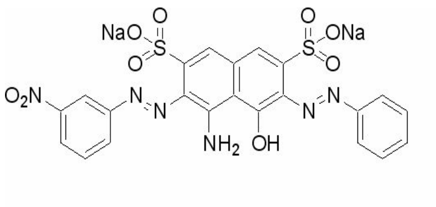
Adsorbate :

The dye was used in this experiment are Acid blue 29 from E merk, AR grade C.I.No.-20460, Mol.Wt.= 616.49, Mol Formula= C22H14N6 Na2O9S2.

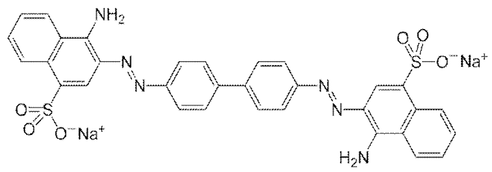
Congo Red (C.I.-22120, Mol.Wt.= 696.665, Mol.formula= $C_{32}H_{22}N_6Na_2O_6S_2$, λ max=510 nm Nature= Anionic dye, Type : Azo Dye).supplied by BDH (India) were used as adsorbate with out further purification.

The stock solution was prepared by dissolving 1 gm of dye in water and made up to the 1000ml stock solution in volumetric flask. From the standard solution. By making 10,30, 50 ppm solution. The concentration of the dye solution was determined by using a spectrophotometer operation in the visible range of absorbance.

Structure of Acid Blue 29 and Congo red :



Acid Blue 29



Congo Red

Experimental Procedure:

The photocatalytic degradation of Acid Blue 29 and Congo Red for both initial concentration and irradiation sample was determined by mean of UV-Visible Spectrophotometer,(model Systronic Model-118) The calibration curve of Acid Blue 29 and Congo Red was obtained at λmax= 602 nm and λmax= 510 nm respectively. The reaction mixture was irradiated with light source UV lamp (PHILIPS-400Watt) at a distance 30cm from the reaction vessel. A double distilled water was used through out the experiment. Kinetics of adsorption was determined by analyzing adsorptive uptake of dye from aqueous solution at different time intervals 15 min. In each experiment an accurately weighted amount of TiO2 and CAC was taken in flask in 100 ml dye solution by adjusting pH of the Acid blue-29 dye solution with addition of requisite volume of NaOH E.Merck India and HCl (E.Merck India). in the different flask at pH 3,4, 5, 6, 7, 8, 9 and 10 the flask were placed under UV lamp the flask were shaken consciously by magnetic stirrer, after certain period (15 Min. Interval) The adsorbent was separated from the solution by centrifugation . the absorbance of the supernant solution was estimated to determine the dye concentration and values of the % of dye removal was found to be maximum at pH 4 therefore pH was finalized at 4 for Acid blue 29 for further experiment. In Congo red dye 100 ml dye solution by adjusting the pH with addition of NaOH and HCl from 3 to 10 pH were placed under 400 watt UV lamp the flask were shaken continuously by magnetic stirrer after certain period (15 Min. Interval) The adsorbent was separated from the solution by centrifugation, the absorbance of the supernant solution was estimated to determine the dye concentration and values of the % of dye removal was found to be maximum at pH 7 therefore pH was finalized at 7 pH for further experiment. Kinetics of adsorption was determined by analyzing adsorptive uptake of dye from aqueous solution at different time interval.

Result and Discussion

Effect of pH:

The pH of is one of the most important factor controlling the adsorption of dye on to the adsorbent. The Acid Blue 29 was maximum at pH 4 is 89.4% and it decreases from 4 to 11 constantly from 89.4 to 36.4% therefore the pH was fixed at 4 for the further experiment.

In case of Congo Red As the pH decreases from 11 to 7 the percentage of adsorption increases from 56.8 to 92.4% and the pH from 7 to 4 the % is decreases from 92.4 to 26.4% Fig.1 shows the effect of pH (2-11) on the percentage removal of Congo Red . The higher Percentage of Removal of dye is obtained at pH 7. There is very slight difference in the percentage removal at 6 to 8. So pH 7 was used for adsorption isotherm (11).

Effect of Contact Time :

The effect of contact time on the amount of Acid Blue29 and Congo Red adsorbed was investigated using 10, 30, 50 ppm initial concentration with 0.5 gm of TiO2 and ZnO respectively . It was found The adsorption percentage was found to be maximum at 180 minutes increases. A maximum values with increase in contact time Fig. 2 but as Concentration of AB-29 and CR increases Percentage of both dyes adsorption decreases from 70.7 to 62.3% and for Congo Red it decreases from 86.5 to 73.1% from 10 ppm to 50 ppm solution .

Effect of Adsorbent dose:

The adsorption dose was studied with 100 ml Acid Blue 29 and Congo Red solution of concentration10, 30 and 50 ppm with varying adsorption dose with 0.2 gm/Lit to 0.6 gm/ Lit. at pH 7 shown in figure 3.The percentage CR removal increase as the adsorbent dose increases. Due to the increase in total number of exchange sites. Experiment were carried out at carbon dosage 200 mg to 600 mg with increase in carbon dosage the percentage of dye removal is also increases.

Effect of Adsorbate :

Initial concentration of the dye AB-29 and CR were changed in order to determine proper dye adsorption keeping the contact time 15 min for both adsorbent at fixed dose 0.2 mg/lit at pH 4 for AB-29 and pH 7 for CR, Fig.4 shows that the amount of the adsorbed qe increased with an increasing the dye concentration However the % removal rate decreases with an increase in the dye concentration. It is also noted that the rate of the removal of the dye as faster at the lower concentration and decreases with an increase in the concentration. It is found that with decreasing concentration of the dye from 1×10^{-5} to 6×10^{-5} .The % removal decreases from 89.4 to 34.5 in AB-29 . The adsorption of the dye was found to decreases constantly with increasing the concentration of adsorbate for AB-29 at 7×10^{-5} is constant indicating a minimum adsorption is pH 4. Whereas for Congo red the % of removal decreases from 92.4 to 61.6 in the concentration range from 7×10^{-5} to $9 \times 10^{-5-}$ for further studies maximum adsorption at pH 7 is used.

Adsorption Isotherm :

In order to optimize the design of an adsorption system to remove the day, It is important to establish the most appropriate correlations for the equilibrium data for each system. Two isotherm model have been tested in the present study; Langmuir and Freundlich model. The applicability of the isotherm equation is compared by judging the correlation coefficient,R^2.

Several mathematical models can be used to describe experimental data of adsorption isotherms . In this work the equilibrium data for Acid Blue 29 on TiO2 and Congo Red on ZnO were modeled with Langmuir and Freundlich models. The details of the linereized Langmuir isotherm are given in the table No.1. in the Fig. 5. The adsorption isotherms there respective plots are shown in Fig.6. The value of the Langmuir constant obtained in this study are presented in table No.1 The Coefficient of correlation for Acid Blue 29 with TiO2 0.2 gm/lit^{-1} obtained from Langmuir expression (R^2= 0.9996) and for Congo Red with ZnO Coefficient of correlation respectively obtained from Freundlich expression (R^2= (0.9999) indicates that Langmuir expression provided better fit for the experimental data of. Acid Blue29 on TiO2 with CAC and Freundlich expression is better fit for the experimental data of Congo Red on ZnO with CAC

Langmuir isotherm:

Langmuir Theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorption layer was unimolecular The theory can be represented by the following equation.

$$Ce/qe=1/bQ0+Ce/q0 \quad \ldots\ldots\ldots (1)$$

Where qe is the amount of dye AB-29 and CR adsorbed per unit mass of adsorbent (mg/g^{-1}) and Ce is the equilibrium concentration of dye AB-29 and CR, Qo and b are Langmuir constant related to the capacity and energy of adsorption respectively . The linear plot of Ce/qe v/s Ce show that the adsorption obeys Langmuir isotherm model for all adsorption(fig.5) The values of Q0 and b were determined for all adsorbent from the intercept and slope of the linear plot of Ce/qe v/s Ce (table1) The good fit for the experimental data and the correlation coefficients R^2 higher than 0.9996 indicates the applicability of Langmuir isotherm model.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor RL which is given by the following equation.

$$RL = \frac{1}{(1+Ka\ Co)} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Where Co (mg/lit^{-1}) is the initial concentration .The values of separation factor is RL, Indicating the nature of adsorption . The adsorption process in between 0 to 1 indicates the adsorption isotherm is favorable. RL indicates the nature of the adsorption isotherm it is given below .

RL values	**Adsorption**
RL>1	Unfavorable
RL=1	Linear
0<RL<1	Favorable
RL=0	Irreversible

The RL Values for the adsorption of dye AB-29 and CR are observed to in the range 0 to 1 indicating that the adsorption process is favorable for type of TiO2 and ZnO respectively.

Freundlich Isotherm : The Freundlich adsorption isotherm model stipulated that the ration of solute adsorbed to the solute concentration is a function of the solution.

Log qe= log Kf +1/(n log Ce)………(3)

Where log Kf is a measure of adsorption capacity and n is the adsorption intensity. The slope 1/n which should have values in the range of 0 to1 for favorable adsorption (12). The value for 1/n below one indicates a normal Freundlich isotherm while 1/n A graph of Log qe vs log Ce shown in figure 5.
Where the values of Kf and 1/n are determined from the intercept and slope of the linear regressions.

The coefficient of correlation was high (R^2=0.9997 and 0.9999 for Acid Blue 29 with TiO2 and Congo Red ZnO respectively) showing the good linearity. The values of Kf and 1/n are determined from the intercept and slope of the linear regretions. (Table1) indicating that the dye is favorable adsorption on the magnitude of Freundlich constant

Adsorption Kinetics :

For the evaluating the adsorption kinetics of Acid blue-29 and Congo red on TiO2 and ZnO were treated with Lagergren first order model express as

Log (qe-qt)=log qe-(k1/2.303)t……(4)

The first order rate constant k1 is obtained form the slope of the plot log(qe-qt) versus time. The coefficient of correlation for the first order kinetic model was not high for all adsorbents and concentration. The estimated values of qe calculated from the equation different from the Expt. Values (Table 2) shows that the model is not appropriate to describe the adsorption process.
Adsorption kinetics were explained by the pseudo – second order model

$t/qt=1/k2*qe^2+t/qe$……………….. (5)

Where K2 is the second order rate constant ($mg^{-1}min^{-1}$). The value of K2 is different initial dye concentration for all adsorbents were calculated from the slope of the respective linear plot of t/qt vs t (fig.8) The correlation coefficients were 0.9927-0.9994, suggest a strong relationship between the parameters and also explain that the process follows the pseudo Second order kinetics. This shows that the adsorption process of AB-29 with TiO2 and CR on ZnO is psuedo second order kinetics..

Conclusion

The present study has revealed that the TiO2 and ZnO with Commercial Activated carbon can be effectively used as a photocatalytic material for the or the removal of Acid Blue 29 and Congo Red dye respectively. Adsorption was influenced by various parameters such as initial pH initial dye concentration and dose of adsorbent. It was observed that ZnO is more effective dye for removal of Congo red while TiO2 is less suitable to remove Congo red therefore ZnO is used to remove the Congo red and TiO2 is used for removal of Acid blue 29. The maximum adsorption of Acid blue 29 and Congo red dye by TiO2 and ZnO respectively. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. The study of the influence of pH of the experimental dye solution on the adsorption potential have reveals the pH values 4 appears to the most favorable for removal of Acid red-29 dye.

The experimental adsorption data have been fitted reasonably well to Langmuir and Freundlich adsorption isotherm. The applicability of Lagergren model suggested the formation of monomolecular layer of the dye on the surface of the adsorbent. It was shown that the adsorption of Acid blue 29 and Congo red fitted by Pseudo second order model.

Table No.1: Langmuir and Freundlich Constant

Dye	Conc.	Time in Min	Langmuir Constant			Freundlich Constant		
			Qo	b	r^2	Kf	1/n	r^2
Acid Blue-29	50 ppm	15	142.86	6.9998	0.9996	1.1023	3.967	0.9849
Acid Blue-29	50 ppm	30	227.27	1.7614	0.9949	1.3395	1.653	0.9876
Acid Blue-29	50 ppm	45	208.45	0.1920	0.9945	9.6074	1.6183	0.9674
Acid Blue-29	50 ppm	60	222.22	4.0909	0.9987	16.031	0.9792	0.9923
Acid Blue-29	50 ppm	75	316.75	2.4193	0.9974	22.205	1.4084	0.9876
Acid Blue-29	50 ppm	90	294.12	3.820	0.9921	35.234	0.5805	0.9281
Acid Blue-29	50 ppm	105	312.5	0.642	0.9951	42.411	1.0987	0.9806
Acid Blue-29	50 ppm	120	333.45	0.566	0.9759	56.298	0.7339	0.9912
Congo Red	50 ppm	15	5.8789	2.352	0.8997	1.4457	1.4589	0.9988
Congo Red	50 ppm	30	4.2854	3.7548	0.8353	3.047	0.451	0.9948
Congo Red	50 ppm	45	4.7589	2.8334	0.7458	4.879	0.2051	0.9878
Congo Red	50 ppm	60	5.2458	1.0458	0.9876	4.879	0.5697	0.9956
Congo Red	50 ppm	75	5.6897	2.3487	0.9519	7.448	0.9234	0.9997
Congo Red	50 ppm	90	6.5598	3.0789	0.9325	2.852	0.948	0.9999
Congo Red	50 ppm	105	5.879	4.038	0.9158	3.761	0.7955	0.9971
Congo Red	50 ppm	120	6.8972	3.784	0.947	6.154	0.9234	0.9926

Table No.2 : Comparison of adsorption rate constant, calculated and experimental qe values for different initial concentration and adsorbent dose for Pseudo First order and Pseudo Second order reaction.

Adsorbent dose	Adsorbent	Dye	Conc. in mg/lit^{-1}	qe expt. mg./gm	Pseudo First order			Pseudo Second order			
					qe cal.	K_1	r^2	qe cal	K_2	r^2	h
2gm /Lit	TiO2	Acid Blue-29	10 mg/Lit^{-1}	32.55	41.81	0.0175	0.9394	34.19	0.8540	0.9994	0.5563
2gm /Lit	TiO2	Acid Blue-29	30mg/Lit^{-1}	95.25	100.6	0.0154	0.9836	92.57	0.5484	0.9927	1.5628
2gm /Lit	TiO2	Acid Blue-29	50mg/Lit^{-1}	154.41	137.68	0.127	0.9947	156.98	0.3839	0.9927	2.6798
2gm /Lit	ZnO	Congo Red	10 mg/Lit^{-1}	5.56	4.167	0.0384	0.9458	5.321	0.0335	0.9965	1.2897
2gm /Lit	ZnO	Congo Red	30mg/Lit^{-1}	16.47	14.89	0.0199	0.9574	16.24	0.0057	0.9947	3.5687
2gm /Lit	ZnO	Congo Red	50mg/Lit^{-1}	25.89	24.634	0.0013	0.9875	25.87	0.0076	0.9996	59.879

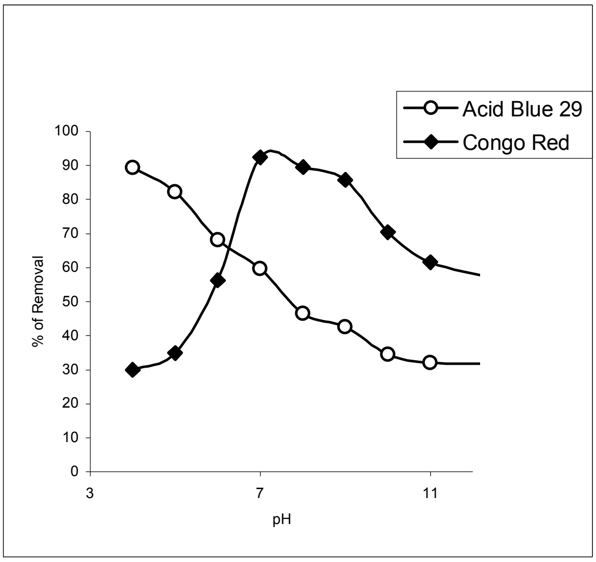


Fig. 1. Effect of pH on adsorption of Acid blue 29 and Congo Red at 50 ppm

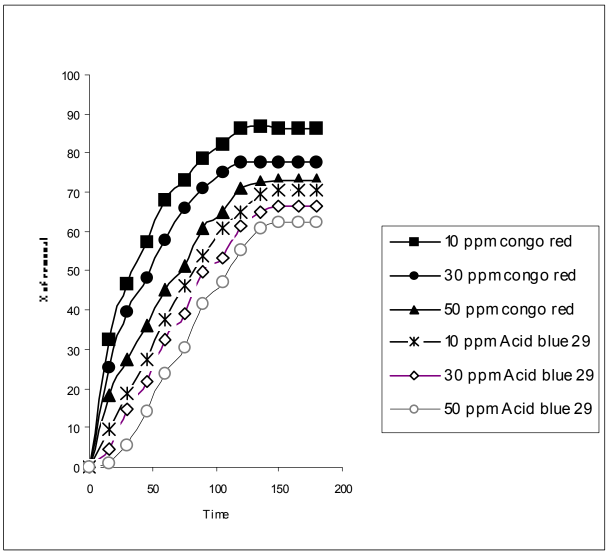


Fig. 2. Effect of contact time on adsorption of Acid blue 29 and Congo red

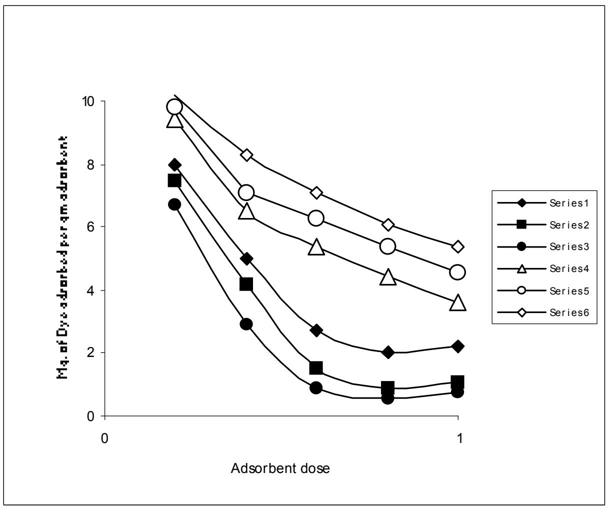


Fig. 3. Effect of adsorbent dose on Acid blue and Congo red

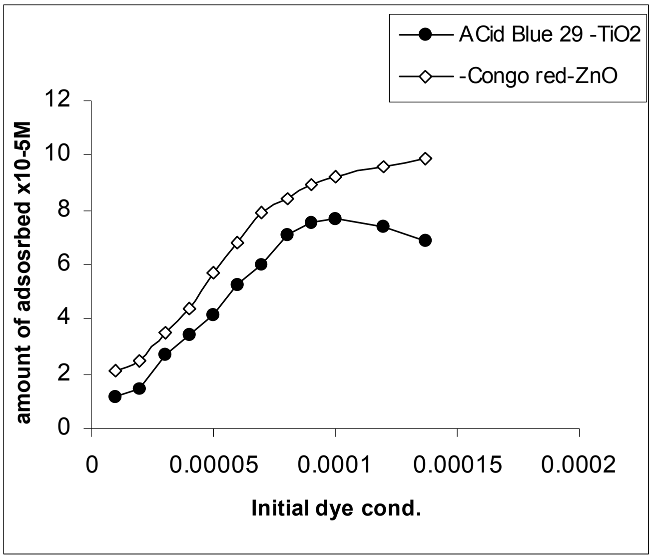


Fig.4. Effect of initial dye concentration on the adsorption of acid blue by TiO2 and Congo red by ZnO

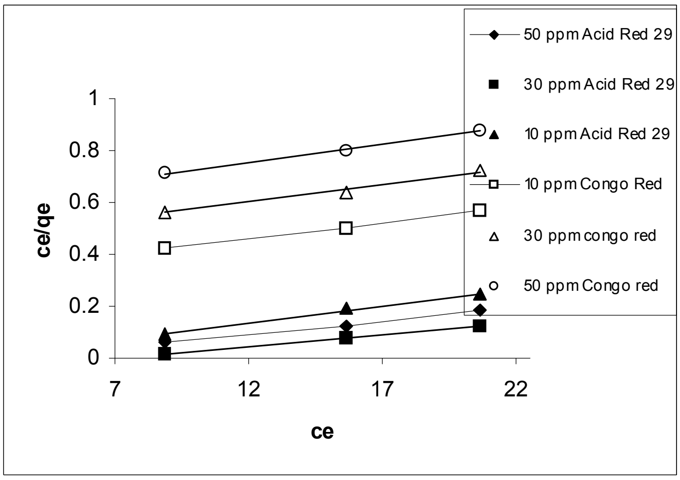


Fig.5. Langmuir adsorption Isotherm of Acid blue 29 and Congo red by using TiO2 and ZnO with CAC

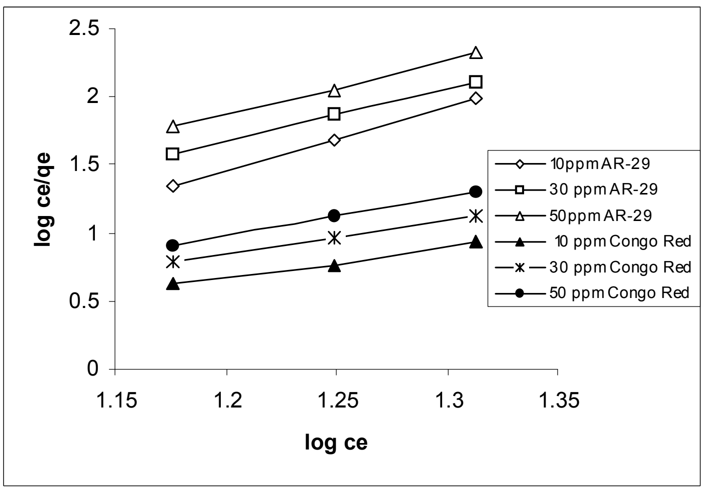
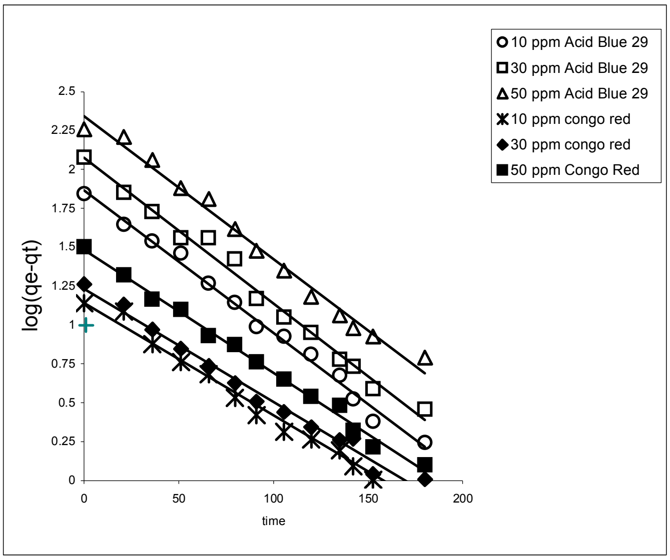


Fig.6. Freundlich adsorption isotherm of Acid Blue and Congo Red by TiO2 and ZnO with CAC



Fig, 7. Lagergren first order plot of Acid blue and Congo red on TiO2 and ZnO

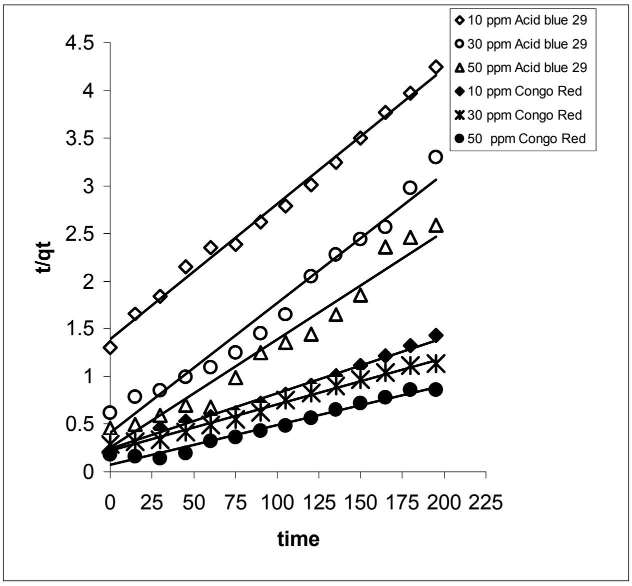


Fig 8. Pseudo Second order of Acid blue and Congo red on TiO2 and ZnO

References

1. Arami,M, Limaee. N.Y. Mahmoodi. N.M. Tabrizi. N.S. Removal of dyes from colourd textile wastewater by adsorbent: equilibrium and kinetic studies. Journal of Colloid and interface Science. , 2005, 288.371-376
2. D. Jalajaa., M.Manjuladevi.,S.V. Saravanan. Removal of acid dye from textile waste water by adsorption using Activated carbon preapared from pomegraneta rind., Pollution Research.,2009, 28(2) : 287-290.
3. S.A. Saad, S, Daud, F.H. Kasim M.N. Saleh, Metylene blue removal from simulated wastewater by adsorption using treated oil palm empty fruit bunch, ICOSM.,2007, 293-296
4. N. Kanan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons a comparative study, Dyes and pigment., 2001,51, 25-40.
5. N. Kannan anf G.G. Nagnathan, Photo catalytic degradation of Saferanine dye on semiconductor by UV radiation IJEP., 200727(12): 1103- 1108.
6. Parra, S., V. Sarria, S. Maloto, P. Periner, and C. pulgarin. Photocatalytic Degradation of attrzine using suspended and supported TiO2. Jour. Applied Catalyssis.B: Environmental ., 2004. 51: 107-116.
7. JCPDS-ICDD reference oattern database, International center for Diffraction data

.Philips Analytical X ray. Almelo, Release, 1996, 46.

8. Rajeev Jain and shalini Shirkarwar , Removal of hazardous dye congo red removal from waste material., Journal.of hazardous materials., 2008,152,942-948.

9. A.K.Patil and V.S. Shrivastava , Adsorption of Congo Red from aqueous solution using Banana plant waste material .,Asian Journal of Chemical and Environmental 2008, 1(4) 20-26.

10. Meahkw. V. markovska, M. Mincheva and A.E. Rodrigues (2001) Adsorption of basic dues in granular activated carbon and natural zeolite. Water research., 2001, 35, 3357-3366

11. S.Senthilkumar, P.Kalaamani, K.Porkodi, P.R.Varadarajan and C.V. Subburaam , Adsorption of dissolved reactive red dye from aqueous phase on to activated carbon prepared from agricultural waste Biosour. Technol., 2006, 97, 1618-1625

12. K. Fytianos, E. Voudras and E. Kokkalis, sorption desorption, behavior Of 2,4 dichlorophenol by marine sediments , Chemosphere., 2000,40,735- 741.

13. F.Haghseresht and G. Lu, Adsorption characteristics of Phenolic compound on to coal reject derived adsorbent, Energy fuels., 1998 ,12,1100-1107

*****