Characteristics and Kinetics of Cationic and Anionic dyes Adsorption on Soil Colloids

R. Murali

Department of Chemistry, Nanjil Catholic College of Arts and Science, Kaliyakkavilai-629153, Kanyakumari (Dt), Tamilnadu, India

Abstract— **Colloids isolated from soil were used as adsorbents for organic dyes such as alizarin red and methylene blue. The mineralogical composition of colloids determined by XRD revealed that the colloids were made up of quartz, calcite and kaolinite. The experiments carried out at different pH values for the adsorption of dyes showed that the adsorption of alizarin red on colloids was high at low pH of 2.5 and decreased with increasing pH of solution. In contrast to this, the adsorption of Methylene blue was found to increase with increasing pH. Pseudo first order and second order kinetic models were applied for the adsorption experiments with different initial dye concentrations and intra particle diffusion was found to be the major contributor to the adsorption behavior.**

Keywords-- **adsorption, coagulation, dye, intraparticle diffusion, Soil colloids**

I. INTRODUCTION

Synthetic complex organic dyes are widely used as colouring material in many textile dyeing industries [1]. Most of dye compounds synthesized are resistive to light, pH and microbial attack which reduces the biological degradation of dyes in water. Dyes absorb and reflect sunlight in water, thus hampering the growth of bacteria and photosynthesis in aquatic plants [2]. This property itself prompts the removal of dyes from the effluents, as it is a major environmental issue. The methods for the removal of dyes from effluents can be divided into three broad processes such as physical, chemical and biological processes [3]. Of the many techniques available for colour removal from the textile effluents, adsorption technology is considered to be a prominent method in terms of cost, simplicity and handling [4]. Adsorption can be divided into two types viz physisorption which occurs due to the weak interparticle bonds between adsorbent and adsorbate, for example van der Waals, dipole-dipole and chemisorption which occurs due to strong interparticle bonds between adsorbent and adsorbate [5].

Many adsorbents have been used for the removal of coloured and colourless organic pollutants from industrial effluents.

Of this activated carbon has been widely studied as an adsorbent for the removal of various dyes [6-10]. A wide variety of materials such as natural manganese mineral [11], fly ash [12], activated clay [13], activated carbon and natural zeolite [4] have been used for the dye removal. Solid waste from leather industry has been used as adsorbents for the removal of methylene blue and reactive red from the aqueous media [14]. It has been reported that the adsorption of acidic dye on activated clay is smaller than that of the basic dyes [15]. As the activated clays being negatively charged, the adsorption of anionic dyes would be less suggesting the weak interaction between the activated clay and anionic dyes. Investigations into the efficiencies of inorganic adsorbents bauxite, activated fullers earth and synthetic clay relative to activated carbon for the removal of reactive dyes from solution have concluded that the synthetic clay is most effective adsorbent as compared to activated carbon over the pH range of 5.5 to pH 8.5 for the removal of reactive dyes thus highlighting the role of clay materials on dye removal [16]. A number of studies are available on the adsorption of basic dyes on variety of adsorbents [17-20].

Although number of studies is available on the adsorption of dyes from aqueous solution using various materials as adsorbents, using of soil colloids for the adsorption of dye is scarce. In this work, we have investigated the adsorption of alizarin red and methylene blue on colloids at different pH. The kinetics characteristics on the adsorption of dyes were investigated using bench scale batch tests to understand adsorption mechanism on colloids.

II. MATERIALS AND METHODS

The dyes used in the adsorption experiments are anionic alizarin red and cationic methylene blue. The alizarin red dye is an anthraquinone derivative obtained from the root of the madder plant and is commercially available. Methylene blue is a thiazine dye, which is widely used in colouring paper, dyeing of cotton and wools and hair dyes among others [21].

A. Colloid separation

Separation of colloidal particles was achieved by mixing 100 g of soil sample with 500 mL distilled water in a beaker. The mixture was stirred overnight using mechanical stirrer. The soil mixture was then centrifuged for 15 minutes at 750 rpm to settle the solids although 3.5 minutes of centrifugation at 750 rpm is known to be sufficient to separate the native colloid particles from soil [22]. So as to ensure a better separation and retention of colloids, centrifugation was carried out for 15 minutes.

The efficiency of separation of the non colloidal particulates could be assured by the value of the relative centrifugal force which turns out to be 25.12 [23]. This value is sufficiently large to separate all suspended matter except the colloidal particle. The supernatant colloidal solution was collected and concentrated by flocculation with 0.5 M $CaCl_2$ solution, to yield a solid deposit that was separated and dried.

B. Characterization

The mineralogical composition of colloidal particles was determined by powder X-ray diffraction analysis (Panalytical, X'per PRO, Cu K, 2.2KW Max). Elemental content of colloids was measured by Scanning Electron Microscopy combined Energy Dispersive X- ray analysis. Transmission electron microscopy (Philips, Tecnai 20) images were taken to determine the shape of colloidal particles in the suspensions.

C. Adsorption experiments

Adsorption of dye from their aqueous solutions by colloids was measured by placing 50 mL of dye solution with a concentration range of 40-200 mg/L in contact with 20 mg of colloidal aggregates in a series of beakers at the pH of 2.5, 6.5 and 9.5 and at temperature of 30±2°C. The pH was varied with 0.1M NaOH/HNO$_3$ solutions. Samples were stirred by using magnetic stirrer with constant speed to maintain the contents completely mixed for about 6h. After equilibration, samples were centrifuged at 3000 rpm for 15 minutes. The concentration of the supernatant solution was measured with UV-Visible spectrophotometer (UV 2450, Shimadzu) at the wavelength of 520 nm and 665 nm for alizarin red and methylene blue respectively. A calibration curve was constructed by measuring the absorbance of known concentration of dye solution. From this plot, the concentration of unknown samples was determined from its absorbance. The quantity of adsorbed dye on colloidal particles was calculated as the difference between initial concentration and concentration at equilibrium.

D. Adsorption Kinetics

In the case of kinetic experiments the same procedure described earlier was performed with initial concentrations ranging from 50- 200 mg L^{-1}. The volume of dye solution and the quantity of adsorbent taken was 50 mL and 20 mg respectively. The samples were withdrawn from the beaker at definite time intervals and analyzed for dye concentration with UV-Visible spectrophotometer. The amount of dye adsorbed at definite time intervals was determined by using the formula given below

$$Q_t = (C_0 - C_t)V/W \qquad (1)$$

Where C_0 is the initial concentration of dye solution and C_t is the concentration of dye in the liquid phase at time t (mg L^{-1}) respectively. V is the volume of the dye solution (in liters) and W mass of the colloid adsorbent (g).

III. RESULTS AND DISCUSSION

The X ray diffraction pattern of colloids is given in Figure 1. The mineral composition colloids are Quartz, calcite and kaolinite with the 2θ values of 27, 30 and 28 reported in literature [24, 25]. The elemental content of colloids determined by EDX spectrum is given in Table I. It is evident that the percentage of indicator elements of colloids such as Si and Al is high in the sample. Transmission Electron Microscopy image of soil colloids (Figure 2) shows the presence of rod shaped and highly irregular colloidal particles in the suspensions.

A. Effect of pH

The effect of pH on the adsorption of dye was investigated by varying the solution pH over the range of 2.5 to 9.5 with 0.1 N NaOH/HNO$_3$ and the results are shown in Figure 3a & 3b. It is evident from Figure 3a that the adsorption capacity of colloids for the alizarin red is found to be high at pH 2.5 than at pH 6.5 and 9.5.
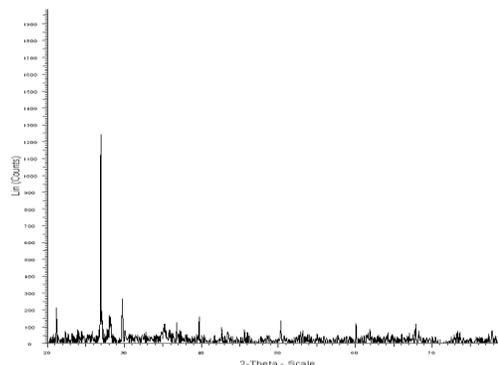

Fig.- 1: X ray diffraction pattern of colloids

The colloids used in this adsorption experiments consists of quartz and kaolinite minerals and it has been reported that isoelectric point for quartz is approximately 3 and for kaolinite it is between 3.3 to 5, below which the colloidal particles becomes positively charged [26, 27]. Thus due to the electrostatic attraction between dye and colloid, the higher amount of anionic alizarin red dye gets adsorbed on the positively charged colloidal particles at a pH of 2.5. But, as the pH increases the colloidal particles get negative charge that leads to the decrease in the adsorption of alizarin red.

Table I.
Elemental Content of Colloids used in the Adsorption experiments

Element	Weight (%)	Atomic (%)	Compound (%)
Mg	2.38	2.14	3.95
Al	9.31	7.55	17.60
Si	26.16	20.38	55.97
K	2.19	1.23	2.64
Ca	6.53	3.56	9.13
Ti	0.57	0.26	0.95
Fe	7.59	2.97	9.76
O	45.27	61.90	

The repulsion between the negatively charged sites on colloidal surface and the dye causes this low adsorption at high pH. It has also been reported that surface charge of colloids becomes more negative with increasing pH [28]. Therefore the adsorption of the alizarin red on the colloidal particles is likely to be less.
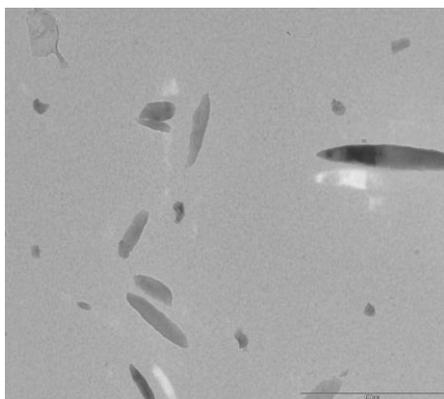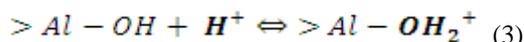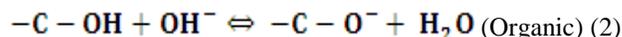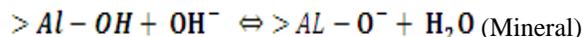

Fig.- 2: Transmission Electron Microscopy image of colloids

However, the adsorption of methylene blue shows a different trend in contrast to the alizarin red. It is observed from Figure 3b that the maximum amount of adsorption of methylene blue occurs at pH of 9.5. The mutual attraction between the negatively charged colloidal surface and the cationic methylene blue dye causes the enhanced adsorption at high pH. The surface charge of the colloids is attributed to the pH of the dye solution in which it is added. It gets negative charge in alkaline medium and positive charge in acidic medium as shown below

$$> Al - OH + OH^- \Leftrightarrow > AL - O^- + H_2O \text{ (Mineral)}$$

$$-C - OH + OH^- \Leftrightarrow -C - O^- + H_2O \text{ (Organic) (2)}$$

$$> Al - OH + H^+ \Leftrightarrow > Al - OH_2^+ \text{ (3)}$$

At low pH values of dye solution, the positive charge on the surface of colloid increases and this causes repulsion between the cationic methylene blue molecules and the colloidal surface, leads to the decrease in adsorption.

It was found that the Freundlich adsorption isotherm represented the adsorption behavior of dye on colloids and it is given in Table II. The adsorption capacity (K_F) and slope N of colloids for alizarin red decreases with respect to the increase in solution pH. In the case of methylene blue, maximum adsorption capacity (K_F) of colloids increased with increasing pH of dye solution. In this case the N value shows the increasing trend.
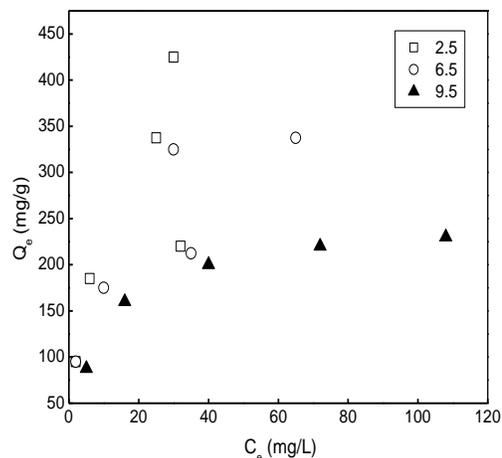
(a)
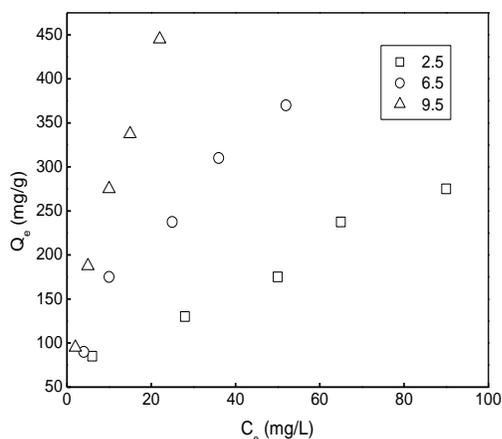
(b)

Fig. -3: Effect of pH on the adsorption of (a) Alizarin red (b) Methylene blue on colloid

The increase in the correlation coefficient value for the adsorption of alizarin red from 0.89 to 0.96 shows the linear relationship exist between the concentration and adsorbed amount of dye.

A favorable Langmuir adsorption isotherm is obtained as reflected in the correlation coefficient (R^2) values for alizarin red at pH 9.5 and for methylene blue at pH 6.5. While the monolayer adsorption capacity (Q_0) is decreased with the increase in solution pH for alizarin red, the methylene blue showed increasing trend with increase in pH.

A comparison of the adsorption capacity of the soil colloids with other adsorbents is given in Table III. The results prove the adsorption capacity of soil colloids over other adsorbents reported in literature [14, 21, 29, 30-32].

B. Adsorption kinetics

The effect of initial dye concentration on the rate and extent of adsorption of colloids were studied in a range of 50-200 mg·L^{-1} with 20 mg of colloids at room temperature (30±2°C) and the experimental data is shown in Figure 4a & 4b.

It can be seen that the rate of adsorption increased with time and attains a plateau after 5 hr. The kinetic data have been analyzed using the pseudo first and second order model.

Pseudo first order equation

The adsorbed amount of dye at different time intervals on colloids was calculated with the formula (1). The kinetics of dye adsorption on colloid was studied using the pseudo first order equation given below

$$dq/dt = K_1 (q_e - q_t) \qquad (4)$$

Where q_e is the amount of dye adsorbed at equilibrium per unit weight of adsorbent (mg·g^{-1}), q_t is the amount of dye adsorbed at time t (mg·g^{-1}) and K_1 is the adsorption constant. The linearized form of the above equation as a function of time is

$$log (q_e - q_t) = log q_e - K_1 t/2.303 \qquad (5)$$

Where k_1 is the first-order rate constant

Plots of the linearized equation were constructed and the constants were calculated from the slopes and intercepts of the plots of log (q_e-q_t) vs time.

The correlation coefficient values were found to be low and the calculated q_e values did not agree with the experimental q_e values. Thus the adsorption of alizarin red and methylene blue does not follow pseudo first order kinetics.

Table II(a).
**Freundlich isotherm Parameters for the Effect of pH**

Dye	(mg·g−1)/(L.mg−1)			N			R^2		
pH	2.5	6.5	9.5	2.5	6.5	9.5	2.5	6.5	9.5
Methylene blue	35.4	44.6	69.1	0.42	0.53	0.54	0.9709	0.9911	0.9693
Alizarin red	75.8	74.1	58.8	0.42	0.35	0.30	0.8931	0.9412	0.9657

Table II(b).
Langmuir isotherm Parameters for the Effect of pH

Dye	Q_0 (mg·g^{-1})			b (L.mg^{-1})			R^2		
pH	2.5	6.5	9.5	2.5	6.5	9.5	2.5	6.5	9.5
Methylene blue	370.3	476.1	555.5	0.027	0.063	0.150	0.9198	0.9843	0.9025
Alizarin red	344.8	370.3	256.4	0.290	0.117	0.111	0.8621	0.9477	0.9996
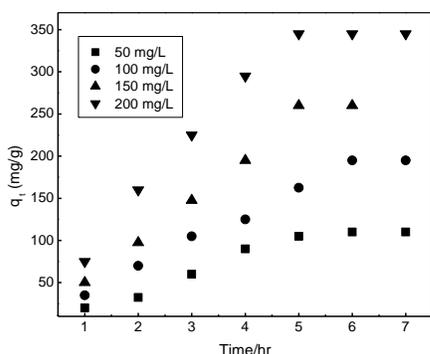
(a)
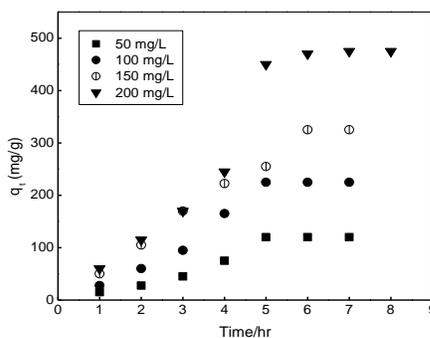
(b)

Fig. -4: The adsorbed amount of dye at different initial concentrations vs time (a) Alizarin red (b) Methylene blue

Pseudo second order equation

The kinetics of adsorption of dye on colloid was studied using the pseudo second order equation given below

$$dq_t/dt = K (q_e - q_t)^2 \qquad (6)$$

Where K is the pseudo second order rate constant (g·mg^{-1}·h^{-1}), q_e is the adsorbed amount of dye at equilibrium (mg·g^{-1}) and q_t is the adsorbed amount of dye at time t (mg·g^{-1}). Integrating equation (6) for the boundary conditions t= 0 to t= t and q_t =0 to $q_t = q_t$, gives

$$1/(q_e - q_t) = 1/q_e + K_t \qquad (7)$$

The linear form of the above equation after integration is

$$t/q_t = 1/(Kq_e^2) + (1/q_e)t \qquad (8)$$

The intercept and slope of the plot of t/q_t vs t gives the value of K and q_e respectively. The correlation coefficient values of the pseudo second order model were low and in this case too the calculated q_e values did not match the experimental q_e values. It suggests that the adsorption of dye does not follow second order kinetics.
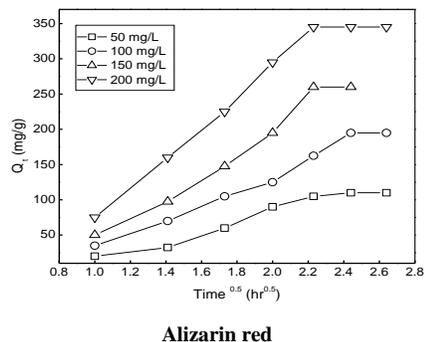
C. Intra-particle diffusion studies

Weber and Morris stated that if intra-particle diffusion is a rate controlling factor, uptake of adsorbate varies with square root of time [33]. It is given by the formula

$$Q_t = K_p t^{0.5} \qquad (9)$$

Where k_p intra particle diffusion rate parameter.

The possibility of intraparticle diffusion was investigated by plotting amount of dye adsorbed (Q_t) vs $t^{0.5}$ at different initial concentration of dye in solution. It is observed from Figure 5 that the amount of dye adsorbed on colloid increases gradually and attains equilibrium. The initial curve portion is attributed to the surface adsorption where as the linear equilibrium portion shows the intra-particle diffusion effect.

Alizarin red
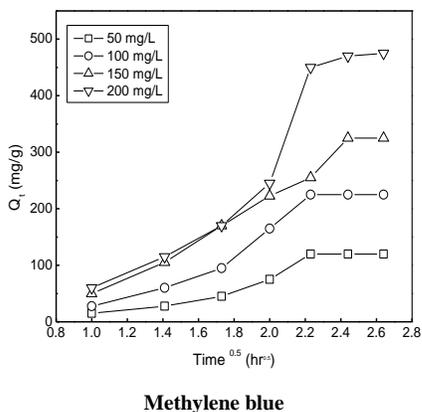
Methylene blue

Fig.- 5: Intra-particle diffusion plot for the adsorption of dye on colloid

The linear plot of $t^{0.5}$ and Q_t indicates the intra-particle diffusion effect of dyes on colloid and this would be a rate controlling step if this line passed through the origin. However, the line do not pass through the origin shows the intraparticle diffusion occurs in the process and it is not the only rate controlling step but other processes such as surface adsorption also involved. The rate constant for intra particle diffusion coefficient $K_p(mg \cdot g^{-1} \cdot hr^{0.5})$ was determined from the slope of the linear plot of Figure 5 and the values of K_p over the concentration range 50-200 $mg \cdot L^{-1}$ are 63.43, 104.75, 158.69 and 178.20 for alizarin red 76.14, 140.88, 179.91 and 293.28 for methylene blue. The intraparticle diffusion coefficient (K_p) increase with a rise in concentration of dye solution. The correlation coefficient values were found to be greater than 0.98 suggesting the intraparticle diffusion. As the colloidal material is crystalline as is evident from the sharp peak in X ray diffraction, intra particle diffusion occurs through the space between the lattice layers. The increase in rate of adsorption and amount adsorbed with concentration is indicative of a system controlled by intraparticle transport.

Table III.
Comparison of adsorption capacities of various adsorbents

Adsorbent	Dye	Adsorption $(mg \cdot g^{-1})$	Reference
Solid waste from leather industry	Methylene blue Reactive red	80.00 163.0	[14]
Montmorillonite Activated clay	Basic green 5	127.6 271.3	[32]
Natural Tripoli	Methylene blue	16.60	[21]
Sludge ash	Methylene blue	1.60	[29]
Activated carbon	Congo red	21.10	[30]
Burnt clay	Congo red	22.80	[31]
Soil colloids	Methylene blue	555.5	Present study

IV. CONCLUSIONS

The colloidal particles isolated from soil adsorb dyes effectively from the aqueous solution. The adsorption dyes at different pH values show that colloid adsorption is sensitive to pH of the aqueous solution. The high adsorbed amount of contaminants on colloid is indicative of surface adsorption and intraparticle diffusion processes occurring in the experiments. The presented results can be used to better understand the adsorption and transport of dyes released from industries in natural environments and possibly be used to remediate the contaminants.

REFERENCES

[1] Tsai, W.T., Chang, C.Y., Ing, C.H. and Chang, C.F. 2004 J. colloid interface sci. 275, 72.

[2] Slokar, Y.M. and Le Marechal, M. 1998 Dyes. Pigm. 37, 335.

[3] Hao, O.J., Kim, H. and Chiang, P. C. 1999 Crit. Rev. Environ. Sci. Technol. 30, 449.

[4] Meshko, V., Markovska, L., Minchev, M. and Rodrigues, A.E. 2001 Water Res. 35(14), 3357.

[5] Allen, S. J. and Koumanova, B. 2005 Journal of the University of Chemical technology and Metallurgy. 40, 175.

[6] Jain, A. K., Gupta, V. K., Jain, S. and Suhas. 2004 Environ. Sci. Technol. 38(4), 1195.

[7] Hameed, B. H. Din, A.T.M. and Ahmad, A. M. 2007 J. Hazard. Mater. 141, 819.

[8] [8] Chern, J. M. and Huang, S. N. 1998 Ind. Eng. Chem. Res. 37(1), 253-259.

[9] Ruth, Yu-Li Yeh. and Thomas, A. 1995 J Chem Tech Biotechnol. 63, 48.

[10] Kannan, N. and Sundaram, M. M. 2002 Water Air Soil Pollut. 138, 289.

[11] Liu, R. and Tang, H. 2000 Water Res. 34(16), 4029.

[12] Albanis, T. A., Hela, D. G., Sakellarides, T. M. and Danis, T. G. 2000 Global Nest: the. Int. J. 2(3), 237.

[13] Hsu, Y. C., Chiang, C. C. and Yu, M. F. 1997 Sep. Sci. Technol. 32, 2513.

[14] Oliveira, L. C. A., Goncalves, M., Oliveira, D.Q.L., Guerreiro, M. C., Guilherme, L.R.G. and Dallago, R. M. 2007 J. Hazard. Mater. 141(1), 344.

[15] Chiang, C. C., Hsu, Y. C. and Chin, J. 1997 Colloid Interface Sci. 20, 215.

[16] Lambert, S. D., Graham, N.J.D., Sollars, C. J. and Fowler, G. D. 1997 Wat. Sci.Tech. 36, 173.

[17] Chu, H. C. and Chen, K. M. 2002 Process Bio Chemistry. 37(6), 595.

[18] Nassar, M. M. and Majdy, Y. H. 1997 Chem. Eng. J. 66(3), 223.

[19] Lata, H., Garg, V. K. and Gupta, R. K. 2007 Dyes Pigm. 74, 653.

[20] McKay, G., El-Geundi, M. and Nassar, M. M. 1988 Water Res. 22, 1527.

[21] Alzaydien, A. S. 2009 Am. J. Environ sci. 5(3), 197.

[22] Barton, C. D., and Karathanasis, A. D. 2003 J. Environ. Studies. 60, 395.

[23] Upadhyay, A., Upadhyay, K., and Nath, N. 1993 Biophysical chemistry Principles and Techniques, Himalaya Publishing House, Bombay.

[24] Atteia, O., Perret, D., Adatte, T., Kozel, R. and Rossi, P. 1998 Environmental Geology. 34(4), 257.

[25] Mashal, K., Harsh, J. B., Flury, M., Felmy, A. R. and Zhao, H. 2004 Environ. Sci. Technol. 38, 5750.

[26] Hendershot, W. H. and Lavkulich, L. M. 1983 Soil Sci. Soc. Am. J. 47, 1252.

[27] Ryan, J. N. and Gschwend, P. M. 1994 Environ. Sci. Technol. 28, 1717.

[28] Sen, T. K., Mahajan, S. P. and Khilar, K. C. 2002b AIChE Journal. 48, 2366.

[29] Weng, C. H. and Pan, Y. F. 2006 Colloids surfaces A: Physicochem. Eng. Aspect. 274, 154.

[30] Arivoli, S., Sundaravadivelu, M. and Elango, K. P. 2008 Ind. J. Chem. Tech. 15, 130.

[31] Mumin, M. A., Khan, M.M.R., Akhter, K. F. and Uddin, M. J. 2007 Int. J. Environ. Sci. Tech. 4(4), 525.

[32] Shiau, C. and Pan, C. 2004 Separation science and technology. 39(8), 1733.

[33] Weber, W. J. and Morris, J. C. 1963 J. Sanit Eng. Div. ASCE. 89, 31.

Corresponding author previous address:

Applied Chemistry Department, Faculty of Technology and Engineering, The M S University of Baroda, Vadodara-390001, Gujarat, India

Contact Number: +91 7708334913