iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 2 **Issue:** Issue- III **Month of publication:** November 2014

DOI:

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Removal of a Model Textile Dye from Effluent using fenugreek powder as an adsorbent

Ambiga Devi. J
Department of Chemical Engineering, Sri Venkateswara College of Engineering, Sriperumbudur

Abstract: The adsorption of methylene blue (model textile dye) on fenugreek powder was studied on batch modes of operation. The operational parameters investigated include initial dye concentration, pH of solution (3.7-9.7), and adsorbent dose (0.2-2.0g/L).The experimental data were analysed using Langmuir and Freundlich isotherm model. The Langmuir isotherm model fits the data very well for the methylene blue on fenugreek powder. Pseudo-first-order and pseudo-second-order kinetic were used to analyse the kinetic data. Kinetic studies showed that the adsorption followed a pseudo-second-order model. The pseudo-second-order kinetic data fit well on whole system for the dye studies.
Keywords- adsorption; methylene blue; fenugreek

I. INTRODUCTION

Colours play an important role in many industries such as paper, textile, rubber, cosmetic. Dyes are released into wastewaters from various industrial units, mainly from the dye manufacturing and textiles and other fabric finishing [1]. The textile finishing's' wastewaters contain organic dyes, chemicals, auxiliaries, salts, surfactants, heavy metals, mineral oils, and others. They are coloured and have extreme pH, COD, BOD and AOX values [2]. Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack [3]. Hence, their presence in wastewater is unwarranted.

Wastewater pollution will effect on public water supplies and cause some disease such as diarrhoea, cholera, typhoid fever, e-coli infections and diphtheria. Diseases are result from heavy metals (mercury, lead, arsenic) and organic contamination (benzene, phenol, PCB) of the water. Dyes also can cause deterioration in human's health. Some dyes are found to be toxic, mutagenic and carcinogenic [4].

Some regulations have been enacted by government to regulate the effluent wastewater discharged. The purpose of those regulations is to control and limit some parameter in the effluent discharged by the industries. One of the regulation is the Environmental Quality (Sewage and Industrial Effluents) Regulation, 1979, limits the colour present in the final discharged by industries to 10 Hazen for standard and 50 Hazen for Standard B (Environmental Quality Act, 1974).

In this study, methylene blue was chosen as a target contaminant to characterize the adsorptive properties of fenugreek powder as it is a common cationic dye used in the medical, textile and printing industries [5]. Methylene blue (MB), chemical formula: $C_{16}H_{18}N_3SCl$; FW: 319.86 $gmol^{-1}$,max: 662nm, (class: thiazine, C.I. classification Number:52015) is the most important basic dye. At room temperature it appears as a solid, odourless, dark green powder that yields a blue solution when dissolved in water. The adsorbate methylene blue was chosen as a model dye because of its well-known adsorption characteristics.[6].

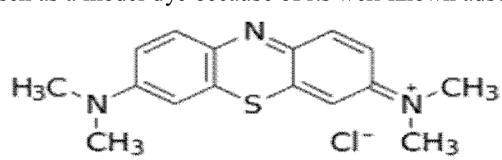


Figure 1. The structure formula for methylene blue

On the other hand, Major fenugreek-producing countries are Afghanistan, Pakistan, India, Iran, Nepal, Bangladesh, Argentina, Egypt, France, Spain, Turkey and Morocco. The largest producer is India, where the major producing states are Rajasthan, Gujarat, Uttarakhand, Uttar Pradesh, Madhya Pradesh, Maharashtra, Haryana, and Punjab. Rajasthan accounts for over 80% of India's output. This powder is suitable used for the removal of methylene blue in this study due to its abundance amount in country such as India. These natural adsorbents are not only low cost, but also save the disposal cost and prevent the on-site burning. Although many low-cost agricultural adsorbents have been studied for dye removal purposes, studies of fenugreek powder as an economical adsorbent have not yet been researched. Using of fenugreek to as a natural bio-adsorbent can decrease the organic waste. Therefore, removal of methylene blue using the low cost fenugreek powder had been carried out in this research to study the efficiency of fenugreek powder as an adsorbent. Besides that, this research also aim to study the adsorption capacities of methylene blue fenugreek with the effect of dye concentration (25-100mg/L), dosage of fenugreek powder

International Journal for Research in Applied Science & Engineering Technology (IJRASET)

concentration, and pH (3.7-9.7). Finally, this research will also investigate the isotherm and kinetics of methylene blue onto fenugreek powder.

II. MATERIALS AND METHODS

A. Materials

Fenugreek powder was collected from agriculture lands at Rajasthan. The fenugreek seeds were washed with raw water to remove impurities. The seeds were washed with distilled water again and dried in hot air oven at 105^{o}C till they become crisp. The dried seeds were first hand crushed and then using Disc Mill Crusher to crush it into powder form. Then sieve shaker issued to sieve the fenugreek powder into size of range 150µm-300µm. The methylene blue (MB) used in this study having molecular weight of 319.85222 g/mole and chemical formula of $C_{16}H_{18}ClN_3S$. MB concentration in the sample solution was determined using a UV-Vis Hitachi U 2810 Spectrophotometer at a wavelength of 662 nm. MB (1000mg/L) in stock solution was prepared and diluted to the required initial concentration, i.e. 25-100mg/L using distilled water. The experiment was carried out under room temperature. All reagents used in this study were of analytical grade chemicals.

B. Batch Adsorption System

For batch equilibrium studies, adsorption isotherms were performed in a set of 4 Erlenmeyer flasks 250mL. 100mL solutions of dye with different initial concentrations (25-100mg/L) were placed in these Erlenmeyer flasks. The optimum pH of the solutions was used. 0.1g/10ml of fenugreek was added to individual dye solutions. The final concentration of dye in the solution were measured at its wavelength λmax (nm), using UV–vis spectrophotometer.

The amount of adsorption at equilibrium time t, qe (mg/g) was calculated using this equation:

$$Qe = \frac{(Co - Ce)V}{W} \quad (1)$$

Where, Co= the liquid-phase concentrations of dye at initial(mg/L); Ce = the liquid-phase concentrations of dye at equilibrium (mg/L) ; V = volume of the solution, (L); W =mass of dry adsorbent used, (g).

In batch kinetic studies, the procedures of these experiments are basically identical to those of equilibrium tests described above. The samples were taken at fixed time intervals, and the concentrations of dye were measured using UV–vis spectrophotometer. The amount of adsorption at time t for every time interval, Qt (mg/g), is calculated by using this equation:-

$$Qt = \frac{(Co-Ct)V}{W} \quad (2)$$

Where, Ct= the liquid-phase concentrations of dye at time t when the aqueous samples were taken (mg/L); Ce = the liquid-phase concentrations of dye at equilibrium (mg/L); V =volume of the solution (L); W = mass of dry adsorbent used (g).

Several operation parameters were also investigated in the batch adsorption studies, including effect of solution pH, initial dye concentration and adsorbent dose.

For the effect of solution pH, acid and alkali were prepared for adjustment of solution pH. The acid and alkali uses for adjustment pH are HCl and NaOH. 0.1N NaOH and 0.1N HCl were required for adjusting pH range from 3.7-9.7. The effect of pH were studied using 0.2g (dry basis) fenugreek powder, 25 mg/L methylene blue (100 mL) at room temperature and contact time equal to 3 hours and 24 hours respectively. The amount of adsorption at 3 hours, q3 (mg/g) and equilibrium time t, qe (mg/g) is calculated using (1) and (2).

Different initial concentration of methylene blue ranging from 25 to 100 mg/L was prepared and placed in four Erlenmeyer flask, each 100mL. The effect of initial concentration and contact time were studied using 0.2g (dry basis) fenugreek powder. Experiments were carried out at room temperature and speed equal to 150 rpm.

Different initial dose of fenugreek powder ranging from 0.2g-2.0g was prepared and placed in six Erlenmeyer flask, each 100mL. The effect of adsorbent dosage and contact time were studied using 50mg/L methylene blue. Experiments were carried out at room temperature and speed equal to 150 rpm.

C. Adsorption Isotherm and Kinetic Study

The isotherm experiments were carried out to obtain the maximum adsorption capacity and parameters as affected by solution's pH. The adsorption isotherm data was analysed according to two adsorption isotherm models, which are Langmuir and Freundlich, while for the kinetic study, pseudo-first-order and pseudo-second-order models were used to test the experimental data to investigate the mechanism of adsorption [8].

Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

III. RESULTS AND DISCUSSIONS

A. Effect of Solution pH

Base on Fig 2. , it shows that the pH of solution has significantly affected the adsorption of methylene blue on fenugreek powder. The higher the pH, the more effective the adsorption of methylene blue on fenugreek powder. Fenugreek powder achieved its optimum adsorption capacity at pH 9.7. From the amount of 3 hours and the 24 hours, we found that the adsorption capacity of methylene blue on fenugreek powder is higher at alkaline condition as compare to acid condition. The adsorption of methylene blue onto adsorbent surface is influenced by the surface charge on the adsorbent and the initial pH of the solution [9]. The surface charge of fenugreek powder is strongly related to the solution pH. The fenugreek powder consists of polar functional groups such as hydroxyl (-OH) and carbonyl (>C=O) which will be influenced by the pH. As the pH of the solution increases, the number of negatively charge sites increased. This is because a strong electrostatic attraction exists between the positively charged cationic dye and the negatively charged fenugreek powder surface due to the ionization of fenugreek powder. As a result, a negatively charged surface site on the adsorbent favours the adsorption of dye [10].

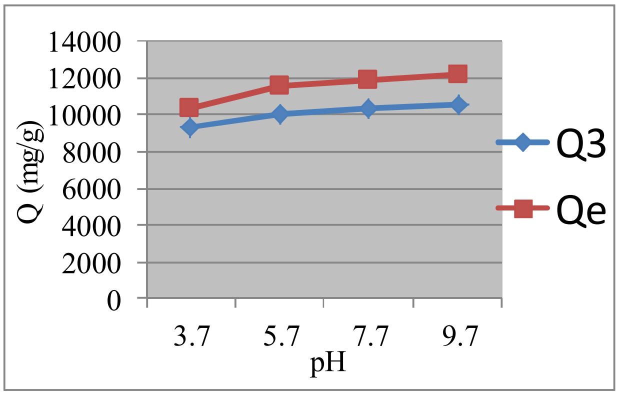


Figure 2. Effect of pH on the adsorption of methylene blue on fenugreek Powder

B. Effect of initial concentration of dyes

The initial methylene blue concentration plays an important role in affecting the capacity of methylene blue to adsorb onto fenugreek powder. Fig. 3 shows that adsorption capacity is increases from 88.3% to 96% as the concentration increased from 25 to 100mg/L. The higher the methylene blue concentration is, the stronger the driving forces of the concentration gradient so the adsorption capacity will be higher.

The reaction of the adsorption is very fast, the amount of dye will reach a constant value while the contact time increases. This constant value is called equilibrium point which means that the maximum of dye can be adsorb by the adsorbent. The time profile of dye uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of adsorbent [11].

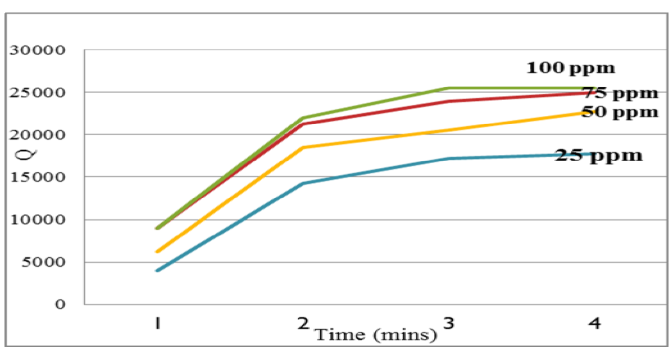


Figure 3. Effect of initial dye concentration and contact time on the adsorption of methylene blue on fenugreek powder.(0.2g, pH 9.7, room temperature)

C. Effect of adsorbent dose on adsorption capacity

Fig. 4 illustrates that the adsorption capacity was increased with the increment of adsorbent dosage. The adsorption capacity is increases from 86.5% to 98% as the adsorbent dosage was increased from 0.2g/L to 2.0g/L. Higher uptake was obtained when

Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

the dosage was low. This indicated that with an increased mass of adsorbent, more surface area is made available and therefore the total number of sites increases [12].

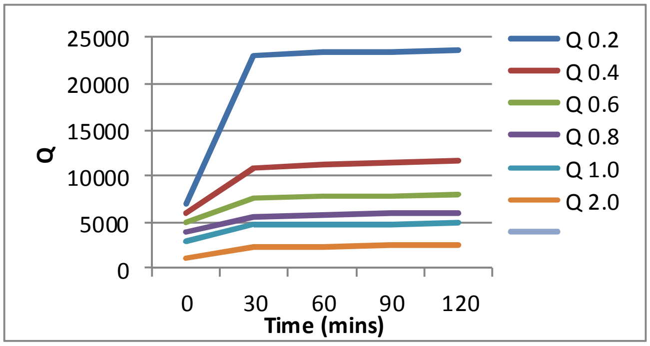


Figure 4. Effect of adsorbent dose and contact time on the adsorption of methylene blue on fenugreek powder (50mg/L, pH 9.7, room temperature)

D. Adsorption Isotherm

Fig. 5 show the Langmuir isotherm plot Ce/ qe versus Ce. The slope of this plot equivalent to 1/ Qo when it intercepts represent 1/QoKL. Table 1 list the computed maximum adsorption capacity, Qo of methylene blue onto fenugreek powder. The experimental maximum adsorption capacity is 25000 mg/g.

The Freundlich model is an empirical equation that assumes heterogeneous adsorption due to the diversity of adsorption sites [13]. Fig. 6 show the plot of ln qe versus ln Ce, enables the constant KF and exponent n to be determined. The value of KF and n are presented in Table 1. KF also use to estimate the quantity of dye adsorbed on adsorbent for an equilibrium concentration. From the Table 1, the slope 1/n calculated to be 0.41 indicates that the adsorption of methylene blue onto fenugreek powder follows the Langmuir isotherm. Favourable adsorption tends to have Freundlich constant n > 1. The value of n is 2.498 which indicate favourable adsorption condition. The Freundlich constant n obtained is between 1 and 10 and 1/n is closer to zero than 1. This shows that the fenugreek powder used in this adsorption studies have heterogeneous surface.

By comparing the correlation coefficient, R^2

Value shown in Table 1, the Langmuir model obtained a better fit of the experimental data compare to Freundlich model. This result shows that the adsorption isotherm with fenugreek powder can be best described by Langmuir equation. The Langmuir adsorption model shows that the formation of monolayer coverage of adsorbate at the outer surface of adsorbent.

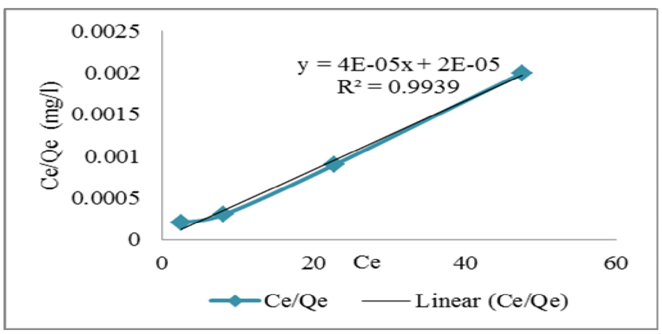


Figure 5. Langmuir isotherms for the removal of methylene blue by adsorption of fenugreek powder.

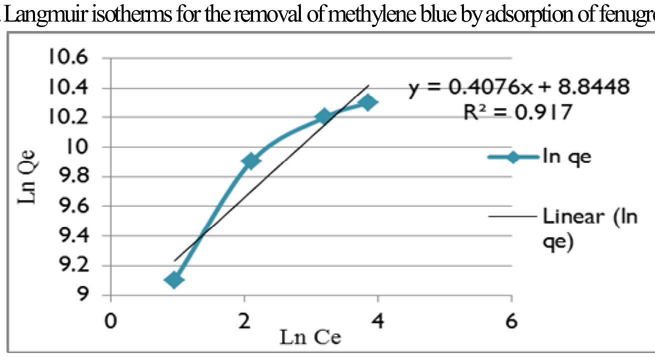


Figure 6. Freundlich isotherms for the removal of methylene blue by adsorption of fenugreek powder.

Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

TABLE I. Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption capacity of methylene blue onto fenugreek powder

Langmuir Isotherm	Freundlich Isotherm
Q_{emax}= 25 000 mg/g	N = 2.5
K_d =2.0 dm^3/mg	1/n = 0.41
R^2 = 0.9939	R^2 = 0.917

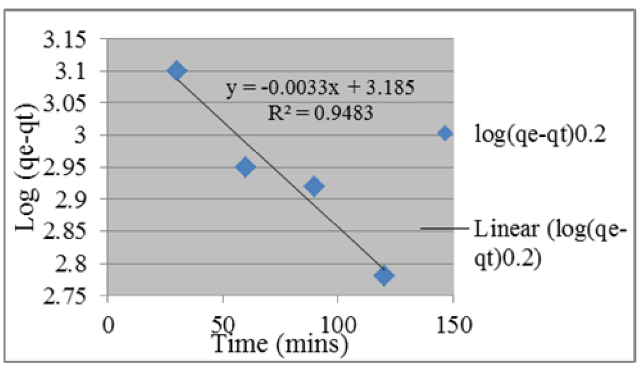
E. Kinetic Study

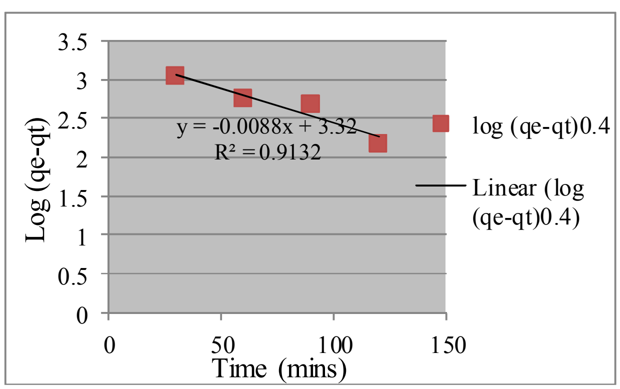
Fig. 7 shows the Pseudo-first-order kinetics of methylene blue adsorption onto fenugreek powder at various adsorbent doses, while Fig. 8 shows the Pseudo-second-order kinetics of methylene blue adsorption onto fenugreek powder at various adsorbent dose. Qe_{cal} and k_1 were determined from the slope and intercept of the plot of Fig. 7 while qe_{cal} and k_2 were determined from the slope and intercept of the plot of Fig. 8.

From the Fig. 7, the kinetic data did not fit well with the pseudo-first-order model. Usually pseudo-first-order equation does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption process [14]. The R^2 for the result are low in pseudo-first-order which is in range of 0.901 to 0.997 and the qe and qe_{cal} also have big differences. Therefore, the adsorption of methylene blue onto fenugreek powder does not follow the pseudo-first-order model.

The plot of t/qt versus t as in Fig. 8 shows a linear relationship with intercept very close to zero. This means that the pseudo-second-order kinetics is applicable. The results show that the unit adsorption (q) for methylene blue increases from 2500 to 25000 mg/g with the decrease in mass of adsorbent from 2g to 0.2g. The correlation coefficients of the pseudo-second-order model for the linear plots are between 0.9945 to 0.9996. The second-order rate constant values show that this adsorption system is a pseudo-second-order model as the values of qe and qe_{cal} are almost the same. Therefore, the pseudo-second-order adsorption mechanism is predominant.

For the both pseudo-first-order and pseudo-second-order model, as the adsorbent dose increase the qe_{cal}(mg/g) decrease significantly.





Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

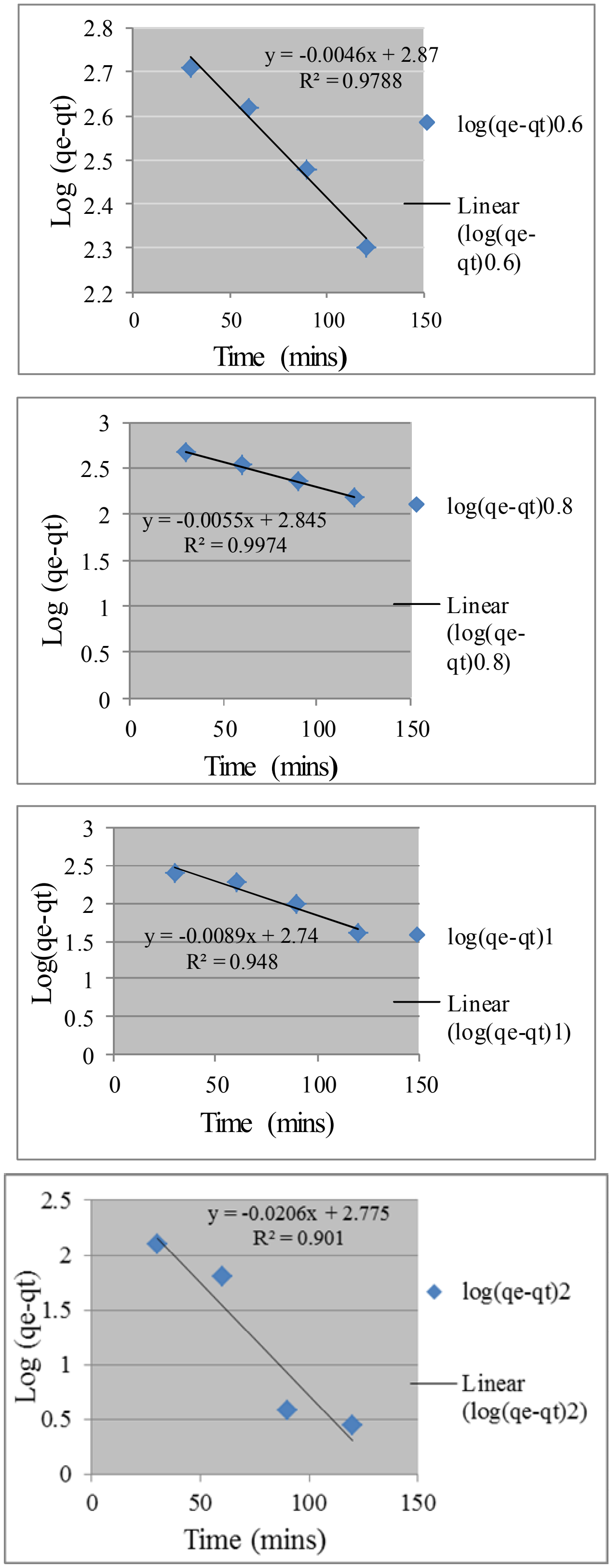
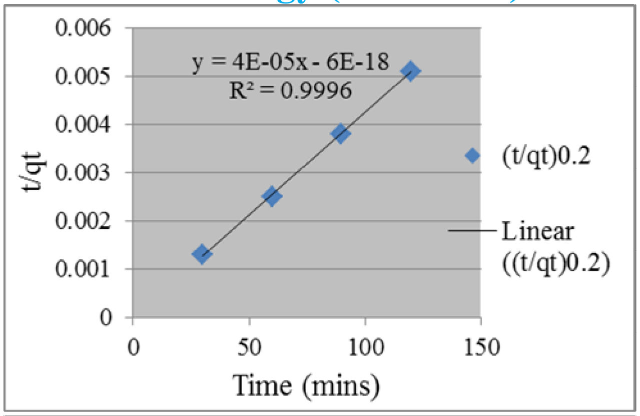
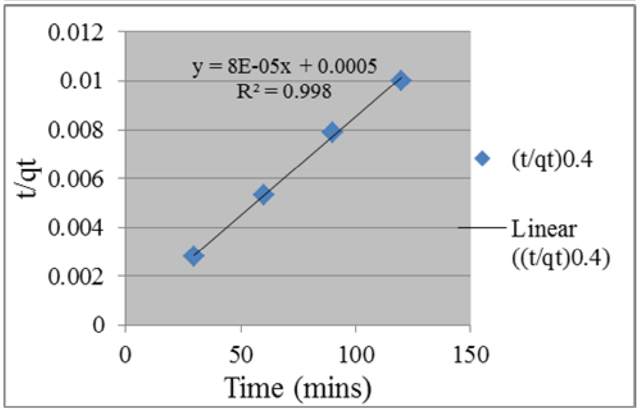
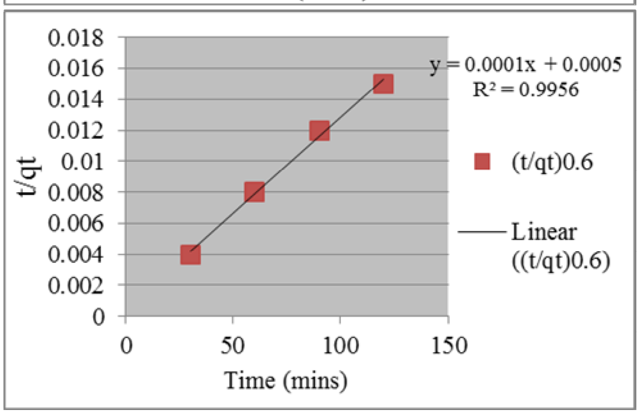


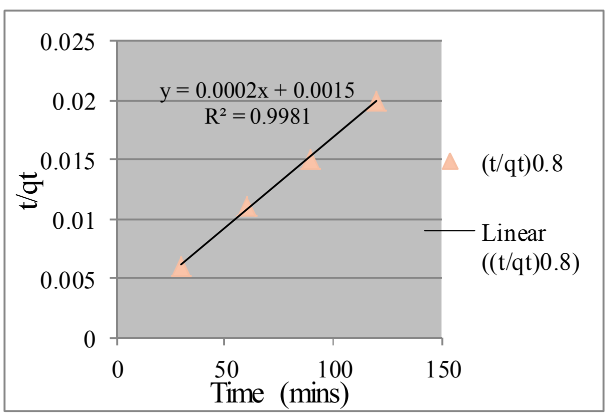
Figure 7. Pseudo-first-order kinetics of methylene blue adsorption onto fenugreek powder at various adsorbent dose.

Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

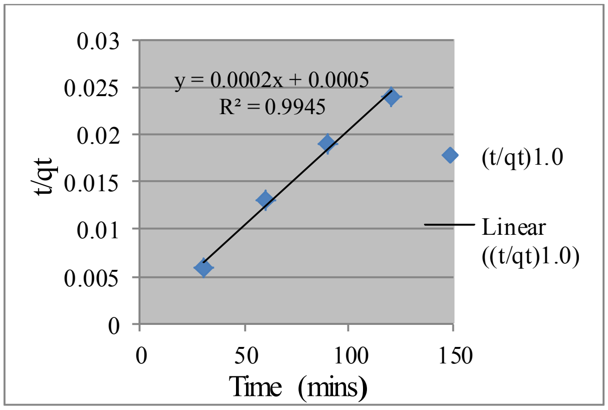








Special Issue-3, November 2014
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)



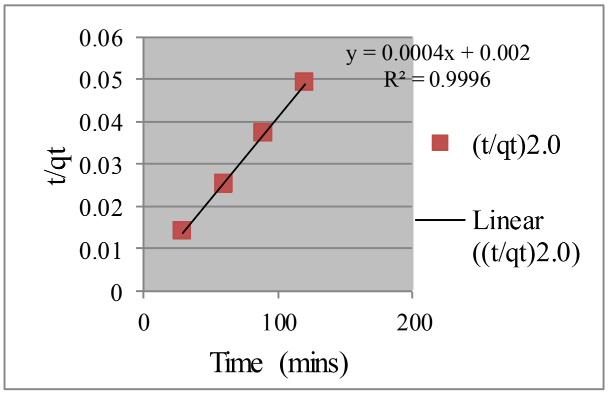


Figure 8. Pseudo-second-order kinetics of methylene blue adsorption onto fenugreek powder at various adsorbent dose.

TABLE 2 Kinetics parameters of methylene blue adsorbed onto fenugreek powder at different adsorbent dose

Adsorbent Dose (g/l)	q_e	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
		qe_{cal} (mg/g)	K_1 (min^{-1})	R^2	qe_{cal} (mg/g)	K_2	R^2
0.2	23750	1531.1	0.0076	0.9483	25000	0.4	0.9996
0.4	11725	2089.3	0.02	0.9132	10000	0.2	0.998
0.6	7916.7	741.3	0.01	0.9788	5000	0.4	0.9956
0.8	5937.5	699.8	0.013	0.9974	5000	0.13	0.9981
1.0	4900	549.5	0.02	0.948	5000	0.4	0.9945
2.0	2435	595.7	0.047	0.901	2500	0.2	0.9996

IV. CONCLUSION

From this study, it may be concluded that the removal of methylene blue from aqueous solutions by adsorption on fenugreek powder has been found to be useful for controlling the water pollutions due to dyes. Adsorption of methylene blue on fenugreek powder is influenced by the pH level. For the first 3 hours and after it reaches the equilibrium point, adsorption capacity increase as the pH increase from range 3.7-9.7. The contact time is significant importance in the adsorption of methylene blue on fenugreek powder. It takes about 120 minutes for initial concentration (25-100mg/L) to reach equilibrium point.
The adsorption of methylene blue onto fenugreek powder follows the Langmuir isotherm. The pseudo-second-order adsorption mechanism is predominant compare to pseudo-first-order adsorption mechanism. The optimum pH for the adsorption of

fenugreek powder is pH 9.7.

The advantages of an adsorption system for water pollution control are less investment in terms of both initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared to the conventional biological treatment processes [15]. Adsorption techniques are useful for controlling the extent of water pollution due to dyes.

Fenugreek powder is a material showing the pronounced removal of dyes from aqueous solutions in alkaline condition. It is easily available in the countryside and has the potential to be used for the small industries which produced dyes as their effluent. The data from this study may be useful for designing an economically cheap treatment process for removal of methylene blue from industrial effluent.

V. ACKNOWLEDGMENT

A word of appreciation to Sri Venkateshwara College of Engineering for providing all the equipment, laboratory devises and material for the running of the project purpose

REFERENCES

[1] P. Janos, H. Buchtova, M. Ryznarova. Sorption of dyes from aqueous solutions onto fly ash, Water Res. (2003)37, 4938–4944.

[2] Vera, G., Aleksandra, V. and Marjana, S. Efficiency of the Coagulation/ Flocculation Method for the Treatment of Dye Bath Effluents. Dyes and Pigments, (2005), 67,93-97

[3] Pagga, U.M. and Taeger, K. Development of a method for adsorption of dyestuffs on activated sludge, Water Resources, (1994), 28, 1051-1057.

[4] Chen, K.C., Wu, J.Y., Huang, C.C., Liang, Y.M. and Hwang, S.C.J. Decolourization of azo dye using PVA-immobilized microorganisms, J. Biotechnology.(2003) 101,241–252.

[5] C. H. Weng, Y. T. Lin, T. W. Tzeng. Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder, J.Hazard. Mater. (2009)170, 417-424

[6] V.Ponnusami*, V.Gunasekar, S.N.Srivastava. Kinetic of methylene blue removal from aqueous solution using gulmohar (Delonix regia) plant leaf powder: Multivariate regression analysis, J. Hazard Mater.(2009) 169,119-127

[7] Chau T. Tran and David A. Mitchell. Pineapple Waste -A Novel Substrate For Citric Acid Production By Solid-State Fermentation. Biotechnology Letters. (0ct.1995).Volume 17 No.10 p.1107-1110

.[8] Azza Khaled, Ahmed El Nemr , Amany El-Sikaily, and Ola Abdelwahab. Removal of Direct N Blue-106fromartificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies. Journal of Hazardous Materials 165 (2009)100–110

[9] X.S.Wang, Y.Zhou, Y.Jiang, C.Sun, The removal of basic dyes from aqueous solutions using agricultural by-products, Journal of Hazardous Materials 157(2008)374-385

[10] Gurusamy, A., Lai Yi Ling and Jiunn-Fwu Lee .Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis .Journal of Hazardous Materials, (2008)152, 337–346.

[11] P.K.Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid yellow 36, Dyes and Pigments 56(2003) 239-249.

[12] N. Yeddou, A. Bensmaili. Kinetic models for the sorption of dye from aqueous solution by clay-wood sawdust mixture, Desalination,(2005) 185, 499-508

[13] B.H.Hameed, Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste, Journal of Hazardous Materials 158 (2008) 499-506

[14] G.McKay, Y.S.Ho, The sorption of lead (II) on peat, Water Research 33 (1999) 578-584

[15] Gupta, G.S., Prasad, G., Panday, K.K. and Singh, V.N. Removal of chrome dye from aqueous solutions by fly ash, Water Air and Soil Pollution, (1988) 37, 13-24

[16] El-Geundi, S.M., "Colour Removal from Textile Effluents-by Adsorption Techniques" Water Res.25,271-273, 1991.

[17] Ho, Y.S. and McKay, G. "Sorption of Dye from Aqueous Solution by Peat", Chemical Engineering Journal,70, 115-124, 1998.

[18] Ho, Y.S. and McKay, G., "The Kinetics of Sorption of Basic Dyes From Aqueous Solution by Sphagnum Moss Peat", Can J. Chem. Eng., 76 (4), 822-7, 1998.

[19] Ho, Y.S. and Ofomaja A.E., "Effect of Calcium Competition on Lead Ion Sorption by Palm Kernel Fibre"Journal of Hazardous Material B120, 157-162, 2005b

[20] Bhattacharyya K.G. and Sharma, A., "Kinetics and Thermodynamics of Methylene Blue Adsorption on Neem Leaf Powder" Dyes and Pigments, 65, 51-59,2005.

[21] Lagergren, S., "About the Theory of So- Called Adsorption of Soluble Substances", Vetenskapsakademiens.Handlingar, Band 24(4) 1-39, 1898

[22] McKay, G., Blair H.S. and Garden, J.R., "Adsorption of Dyes on Chitin. Equilibrium Studies", J. Appl. Polym. Sci. 27, 3043-3057, 1983

[23] Strivastava, K.A., Gupta, S.K., and Iyer, M.V.S.,"Colour Removal from Paper Mill Waste", J. of Inst.Public Health Eng. India, Part 2/3, 59-64, 1984.

[24] Temkin, M.I., Pyzhev, V.,"Kinetic of Ammonia Synthesis on Promoted Iron Catalyst", Acta physiochim.