

Comparative Study of Kinetics of Removal of Fuchsin Basic from Aqueous Solutions Using Biosorbents

Satish Patil¹, Jayesh Patil², Naseema Patel³

^{1,2}Department of Chemistry, A.P.ScienceCollege,Nagothane – 402106 (MS), India

³Department of Chemistry, Yeshwant College, Nanded – 431602 (MS), India.

Abstract: Adsorption studies of Fuchsin Basic (FB) on six different agricultural wastes / natural materials were carried out by batch experiments. The parameters studied include initial dye concentration, adsorbent dose, pH, agitation time, agitation speed, particle size of adsorbent and temperature. The best fitting isotherm models were found to be Langmuir and Temkin. The monolayer (maximum) adsorption capacities (q_m) were found between 166.667 to 250 mg/g for adsorbents under study. Among the kinetic models, Lagergen pseudo - second order model best fits the kinetics of adsorption. Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. Adsorption was found to increase on increasing pH, increasing temperature, increasing agitation speed and decreasing particle size. Thermodynamic analysis showed negative values of free energy change indicating adsorption was favourable and spontaneous, small positive values below 40 KJ/mole of enthalpy change indicating endothermic physical adsorption and positive values of entropy change indicating increased disorder and randomness at the solid- solution interface of FB with biosorbents. Adsorption capacity of pineapple peel powder towards FB was found to be more than other adsorbents under study.

Keywords: Adsorption isotherm, FuchsinBasic, biosorbents, kinetic and thermodynamic parameters.

I. Introduction

The discharge of synthetic dyes into wastewaters from the textile industries has raised much concern because of potential health hazards associated with entry of toxic components into the food chains of human and animals. Over 10,000 dyes with an annual production of over 7×10^5 metric tons worldwide are commercially available and 5–10% of the dye stuff is lost in the industrial effluents. The coloration of water by the dyes may have an inhibitory effect on photosynthesis, thus affecting aquatic eco-systems. Dyes may also be problematic if they are broken down anaerobically in the sediment as toxic amines which are often produced due to incomplete degradation by bacteria. Some of the dyes or their metabolites are either toxic or mutagenic and carcinogenic.

The most popular treatment methods for textile wastewater are combinations of biological treatment, chemical coagulation and activated carbon adsorption [1-2]. Adsorption onto activated carbon is proven to be very effective in treating textile wastes. However, in view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost adsorbents. Such types of adsorbents include coir pith [3], modified clays[4], oxihumolite [5]and fly ash [6].

In the present study removal of fuchsin basic from aqueous solution using some agricultural wastes / solids as adsorbents were investigated.

II. Material And Methods

1.1 Adsorbent

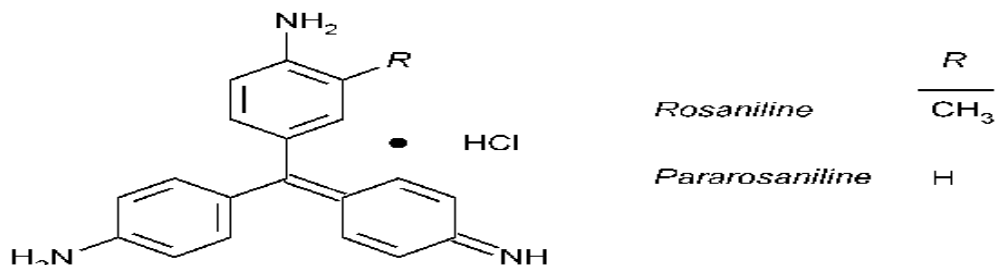
Adsorbents used in the present study are:

1. Pineapple (*Ananascomosus*) peel powder (PPP)
2. Mangrove plant (*Sonneratiaapetala*) fruit powder (MPFP)
3. Coconut (*Cocosnucifera*)coir pith (CCP)
4. Mango (*Mangiferaindica*) leaf powder (MLP)
5. Toor plant (*Pisumstativum*) leaf powder (TPLP)
6. Tamarind (*Tamarindusindica*) fruit shell powder (TFSP)

Mature materials of all above biosorbents were collected from Konkan region of Maharashtra state in India and washed thoroughly with distilled water to remove dust and other impurities. Washed materials were dried for 10 days in sunlight. Dried materials were grounded in a domestic mixer- grinder after removing non required parts separately. After grinding, the powders were again washed and dried. Different sized powders of each adsorbent were sieved through Jayant's sieves and stored in plastic bottle containers for further use.

2.2 Dye solution

Fuchsin Basic (FB), a basic dye which is mixture of rosaniline and pararosaniline hydrochlorides. It is Benzenamine,4-[(4-aminophenyl)(4-amino-2,5-cyclohexadien-1-ylidene)methyl-2-methyl],monohydrochloride. It contains the equivalent of not less than 88 % of rosaniline hydrochloride with molecular formula $C_{20}H_{19}N_3.HCl$. In dye classification it is classified as C.I.Basic Violet 14 monohydrochloride [632-99-5].



A stock solution of 1000 mg/l was prepared in double-distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

2.3 Methods:

Standard solution (8 mg/l) of the FB was taken and absorbance was determined at different wavelengths using Equiptronics single beam u.v. visible spectrophotometer to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance ($\lambda_{max} = 550$ nm) as determined from the plot, was noted and this wavelength was used for measuring the absorbance in the present study. pH of solutions were adjusted using 1M HCl and 1M NaOH by Equiptronics pH-meter.

The efficiency of adsorbents is evaluated by conducting laboratory batch mode studies. Specific amounts (25mg) of adsorbents were shaken in 25 ml aqueous solution of dye of varying concentration for different time periods at natural pH (≈ 7) and temperature ($\approx 303K$). At the end of pre-determined time intervals, adsorbent was removed by centrifugation at 10000 rpm and supernatant was analyzed for the residual concentration of FB, spectrophotometrically at 550 nm wavelength.

Also variation in pH, adsorbent dose, particle size, agitation speed and temperature were studied.

The values of percentage removal and amount of dye adsorbed were calculated using following relationships:

$$\text{Percentage removal} = [(C_i - C_f) / C_i] \times 100$$

$$\text{Amount adsorbed} = (C_i - C_f) / m$$

Where, C_i = Initial dye concentration, C_f = Final dye concentration, m = Mass of adsorbent in g/l.

2.3.1 Effect of contact time

25 mg of adsorbent of ≥ 120 mesh size with 25 ml of dye solution was kept constant for batch experiments with an initial dye concentration of 150 mg/l were performed at nearly 303K on a oscillator at 230 rpm for 5, 10, 15, 20, 30, 40, 50 and 60 minutes at pH = 7. Then optimum contact time was identified for further batch experimental study.

2.3.2 Effect of adsorbent dosage

Initial dye concentration of 500 mg/l were used in conjunction with adsorbent dose of 1, 2, 3, 4, 5, and 6 g/l. Contact time, pH, agitation speed, temperature and particle size of 30 minutes, 7, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

2.3.3 Effect of initial dye concentration

Initial dye concentration of 100, 125, 150, 175, 200, 225 and 250 mg/l were used in conjunction with adsorbent dose of 1 g/l. Contact time, pH, agitation speed, temperature and particle size of 30 minutes, 7, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

2.3.4 Effect of pH

Initial pH of dye solutions were adjusted to 3, 4, 6, 7, 8 and 11 for 200 mg/l concentration. Contact time, adsorbent dose, agitation speed, temperature and particle size of 30 minutes, 1 g/l, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

2.3.5 Effect of particle size

Three different sized particles of ≥ 120 , $120 \leq 85$ and $85 \leq 60$ meshes were used in conjunction with

200 mg/l dye concentration. Contact time, adsorbent dose, agitation speed, temperature and pH of 60 minutes, 1 g/l, 230 rpm, 303K and 7 respectively were kept constant.

2.3.6 Effect of temperature

303K, 313K and 323K temperatures were used in conjunction with 250 mg/l dye concentration. Contact time, adsorbent dose, agitation speed, particle size and pH of 60 minutes, 1 g/l, 230 rpm, ≥ 120 mesh and 7 respectively were kept constant.

2.3.7 Effect of agitation speed

100, 170 and 230 rpm agitation speeds were used in conjunction with initial dye concentration of 175 mg/l. Adsorbent dose, pH, temperature, contact time and particle size of 1 g/l, 7, 303K, 60 minutes and ≥ 120 mesh respectively were kept constant.

2.4 Desorption Studies:

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH 3, 7 and 11 using dilute solutions of NaOH and HCl. Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual dyes.

For the desorption studies, dye loaded adsorbents from 100mg/l initial dye concentration were used.

2.5 COD Determination Studies

COD of each dye before and after adsorption was determined for 100 mg/l initial dye concentration for the adsorbent with highest adsorbent capacity. Reduction in COD due to removal of dye after adsorption is then tabulated.

III. Results And Discussion

3.1 Effect of contact time

Effect of contact time on adsorption of FB is presented in **Fig. 1**. Uptake of FB was rapid in first 5 minutes and after 30 minutes amount of dye adsorbed was almost constant. Therefore, further batch experiments were carried out at 30 minutes optimum contact time.

In first 5 minutes nearly 69.66 to 92.53% of total dye uptake appears to have been adsorbed in this duration depending upon the adsorption ability of different adsorbents. Later on the process becomes relatively slower and equilibrium conditions are reached within 20 to 30 minutes. Therefore, further batch experiments were carried out at 30 minutes optimum contact time. At equilibrium % removal increased 81.47 to 96.93 % depending upon the adsorption ability of different adsorbents. The adsorption capacity of adsorbents was found to be of the order of PPP > MPFP > CCP > MLP > TPLP > TFSP.

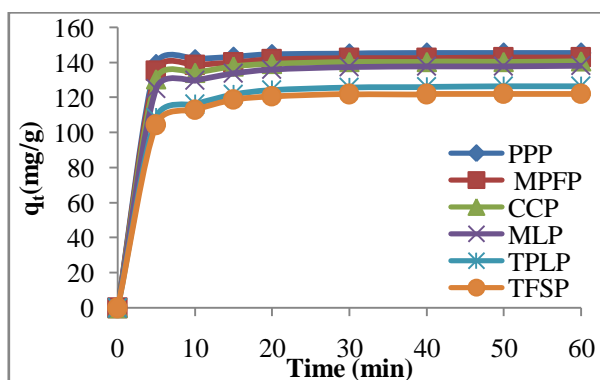


Fig. 1: Effect of contact time on adsorption of FB.

To investigate the mechanism of adsorption, pseudo - first order, pseudo- second order, Natarajan and Khalaf first order, Bhattacharya and Venkobachar first order models were used.

The Lagergen pseudo- first order rate expression is given as

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t \quad (1)$$

Where q_e and q_t are amounts of dye adsorbed (mg/g) on adsorbent at equilibrium and at time t

respectively and k_1 is rate constant of pseudo first order adsorption (min^{-1}). The slope and intercept values of plots $\log(q_e - q_t)$ against t , (**Fig. 2**) were used to determine pseudo first order rate constant (k_1) and theoretical amount of dye adsorbed per unit mass of adsorbent $q_{e(\text{the})}$, respectively. $q_{e(\text{the})}$ were compared with the $q_{e(\text{exp})}$ values in **Table 1**. $q_{e(\text{exp})}$ values differ from the corresponding $q_{e(\text{the})}$ values showed that pseudo first order equation of Langergen does not fit well with whole range of contact time and is generally applicable for initial stage of adsorption.

The Langergen pseudo- second order kinetic model is given as $t/q_t = 1/(k_2q_e^2) + t/q_e$ (2)

Where k_2 is rate constant of second order adsorption ($\text{g/mg}\cdot\text{min}$). The slopes and intercepts of plot of t/q_t against t , (**Fig. 3**) were used to determine $q_{e(\text{the})}$ and k_2 respectively. From highly linear plots it is cleared that there may be a possibility of chemisorption playing a significant role in the rate determining step. The pseudo second order parameters, $q_{e(\text{the})}$, h and k_2 obtained from the plot are represented in **Table 1**. Where h is initial adsorption rate ($\text{mg/g}\cdot\text{min}$), $h = k_2 q_e^2$.

The correlation coefficient R^2 for second order adsorption model has very high values for both the adsorbents ($R^2 \geq 0.999$) and $q_{e(\text{the})}$ values are consistent with $q_{e(\text{exp})}$ showed that pseudo second order adsorption equation of Langergen fit well with whole range of contact time and dye adsorption process appears to be controlled by chemisorption.

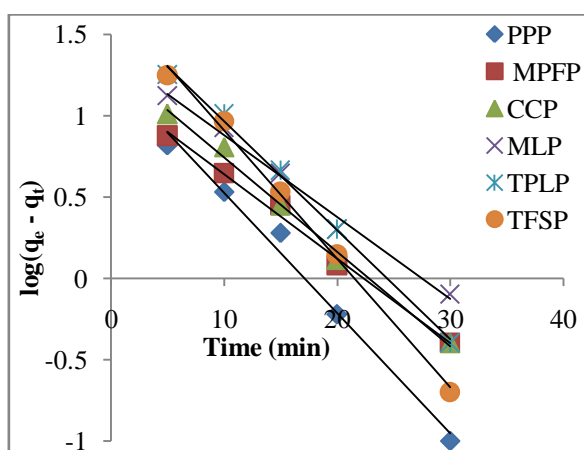


Fig. 2: Pseudo first order plot of effect of contact time on adsorption of FB.

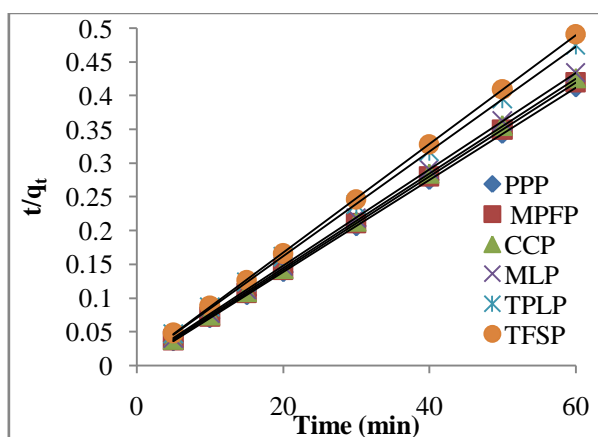


Fig. 3: Pseudo second order plot of effect of contact time on adsorption of FB.

Table 1: Effect of contact time on adsorption of FB

Adsorbent	Initial FB Conc. (mg/l)	Pseudo -first order model				Pseudo -second order model				
		$q_{e(\text{exp})}$ (mg/g)	$K_1(\text{min}^{-1})$	$q_{e(\text{the})}$ (mg/g)	R^2	$q_{e(\text{exp})}$ (mg/g)	K_2 (g/mg/min)	$q_{e(\text{the})}$ (mg/g)	h (mg/g min)	R^2
PPP	150	145.4	0.1704	18.408	0.988	145.4	0.03621	166.67	1006.02	1
MPFP	150	143	0.1175	14.421	0.993	143	0.01811	166.67	503.012	1
CCP	150	140.8	0.1336	21.135	0.994	140.8	0.01633	142.86	333.334	1
MLP	150	138.2	0.1152	24.266	0.99	138.2	0.01225	142.86	250.001	1
TPLP	150	126.4	0.1543	43.551	0.996	126.4	0.00817	142.86	166.667	0.999
TFSP	150	122.2	0.1819	50.350	0.996	122.2	0.01067	125	166.667	0.999

The linearized form of Natarajan and Khalaf first order kinetic equation is presented as

$$\log (C_0/C_t) = (K / 2.303) t \quad (3)$$

Where C_0 and C_t are concentrations of FB (mg/l) at time zero and time t respectively. K is first order adsorption rate constant (min^{-1}) which was calculated from slope of plot $\log (C_0/C_t)$ against t , (Fig. 4, Table 2).

The linearized form of Bhattacharya and Venkobachar first order kinetic equation is presented as

$$\log [1 - U(T)] = - (k / 2.303) t \quad (4)$$

Where $U(T) = [(C_0 - C_t) / (C_0 - C_e)]$

C_e is equilibrium FB concentration (mg/l)

K is first order adsorption rate constant (min^{-1}) which was calculated from slope of plot $\log [1 - U(T)]$ against t , (Fig. 5, Table 2).

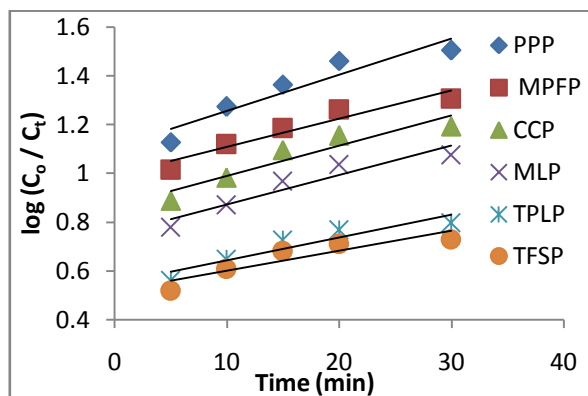


Fig. 4: Natarajan and Khalaf first order plot of effect of contact time on adsorption of FB.

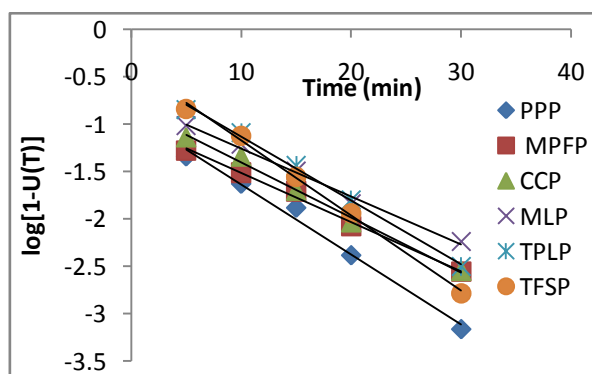


Fig. 5: Bhattacharya and Venkobachar first order plot of effect of contact time on adsorption of FB.

Correlation coefficient values were not high for Natarajan and Khalaf first order equation ($R^2 = 0.818$ to 0.92) and does not fit well but for Bhattacharya and Venkobachar first order equation ($R^2 = 0.98$ to 0.996) values were found high enough and does not fit well at least till attending the equilibrium for adsorption of FB. Steps involved in sorption of the dye by adsorbent includes transport of solute from aqueous to surface of solid and diffusion of solute into the interior of pores, which is generally a slow process. According to Weber and Morris, the intra particle diffusion rate constant (K_i) is given by the following equation

$$q_t = K_i t^{1/2} \quad (5)$$

K_i ($\text{mg g}^{-1} \text{min}^{-1/2}$) values can be determined from the slope of the plots q_t against $t^{1/2}$. Fig. 6 showed a linear relationship after certain time but they do not pass through origin. This is due boundary layer effect. The larger the intercept, the greater the contribution of surface sorption in rate determining step. The intercepts and K_i values of plot q_t against $t^{1/2}$ increased with increase in the initial concentration of dye, (Table 2). Initial portion is attributed to the liquid film mass transfer and linear portion to the intra particle diffusion.

The linearized form of Elovich kinetic equation is presented as

$$q_t = 1 / [\beta \ln(\alpha\beta)] + \ln t / \beta \quad (6)$$

Where α and β are the constants calculated from the intercepts and slopes of plots q_t against $\ln t$, (Fig. 7, Table 2). α and β values are found to be according to the adsorption capacity of the adsorbent. The better adsorption has highest value of initial adsorption rate (α) and lowest value of desorption constant (β) and vice versa. Thus Elovich model also fit well.

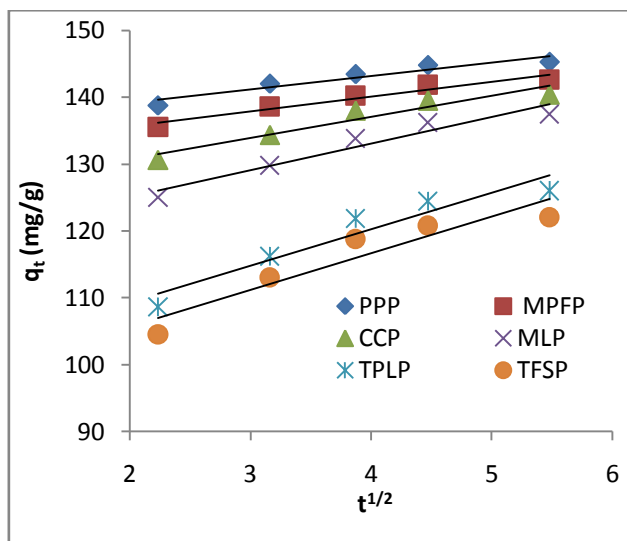


Fig. 6: Intra particle diffusion plot of effect of contact time on adsorption of FB.

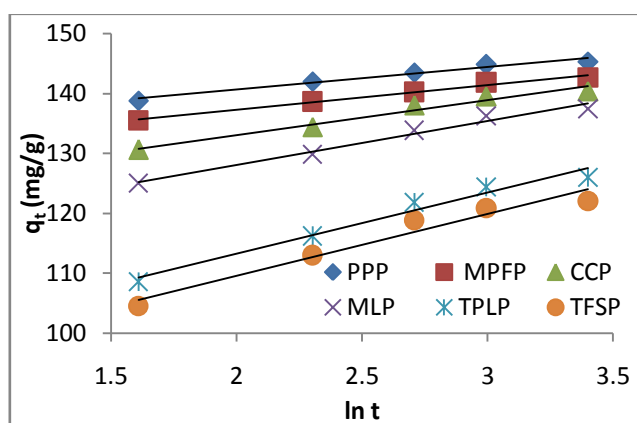


Fig. 7: Elovich plot of effect of contact time on adsorption of FB.

Table 2: Effect of contact time on adsorption of FB

Adsorbent	Initial FB Conc. (mg/l)	Intra particle diffusion model			Elovich Model			Natarajan and Khalaf model		Bhattacharya and Venkobachar model	
		K_i (mg/g/min ^{1/2})	A (mg/g)	R ²	A (mg/g/min)	β (g.mg ⁻¹)	R ²	K (min ⁻¹)	R ²	K (min ⁻¹)	R ²
PPP	150	2.018	135.1	0.91	3.8678	0.2659	0.972	0.0322	0.892	0.1704	0.98
MPFP	150	2.22	131.2	0.944	4.2153	0.2443	0.987	0.0253	0.92	0.1175	0.993
CCP	150	3.143	124.5	0.92	6.1058	0.1718	0.97	0.0276	0.885	0.1336	0.994
MLP	150	3.969	117.1	0.935	7.8097	0.1366	0.979	0.0276	0.905	0.1152	0.99
TPLP	150	5.486	98.31	0.914	11.3845	0.0980	0.972	0.0207	0.869	0.1543	0.996
TFSP	150	5.469	94.79	0.879	11.5123	0.0975	0.952	0.0184	0.818	0.1819	0.996

3.2 Effect of adsorbent dosage

Adsorption of FB was studied by varying the adsorbent dosage. The percentage of adsorption increased (Fig. 8) but amount adsorbed per unit mass of adsorbent decreased (Fig. 9) with increase in dosage of adsorbent from 1 to 6 g/l. For above 95% removal of FB from 500 mg/l initial FB concentration, adsorbent dosage of 3, 4, 4, 5 and 6 g/l were needed for PPP, MPFP, CCP, MLP and TPLP respectively, but for TFSP even for 6 g/l adsorbent dose 95% removal of FB was not observed. It was found that % removal of dye increased but amount of dye adsorbed per unit mass of adsorbent decreased with increased in adsorbent dose from 1 to 6 g/l. As amount of adsorbent increases, number of active sides available for adsorption also increases thus % removal also increases but as all active sides may not be available during adsorption due to overlapping between the active sides themselves and thus amount adsorbed mg/g of adsorbent decreases. The adsorption of dye increased with the sorbent dosage and reached an equilibrium value after certain sorbent dosage.

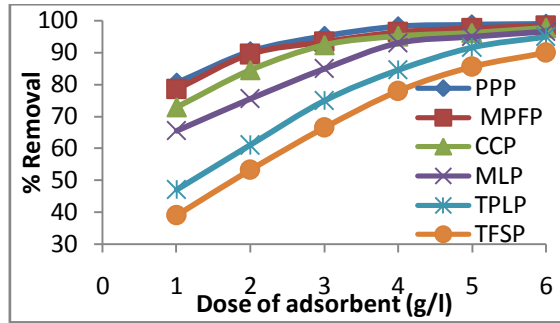


Fig. 8: Effect of adsorbent dosage on adsorption of FB.

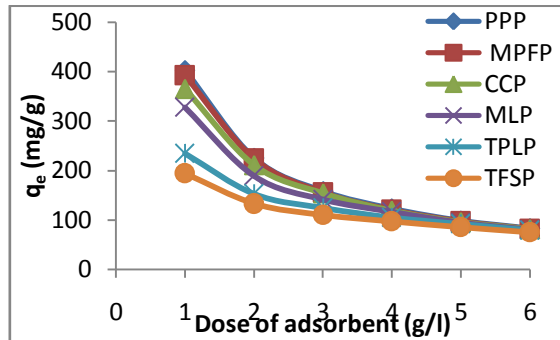


Fig. 9: Effect of adsorbent dosage on amount adsorbed of FB (mg/g)

3.3 Effect of initial dye concentration

Amount of FB adsorbed per unit mass of adsorbent increased (Fig. 10) but % removal decreased (Fig. 11) with increase in initial FB concentration from 100 to 250 mg/l.

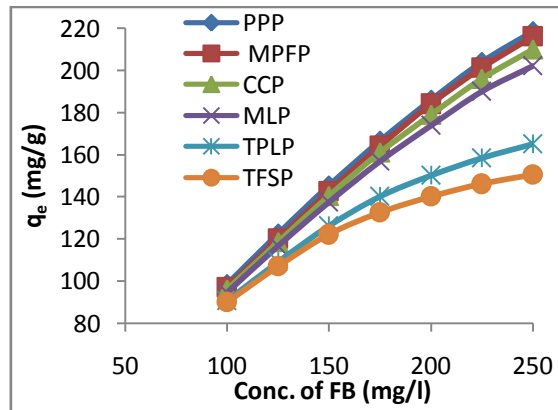


Fig. 10: Effect of initial dye concentration on adsorption of FB.

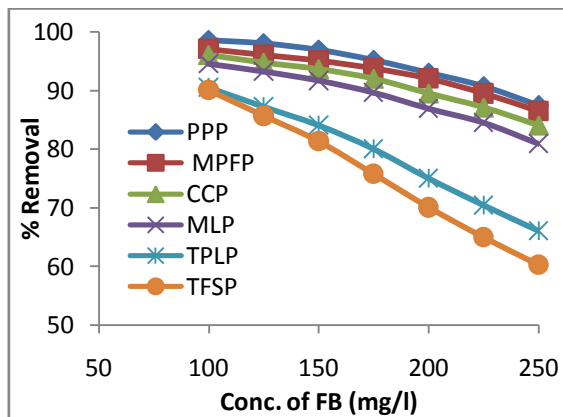


Fig. 11: Effect of initial dye concentration on % removal of FB.

The Freundlich equation was employed for the adsorption of FB onto the adsorbent. The isotherm was represented by

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \quad (7)$$

Where q_e is amount of FB adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of FB in solution (mg/l), K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption respectively. The plots of $\text{log } q_e$ against $\text{log } C_e$ showed good linearity ($R^2 = 0.976$ to 0.989) indicating the adsorption of FB obeys the Freundlich adsorption isotherm, (Fig. 12). The values of K_f and n are given in the Table 3. Values of n between 1 to 10 indicate an effective adsorption[10] while higher values of K_f represent an easy uptake of adsorbate from the solution[9].

The Langmuir isotherm was represented by the following equation

$$C_e / q_e = 1 / (q_m b) + C_e / q_m \quad (8)$$

Where q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg). Linear plots of C_e / q_e against C_e ($R^2 = 0.997$ to 0.999) suggest the applicability of the Langmuir isotherms, (Fig. 13). The values of q_m and b were determined from slopes and intercepts of the plot, (Table 3). The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L , which is defined by the following relation given by Hall[11]

$$R_L = 1 / (1 + bC_0) \quad (9)$$

Where C_0 is initial FB concentration (mg/l). R_L values lies between 0 to 1 indicates favourable adsorption, (Table 4).

The Temkin isotherm is given as

$$q_e = B \ln A + B \ln C_e \quad (10)$$

Where A (1/g) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to heat of adsorption. A linear plots of q_e against $\ln C_e$, ($R^2 = 0.992$ to 0.999) enables the determination of the constants B and A from the slope and intercept, (Fig. 14). The results of the plot are given in Table 3. All the adsorption isotherms fit well for adsorption of FB on the adsorbents under study.

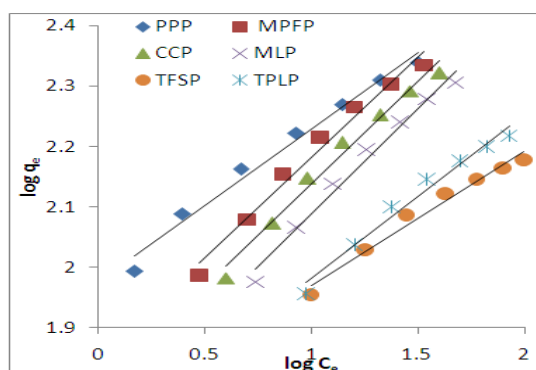


Fig. 12: Freundlich isotherm plot of effect of initial dye concentration on adsorption of FB.

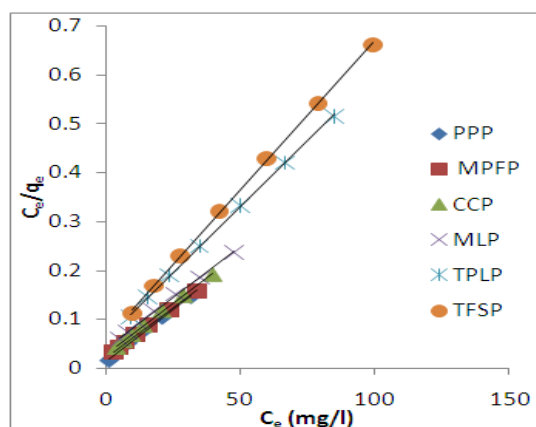


Fig. 13: Langmuir isotherm plot of effect of initial dye concentration on adsorption of FB.

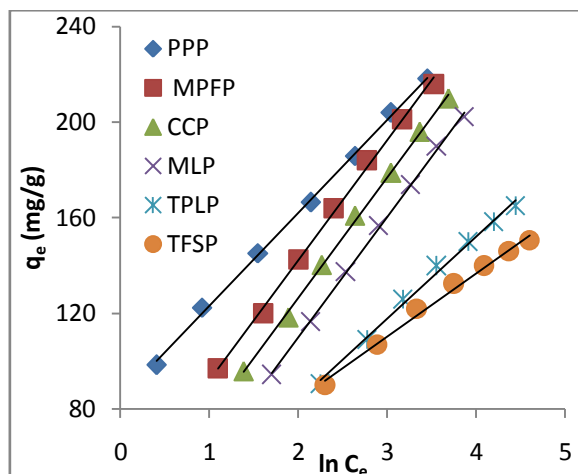


Fig. 14: Temkin isotherm plot of effect of initial dye concentration on adsorption of FB.

Table 3: Effect of initial dye concentration on adsorption of FB

Adsorbent	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	R^2	q_m	b	R^2	A	B	R^2
PPP	94.189	3.953	0.989	250	0.364	0.997	8.812	38.84	0.998
MPFP	70.632	3.012	0.98	250	0.19	0.999	2.299	50.2	0.997
CCP	62.517	2.941	0.983	250	0.143	0.998	1.673	50.31	0.998
MLP	54.45	2.857	0.983	250	0.105	0.999	1.197	50.46	0.999
TPLP	51.05	3.676	0.977	200	0.085	0.999	1.543	34.33	0.994
TFSP	55.976	4.525	0.976	166.667	0.107	0.999	3.232	26.47	0.992

Table 4: Dimensionless separation factor (R_L) calculated from Langmuir constant (b)

Initial FB Conc. (mg/l)	PPP	MPFP	CCP	MLP	TPLP	TFSP
100	0.026764	0.04988	0.065419	0.08676	0.105541	0.085368
125	0.021526	0.040306	0.053029	0.070634	0.086253	0.069481
150	0.018003	0.033816	0.044585	0.059563	0.072926	0.058579
175	0.015471	0.029126	0.038461	0.051492	0.063166	0.050634
200	0.013563	0.025578	0.033816	0.045347	0.05571	0.044587
225	0.012075	0.022801	0.030172	0.040513	0.049829	0.03983
250	0.01088	0.02057	0.02724	0.03661	0.04507	0.03599

3.4 Effect of pH

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of FB from 200 mg/l concentration on different was studied by varying the pH from 3 to 11. The % removal of FB increased with increase in pH from 3 to 11, (Fig. 15).

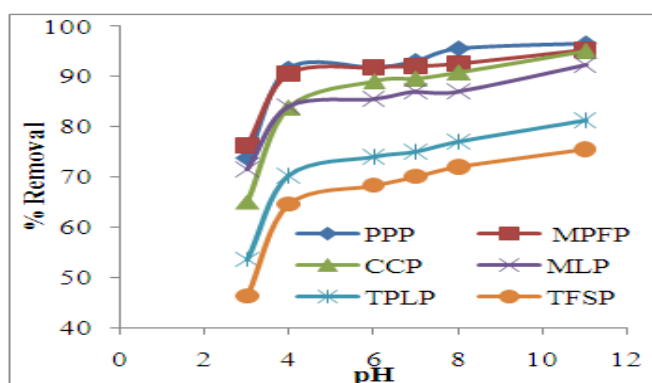


Fig. 15: Effect of pH on adsorption of FB from initial concentration of 200 mg/l.

3.5 Effect of particle size

Adsorption of FB on three sized particles ≥ 120 , $120 \leq 85$ and $85 \leq 60$ mesh of adsorbent was studied for 200 mg/l concentrations of FB. The results of variation of these particle sizes on dye adsorption are shown in Fig. 16. It can be observed that as the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. This is due to larger surface area that is associated with smaller particles. For larger particles, the diffusion resistance to mass transfer is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently amount of dye adsorbed is small.

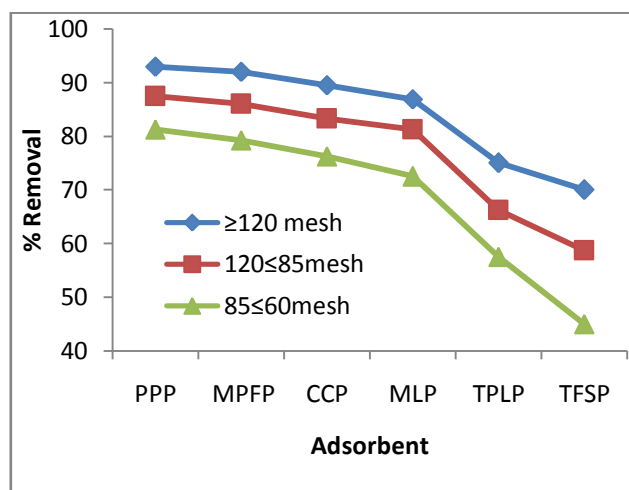


Fig. 16: Effect of particle size on % removal of FB.

3.6 Effect of agitation speed

Sorption is influenced by mass transfer parameters. Fig. 17 illustrates the sorption kinetics of FB from 175 mg/l initial FB solution by biosorbents for different agitation speeds. The amounts adsorbed at equilibrium (q_e) in mg/g were found to increase with increased in agitation speed from 100, 170 and 230 rpm of an oscillator. This is because with low agitation speed the greater contact time is required to attend the equilibrium. With increasing the agitation speed, the rate of diffusion of dye molecules from bulk liquid to the liquid boundary layer surrounding the particle become higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer.

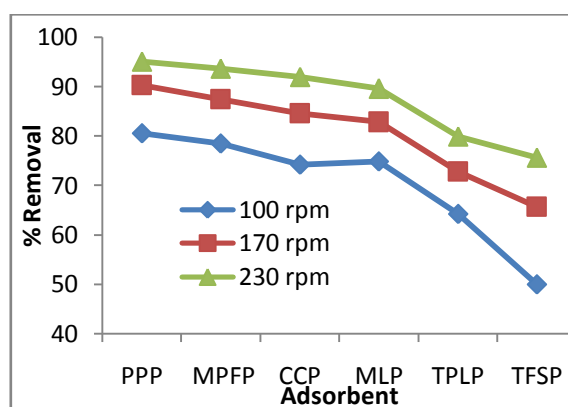


Fig. 17: Effect of agitation speed on adsorption of FB.

3.7 Effect of temperature

Temperature has important effects on adsorption process. Adsorption of FB at three different temperatures (303K, 313K and 323K) onto different biosorbents was studied for 250 mg/l initial FB concentration. The results variations in temperatures on dye adsorption are shown in Fig. 18. It is observed that as the experimental temperature increases from 303K to 323K, the dye adsorption also increases. As the temperature increases, rate of diffusion of adsorbate molecules across external boundary layer and internal pores of adsorbent particle increases [7]. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate[7-8].

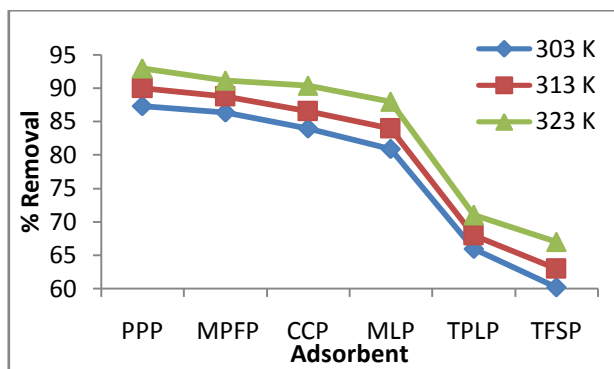


Fig. 18: Effect of temperature on adsorption of FB

Thermodynamic analysis:

Thermodynamic parameters such as change in free energy (ΔG) (kJ/mole), enthalpy (ΔH) (kJ/mole) and entropy (ΔS) (J/K/mole) were determined using following equations

$$K_o = C_{solid} / C_{liquid} \tag{11}$$

$$\Delta G = -RT \ln K_o \tag{12}$$

$$\Delta G = \Delta H - T \Delta S$$

$$\ln K_o = -\Delta G / RT$$

$$\ln K_o = \Delta S / R - \Delta H / RT \tag{13}$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/l), C_{liquid} is liquid phase concentration at equilibrium (mg/l), T is absolute temperature in Kelvin and R is gas constant. ΔG values obtained from equation (12), ΔH and ΔS values obtained from the slope and intercept of plot $\ln K_o$ against $1/T$, Fig. 19 presented in Table 5. The negative value of ΔG indicates the adsorption is favourable and spontaneous. ΔG values increased with increase in temperature and decreased with increase in initial concentration of FB. The low positive values of ΔH indicates endothermic nature of adsorption ΔH values were lie between 11.947 to 26.522 KJ/mole indicates physical adsorption. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of FB with the adsorbent. The adsorbed water molecules, which were displaced by adsorbate molecules, gain more translational energy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface.

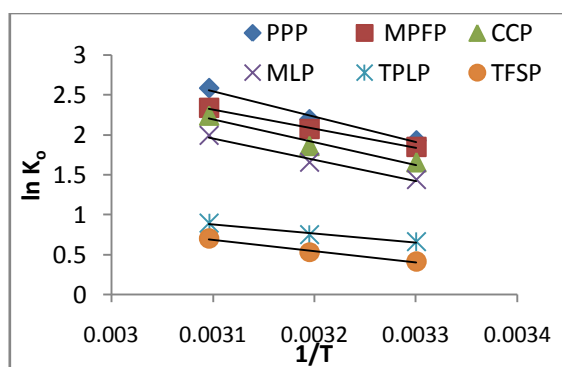


Fig. 19: Von't Hoff plot of effect of temperature on adsorption of FB.

Table 5: Equilibrium constants and thermodynamic parameters for the adsorption of FB

Adsorbent	K _o			ΔG (kJ/mole)			ΔH (kJ/mole)	ΔS (J/K/mole)
	303K	313K	323K	303K	313K	323K		
PPP	6.911	9	13.286	-4.870	-5.718	-6.946	26.522	103.343
MPFP	6.353	7.929	10.364	-4.658	-5.388	-6.279	19.879	80.90353
CCP	5.25	6.44	9.417	-4.177	-4.847	-6.022	23.678	91.62028
MLP	4.23	5.25	7.333	-3.633	-4.315	-5.351	22.323	85.46792
TPLP	1.941	2.125	2.448	-1.671	-1.962	-2.405	9.411	36.51509
TFSP	1.513	1.703	2.03	-1.042	-1.385	-1.902	11.947	42.77553

Desorption Studies: Fig. 20 represents desorption of FB from dye loaded adsorbents at initial pH 3, 7 and 11. For the desorption studies, dye loaded adsorbents from 100 mg/l initial dye concentration are used.

Among the adsorbents at pH 3, least desorption of FB is observed for PPP (12.59%) and maximum for TFSP (26.11%). At pH 7, least desorption of FB is observed for PPP (2.84%) and maximum for TFSP (6.67%). At pH 11, least desorption of FB is observed for PPP (1.52%) and maximum for TFSP (5%).

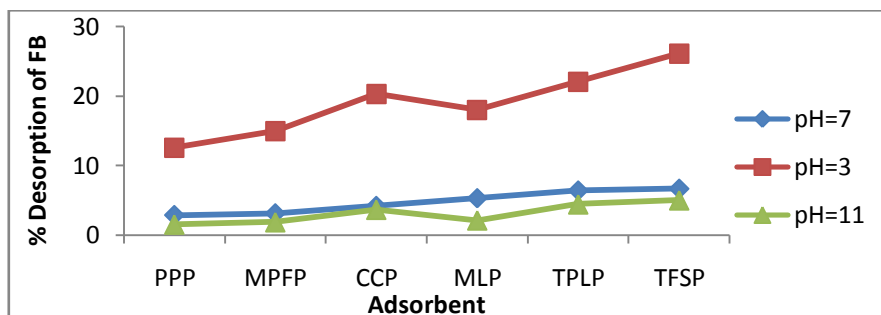


Fig. 20: % desorption of FB from dye loaded adsorbent

Desorption studies showed reverse mechanism. Desorption of dye (organic pollutant) from the surface of adsorbents increased with decrease in pH of solution because adsorbed cationic dye again displaced by H⁺ ions. But only 12.59 to 26.11 % desorption is observed even at pH = 3 indicating chemical adsorption is played a role in adsorption. Chemical adsorption followed by multilayer physical adsorption. Ion exchange mechanism played a minimal role in adsorption.

COD Determination Studies:

COD of before and after adsorption is determined for 100 mg/l initial dye concentration for the adsorbent with highest adsorbent capacity for a particular dye. Reduction in COD due to removal of FB after adsorption is given in Table 6.

Table 6: % Reduction in COD after adsorption

Adsorbent	FB Conc.(mg/l)		COD (mg/l)		% Reduction in COD
	Before adsorption	After adsorption	Before adsorption	After adsorption	
PPP	100	2.1	520	100	80.77

Sharp reduction in COD indicates sorption of FB on biosorbents under study was found to be an excellent technique for wastewater management.

IV. Conclusion

The objective of this paper was utilization of different agricultural waste materials as adsorbents for the removal of fuchsin basic.

The following conclusions have been drawn based on above investigations:

1. These biomaterials have excellent adsorption capacity compared to many other non-conventional adsorbents. They can be used as a low cost attractive alternative for costly activated carbon.
2. Langmuir and Freundlich isotherm parameters ($R^2 \approx 0.99$, $n > 3.4$, $R_L = 0.0187$ to 0.1988) confirmed that the adsorption of FB on these adsorbents was favourable.
3. Bhattacharya and Venkobachar first order kinetic model also showed good linearity ($R^2 = 0.978$ to 0.995)
4. Langmuir and Freundlich isotherm models and Lagergen pseudo -second order kinetic model were found to be best fitting models.
5. The values amount of FB adsorbed per unit mass of adsorbent obtained by Lagergen pseudo -second order model, $q_{e(the)}$ were in consistent with the experimental values, $q_{e(exp)}$ with $R^2 \approx 1$.
6. Intra particle diffusion model showed boundary layer effect and larger intercepts indicates contribution of surface adsorption was high in rate determining step. Adsorption was found to increase on increasing pH, temperature, agitation speed and decreasing particle size.
7. Thermodynamic analysis showed that adsorption of FB on these biomaterials was:
 - a) favourable and spontaneous (negative values of ΔG)
 - b) Endothermic (positive values of ΔH)
 - c) Physical adsorption (small $\Delta H < 30$ kJ/mole)
 - d) Increased disorder and randomness at the solid- solution interface (positive values of ΔS).

8. Adsorption ability of biosorbents towards FB was found to be PPP > MPFP > CCP > MLP > TPLP > TFSP
9. Desorption studies showed chemical adsorption also played a role.
10. Nearly 80% COD reduction showed an excellent method of removal of organic pollutants from waste water using biosorbents.

References

- [1] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption of various carbons- a comparative study, *Dyes and pigments*, 51,2001, 25-40.
- [2] K.G.Bhattacharyya and A.Sharma, Kinetics and thermodynamics of methylene blue adsorption on Neem(*Azadirachta Indica*) leaf powder, *Dyes and pigments*, 65,2005,51-59.
- [3] C. Namasivayam, D.Kavitha, Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, *J. Dyes Pigments*, 54,2002,47-58.
- [4] Z Bouberka, S. Kacha, M, Kameche, S. Elmaleh, Z .Derriche , Sorption study of an acid dye from aqueous solutions using modified clays. *J. Hazard. Mater. B.* 119,2005, 117-124.
- [5] P.Janos, P.Sedivy, M .Ryznarova, Sorption of basic and acid dyes from aqueous solutions onto oxihumolite, *Chemosphere*; 119,2005,881-886.
- [6] S. Wang., Y.Boyjoo , A.Choueib , Z. H.Zhu , Removal of dyes from aqueous solution using fly ash and red mud, *Water Res.*, 39,2005, 129-138.
- [7] S.H.Lin, "Adsorption of disperse dye on various adsorbents", *J.Chem. Tech. Biotechnol.*, **58**, 1993,159-162.
- [8] A.K.Singh, D.P.Singh, K.K.Pandey,V. N.Singh, "Wollastonite as adsorbent for removal of Fe(II) from water," *J. Chem. Technol.*, **42**, 1988,39.
- [9] A.H.Mahvi, A.Maleki,A.Eslami, Potential of rice husk and rice husk ash for phenol removal in aqueous system. *Am. J. Appl. Sci.*, **1 (4)**,2004,321-326.
- [10] J.Potgeiter, S.Vermaak, P.Kalibatonga, Heavy metals removal from solution by Palygorskite clay. *Minerals Engineering*. 2005.
- [11] K. R.Hall,L.C.Eagleton,A.Acrivios, T.Vermeulen, *Ind. Eng. Chem. Fund.*, **5**, 1966
- [12] W.J.Weber , *Principle and Application of Water Chemistry*, edited by Faust S.D. and Hunter J. V. Wiley, New York, 1967.