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Removal of Tartrazine Dye form Aqueous Solutions by Adsorption on the Surface of Polyaniline/Iron Oxide Composite

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***Abstract*—**In this work, a polyaniline/Iron oxide (PANI/Fe_2O_3) composite was chemically prepared by oxidative polymerization of aniline in acid medium, in presence of ammonium persulphate as an oxidant and amount of Fe_2O_3. The composite was characterized by a scanning electron microscopy (SEM). The prepared composite has been used as adsorbent to remove Tartrazine dye form aqueous solutions.

The effects of initial dye concentration and temperature on the adsorption capacity of PANI/Fe_2O_3 for Tartrazine dye have been studied in this paper.

The Langmuir and Freundlich adsorption models have been used for the mathematical description of adsorption equilibrium data. The best fit is obtained using the Freundlich isotherm with an R^2 value of 0.998. The change of Gibbs energy, enthalpy, and entropy of adsorption has been also evaluated for the adsorption of Tartrazine onto PANI/ Fe_2O_3. It has been proved according the results that the adsorption process is endothermic in nature.

***Keywords*—**Adsorption, Composite, dye, Polyaniline, Tartrazine.

I. Introduction

ELECTRICALLY conducting polymers are important in modern technology as they have potential applications in optical and micro-electronic devices, chemical sensors [1], catalysis, anti corrosion, and energy storage systems [2], [3]. Polyaniline is one of the most interesting conducting polymers due to its environmental stability [4]. Practically, Polyaniline can be prepared via chemical or electro-chemical oxidation of aniline in acidic medium [5], [6].

Conducting polymer/Inorganic particle composites with different combinations of the components have attracted more attention since they have interesting physical properties. A variety of oxides such as: Al_2O_3, TiO_2, MnO_2, and Fe_2O_3 have been incorporated into Polyaniline in order to improve its properties [7]-[10].

Color pollution in aquatic environments is an escalating problem. The recalcitrant nature of modern synthetic dyes has led to the imposition of strict environmental regulations. The need for a cost effective process to remove the color from wastewater produced by the textile industry, has been recognized.

Dyes are one of the organic compounds which can color other substances and make them brighter. Synthetic dyes generally have a complex aromatic molecular structure which it probably comes from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. Due to the complex aromatic molecular structure of dyes, these dyes will be more stable and harder to biodegrade [11], [12]. The main technologies used for the treatment of dye-containing effluents are chemical precipitation, adsorption, ion exchange, biodegradation, membrane filtration, coagulation, flocculation, etc. Adsorption is widely used and it is the most versatile as other methods have high capital cost and low efficiency [13], [14].

In this paper, adsorption of Tartrazine dye from aqueous solution on the surface of Polyaniline/Iron oxide (PANI/ Fe_2O_3) has been investigated. Furthermore, thermodynamic parameters of adsorption have been calculated using Freundlich and Langmuir equations.

The effect of temperature in the range of 20-40°C has been studied. It has been found that the amount of adsorption increases when temperature increases. Freundlich and Langmuir equations have been applied for the obtained results.

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II. Materials and Methods

A. Materials

The materials have been used in this research are as follows: Aniline (PARK) which was used after double distillation, Ammonium persulfate, pure Fe_2O_3 (99%), Acetone and Hydrochloric acid (obtained from BDH), and Tartrazine dye (Aldrich, USA) which were used without further purification.

TABLE I
CHARACTERISTICS OF TARTRAZINE

Parameter	Value
Chemical formula	$C_{16}H_9N_4Na_3O_9S_2$
Molecular weight (g/mol)	534.36
C.I. No	19140
Physical form	Orange powder
Soluble in solvents	Water
λ_{max} (nm)	426
C.I. Name	Anionic Dye

B. Methods

1. Dye Solution Preparation

The characteristics of the Tartrazine are given in Table I while Fig. 1 illustrates the Chemical structure of Tartrazine. An accurately weighed quantity of the dye (0.534g) was dissolved in double distilled water to prepare stock solution ($1x10^{-3}$ M). This solution has been used in the experiments to get the desired concentration by successive dilutions, which ranges from 5×10^{-5} to 1.25×10^{-4} M.

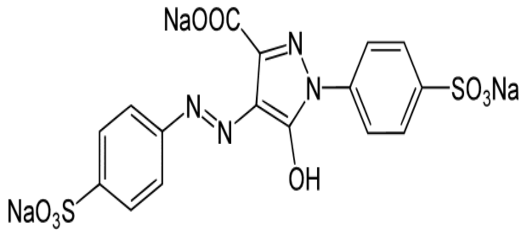

Fig. 1 Chemical structure of Tartrazine

2. Preparation of PANI/Fe_2O_3 Composite

Polyaniline/Iron oxide composite has been prepared by the reported method [15]. The polyaniline/Iron oxide (PANI/Fe_2O_3) composite has been chemically prepared by oxidative polymerization of aniline in acid medium, where 100 ml of (0.1 M) HCl acid has been placed in a beaker of 250 ml; then, 2.28g (0.1M) of $(NH_4)_2S_2O_8$ and 2g of Fe_2O_3 have been added in the beaker. After a period of 10 min of shaking and stirring of the mixture on a magnetic stirrer, 0.625M of aniline has been injected, drop by drop, into the mixture. After injection of 6 ml of this aniline, polymerization has started and a dark green precipitate (PANI/Fe_2O_3) has formed. Then, polymerization has continued for three hours at room temperature.

After that, the formed precipitate has been separated by filtration and the precipitate has been washed several times by the acid solution used in polymerization process. Then it has been washed by distillated water several times in order to remove the acid. Orange methyl has been used to check the removal of acid.

Finally, the precipitate has been washed several times using acetone in order to obtain pure composite. The precipitate has been dried in a furnace in a temperature range of 60-80^{o}C for 24 hours and then it has been properly crushed.

3. The Process of Adsorption

Kinetic Experiments

Batch kinetic experiments has been performed by mixing 0.03g of (PANI/Fe_2O_3) to each 20 ml of dye solution of $1\text{x}10^{-4}$ M concentration at (20,25,30,35, and 40°C), respectively. A series of such conical flasks has been then shaken at a constant speed of 100 rev/min in a water bath shaker. Samples have been collected at different time intervals.

The sample has been taken by a pipette after the separation of the solution by precipitation and filtration using centrifuge (Model 0412-1). Then, the sample has been placed inside a cell of UV-visible spectrophotometer (JENWAY 6305 Spectrophotometer).

The percentage removal of dye solution has been calculated by the following formula:

$$(Adsorpation\%) = \frac{C_o - Ce}{C_o} \times 100 \quad (1)$$

where C_o is the initial concentration of the dye and C_e is the equilibrium concentration of the dye (mol/L).

The equilibrium adsorption capacity of PANI/Fe_2O_3 for Tartrazine dye has been calculated from the following relationship:

$$q_{eq} = \frac{(C_o - C_{eq})V}{W} \quad (2)$$

where q_{eq} is the equilibrium adsorption capacity, C_e is the dye concentration (mol $\cdot L^{-1}$) at equilibrium, V is the volume (L) of solution, and w is the weight (g) of adsorbent.

The amount of Tartrazine dye adsorbed q_t at time t onto the surface of the PANI/Fe_2O_3 has been estimated by the mass balance equation as follows:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (3)$$

Equilibrium Experiments

The effect of the initial dye concentration has been determined by placing 0.03 g of the PANI/Fe_2O_3 composite in 20 ml of dye solution of different initial concentrations (5 x 10^{-5} M, 7.5 x 10^{-5} M, 1 x 10^{-4} M and 1.25 x 10^{-4} M) for 60 minutes at 30±1^{o}C. The concentration of Tartrazine dye left in the supernatant solution was determined by spectrophotometer at a wavelength of maximum absorbance (426 nm).

III. Results and Discussion

A. Surface Morphology Analysis

The scanning electron microscopy (SEM, JMS-6700F) image of PANI/Fe_2O_3 is shown in Fig. 2. It can be seen from the figure that the surface is irregular and porous, which provides a good platform for Tartrazine adsorption.

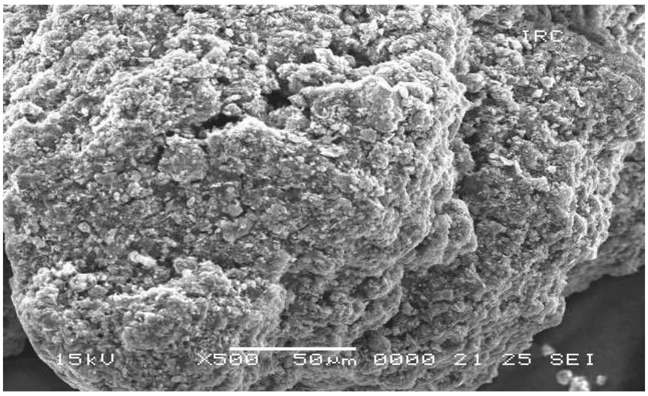

Fig. 2 SEM image of PANI/ Fe_2O_3

B. Effect of Initial Dye Concentration

The effect of initial dye concentration on adsorption efficiency onto PANI/Fe_2O_3 has been explored as shown in Fig. 3. The examined dye concentration on adsorption is in the range of 5x10^{-5} to 1.25 x 10^{-4} (mol.L^{-1}) Tartrazine at temperature 30±1^{o}C in presence 0.03 g PANI/ Fe_2O_3. It can be noticed from the figure that the percentage of Tartrazine removal has decreased with the increase in initial concentration of Tartrazine. Although the percent of adsorption has decreased with the increase in initial dye concentration, the actual amount of dye adsorbed per unit mass of adsorbent has increased with increase in dye concentration. This is because the initial dye concentration supplies the required driving force in order to overcome the resistance facing the mass transfer of Tartrazine between aqueous phase and the solid phase. The increase in initial dye concentration causes an increase in the interaction between dye molecules and PANI/ Fe_2O_3 surface. As a result, the increase of the initial concentration of Tartrazine improves the adsorption uptake of the dye [16].

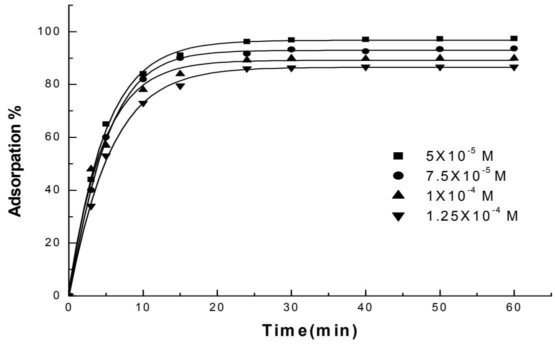

Fig. 3 Effect of initial dye concentration on percent removal at equilibrium at temperature 30°C

C. Effect of Temperature on Adsorption

The effect of temperature in the range of 20-40°C has been studied, where it has been found that the amount of adsorption increases with increasing of temperature. Freundlich and Langmuir equations have been applied for the obtained results.

D. Freundlich Isotherm Modeling

Freundlich model assumes a heterogeneous adsorption surface which has unequal available sites with different adsorption energies [17] and can be represented by:

$$q_{eq} = K_f \cdot C_{eq}^{1/n} \tag{4}$$

The equation could be written in a linear form of Freundlich by taking logarithm of the equation as follows:

$$Ln q_{eq} = Ln K_f + 1/n \, Ln C_{eq} \tag{5}$$

where: q_{eq} is the amount of dye adsorbed at equilibrium, K_f is Freundlich constant related to the sorption, (1/n) is an empirical parameter related to sorption intensity,which varies heterogeneity of the material and C_{eq} is the equilibrium dye Concentration in solution.

It can be noticed that when Freundlich equation has been applied, the obtained results were compatible with the equation, where correlation coefficient (R^2) was approximately 0.998 in most of the cases, as it appears in Fig. 4. Table II shows the values of K_f and n of Tartrazine dye.

TABLE II
FREUNDLICH ADSORPTION CONSTANTS FOR ADSORPTION OF TARTRAZINE PANI/F_2O_3 AT DIFFERENT TEMPERATURE

Temp (°C)	R^2	(1/n)	n	LnK_f	K_f
20	0.996	0.155	6.45	-1.05	0.355
25	0.999	0.156	6.41	- 0.947	0.387
30	0.981	0.171	5.84	- 0.677	0.508
35	0.997	0.217	4.60	- 0.013	0.987
40	0.996	0.242	4.13	0.402	1.490

It can be noticed from Table II that the value of K_f increases with the increase of temperature. This means that the adsorption process increases with increase in temperature (i.e. the process is endothermic). Fig. 4 shows the application of Freundlich on adsorption results at different temperature.

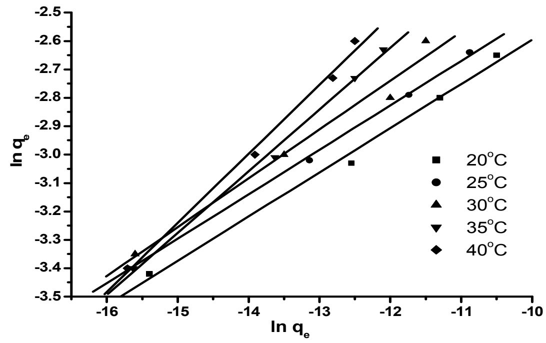

Fig. 4 Freundlich isotherms for adsorption of Tartrazine onto PANI/Fe_2O_3 at different temperature

E. Langmuir Isotherm Modeling

The Langmuir isotherm is the common used isotherm equation for modeling of the sorption equilibrium data [18]. In this model, the uniform energies of adsorption onto the surface are assumed without any transmigration of adsorbate in the plane of the surface. Langmuir model of sorption is a model based on the physical hypothesis in which there is no interaction between adsorbed molecules and the energy of adsorption over the entire coverage surface.

This model imposes that a certain site of the adsorbent is occupied by an adsorbate molecule. No further adsorption takes place at that site, i.e. forming a monolayer of adsorbed species.

The linear form of Langmuir isotherm equation is given by the following equation [19]:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L q_{max}} + \frac{C_{eq}}{q_{eq}} \tag{6}$$

where C_{eq} is the equilibrium concentration of the dye (mol/L), q_{eq} is the amount of adsorbate dye per each gram of composite at equilibrium, q_{max} (mmol/g) is the maximum amount of adsorbed dye corresponding to complete monolayer coverage, K_L(L/mol) is the Langmuir adsorption equilibrium Constant related to the energy of adsorption.

The Langmuir constants can be evaluated from the slope and the intercept of the linear equation.

Fig. 5 shows the application of Langmuir equation for the results of Tartrazine dye adsorbing on the surface of PANI/Fe_2O_3 composite at different values of temperature.

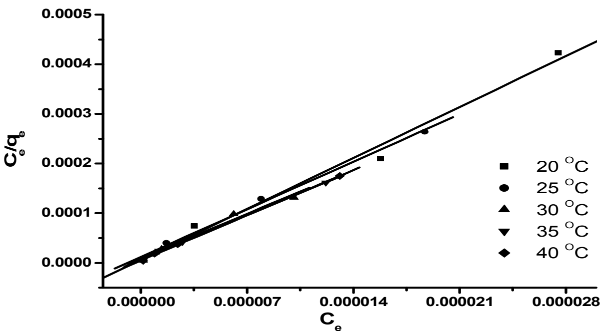

Fig. 5 Langmuir isotherms for adsorption of Tartrazine onto PANI/Fe_2O_3 at different temperature

Table III shows the Langmuir parameters of Tartrazine dye adsorption, which is calculated at different temperature values ranging from 20-40°C. It can be noticed that the value of q_{max} increases with the increase in temperature until it reaches its maximum value at 30°C while it decreases with the increase in temperature when the temperature is above 30^{o}C till the temperature reaches 40°C. This is because the increase in temperature leads to an increase in the speed of adsorption process until a Monolayer of dye molecules is formed on the surface of PANI/ Fe_2O_3 and reaching the equilibrium state. Furthermore, due to the low observed value of contact time, which was about 24 minutes, adsorption process is considered to be a physical adsorption. In addition, because the adhesion of dye molecules is weak in such desorption process starts once the temperature is increased. This causes a decrease in the value of q_{max} at high temperature.

TABLE III
LANGMUIR ADSORPTION CONSTANTS FOR ADSORPTION OF TARTRAZINE ON PANI/F_2O_3 AT DIFFERENT TEMPERATURE

Temp (C^o)	q_{max} mmol/g	$K_L x10^3$ (L/ mol)	K_L (L/mol)	LnK_L	ΔG (KJ/mol)	R^2
20	0.066	104.493	104.493	4.649	-11.324	0.998
25	0.072	133.547	135.547	4.909	-12.168	0.997
30	0.078	149.423	149.423	5.006	-12.610	0.990
35	0.078	214.389	214.389	5.367	-13.526	0.998
40	0.077	166.074	166.074	5.112	-13.302	0.999

F. Thermodynamic Parameters for Adsorption Process

Thermodynamic parameters for adsorption process have been calculated using Langmuir constant (K_L). These parameters have been calculated at different temperature values as shown in Fig. 4. These parameters are the change in enthalpy (ΔH), the change in free energy (ΔG), and the change in entropy (ΔS) associated with adsorption process.

The change in free energy (ΔG) associated with adsorption process can be calculated from this equation:

$$\Delta G = -RT\, Ln\, K_L \tag{7}$$

where: *ΔG is* change in free energy (KJ/mol), R is general gas constant, which equals 8.314J/mol.k, T is Absolute temperature (K), $K_L$is Langmuir constant (L/mol).

Equations (8) and (9) are used to calculate the values of *ΔS, ΔH* :

$$\ln K_L = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

First of all, a graph of LnK_L on the Y- axis and (1/T) on the X-axis is plotted as shown in Fig. 5. The relationship is linear with a slope equals $\frac{-\Delta H}{R}$

ΔH can be calculated using the slope value and then substituted in (9).

Table IV gives the quantitative thermodynamic data of dye on the adsorbent surface of PANI/Fe_2O_3. When the value of ΔH for Tartrazine dye is positive this indicates that the adsorption process is an endothermic process. The negative value of Δ*G* has increased with temperature increase, indicating the feasibility and spontaneity of the adsorption process of Tartrazine onto PANI/Fe_2O_3, while the positive value of Δ*S* revealed the increase in randomness at the solid-solution interface during the adsorption process.

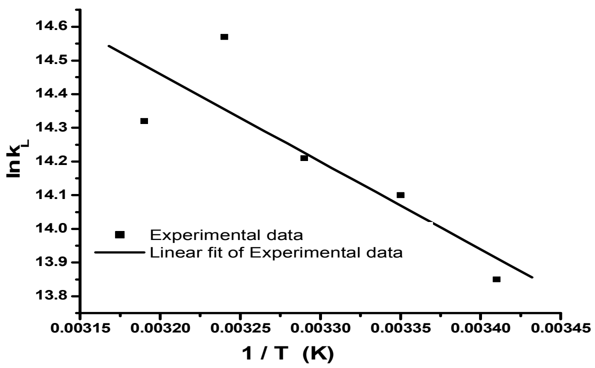

Fig. 6 Plot of lnk_L vs. 1/*T* for the estimation of thermodynamic parameters for adsorption of tartrazine onto PANI/Fe_2O_3

TABLE IV
THE THERMODYNAMIC PARAMETERS OF TARTRAZINE DYE ADSORPTION PROCESS ON THE SURFACE OF PANI/F_2O_3

T K	1/T K^{-1}	K_L L\mol	LnK_L	ΔG KJ/mol	ΔH KJ/mol	ΔS J.mol/K
293.15	0.00341	104.493	4.649	-11.32		
298.15	0.00335	133.547	4.909	-12.16		
303.15	0.00329	149.423	5.006	-12.61	21.220	111.58
308.15	0.00324	214.389	5.367	-13.52		
313.15	0.00319	166.074	5.112	-13.30		

G. Weber–Morris Model

The Intraparticle diffusion model has been tested in order to identify the adsorption mechanism. The Intraparticle diffusion model de-signed by Weber–Morris [20] is given in the following equation:

$$q_t = K_i t^{0.5} + I \quad (10)$$

where: K_i is the Intraparticle diffusion rate constant in ($mmol.g^{-1}.min^{-0.5}$), $t^{0.5}$ is square root of contact time; I is an intercept (mmol. g^{-1}) proportional to the boundary layer thickness.

It should be noticed that the larger value of I, the greater is the boundary layer effect [21], [22].

When Weber–Morris model has been applied on the results of adsorption process obtained in this research, it has been found that graphical shape of this model has linear intersects with Y-axis while it does not passes through the origin, as shown in Fig. 7. This means that the adsorption process is complicated. It also means that both surface adsorption mechanism and adsorption due to diffusion inside Polyaniline iron oxide composite are the responsible for the completion of adsorption process.

The value of intercept gives an indication about the thickness of the boundary layer. When intercept is larger the effect of thickness of the diffusion layer will be greater in adsorption process.

It can be concluded that the amount of adsorbed dye on the surface of ($PANI/Fe_2O_3$) is the sum of adsorption on the surface and the adsorption inside the composite. It can also be noticed that the value of R^2 approaches one which indicates that the application of this model on the results is correct.

Table V shows the values of intercepts (I) and Ki which are calculated by Weber–Morris model on the results of Tartrazine dye adsorption at different initial dye concentration.

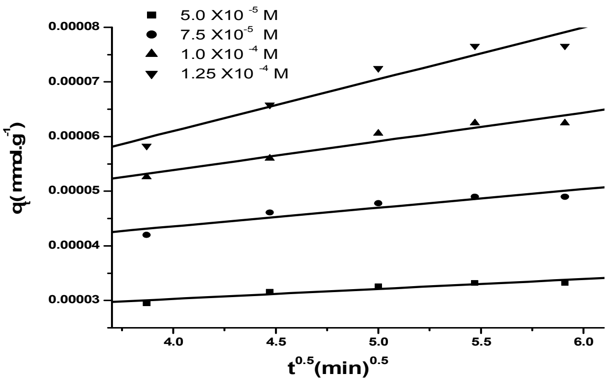

Fig. 7 Intreapartical diffusion plot for adsorption of Tartrazine onto $PANI/Fe_2O_3$ at various dye concentrations

It can be noticed from Table V that the values of K_i, I increase by the increase of initial dye concentration. This can be interpreted according to the effect of potential force due to the gradual change in concentration.

TABLE V
THE VALUES OF INTERCEPTS (I) AND KI WHICH ARE CALCULATED BY WEBER–MORRIS MODEL AT DIFFERENT INITIAL DYE CONCENTRATION

[Dye] mol/L	Intercept (I)	K_i	R^2
5 x 10^{-5}	2.32 x 10^{-5}	1.77 x 10^{-6}	0.942
7.5 x 10^{-5}	2.99 x 10^{-5}	3.40 x 10^{-6}	0.937
1 x 10^{-4}	3.28 x 10^{-5}	5.25 x 10^{-6}	0.964
1.25 x 10^{-4}	2.22 x 10^{-5}	9.61 x 10^{-6}	0.969

IV. CONCLUSIONS

A polyaniline/Iron oxide ($PANI/Fe_2O_3$) composite has been chemically prepared by oxidative polymerization of aniline in medium acid, in presence of ammonium persulphate as an oxidant and amount of Fe_2O_3. This composite has been used to remove Tartrazine dye from aqueous Solution. It has been noticed from this study that physical adsorption is the responsible process for removal of Tartrazine dye from aqueous solutions. It has also been concluded that the amount of adsorbed dye on the surface of ($PANI/Fe_2O_3$) is the sum of adsorption on the surface and the adsorption inside the composite. Furthermore, according to the obtained results, the process is endothermic process. It has been also noticed the percentage of Tartrazine removal decreases with the increase in initial concentration of Tartrazine.

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REFERENCES

[1] J. Huang, S Virji, R. B. Kaner." Polyaniline nanofibers facile synthesis and Chemical sensors". *J. Am chem Soc*, vol.125, pp. 314-5, 2003.
[2] A. Gemeay, I. Mansour, R. G. " El-Sharkawy, A. B Zaki, Catalytic activity of polyaniline/MO_2 Composites towords the oxidative decolorization of organic dyes ", *j,applied Catalysis*, vol. 80, PP. 106-15, 2008.
[3] D. Sazou, kourouzidou, E. pavlidou, "potentodynamic and potentiostatic deposition of polyaniline onstainless steel : electrochemical and structural studies for a potential application to corrosion control Electrochim". *Acta*, vol. 13, PP. 4385-97, 2007.
[4] J.L.Camalet, J.C Lacroix, S.Aeiyach, Chane-ching, K, P.C. Lacaze, "Electrosynthesis of adherent polyaniline films on iron and mild steel in aqueous oxalic acid medium", Synth. Met.,vol.93,pp 133–142 1998.
[5] M. Debajyoti, M.G. irdhar, S. Radhakrishnan, and P. Satish, "Adsorpation of Sulfonated Dyes by poly anilnie Emeradine Salt and Its Kinetes", *J. Phys.Chem*, vol.112,PP. 10153- 10157, 2008.
[6] J. Molina, A. I. del Rio, J.Bonastre, F. Cases. "Electrochemical polymerization of aniline on Conducting textiles of polyester covered with polypyrrole/AQA" J.Europen polymer, PP 11-003, 2008.
[7] K. arthikeyan, M.. Kumar, K. K. S.; Elango, K. P. "Conducting polymer/ alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution". *J. Fluorine Chem* vol, 130,PP, 894–901 2009.
[8] A. Mohamed, Salem, F.Ahmed, Al-Ghonemiy, Ahmed B. Zaki. "photocatalytic degradation of Allura red Quinoline yellow with polyaniline/ TiO_2 nanoComposite", *J applied Catalysis* B, Environmental, vol, 91,PP. 59-66, 2009.
[9] A. Gemeay, I. A. Mansour, R., G. El-Sharkawy, A. B Zaki, "preparation and Characterization of polyaniline/ manganese dioxide Composites and their Catalytic activity", *J. Collod Interface-Sci*. 308,PP. 385-394,2007.
[10] S. Sathianaryanan, S. Syed Azim, G. Ve. Katachaxi, "preparation and Characterization of polyaniline/ manganese dioxide Composites and its anticorrsion performance"*J. Synthetic Metals*,,157, PP.751 – 757, 2007.

[11] S. Seshadri, Bishop, P. L.; Agha, A. M. "Anaerobic/aerobic treatment of selected azo dyes in wastewater". *Waste Manage*. vol 15,PP 127–137,1994.
[12] G.Renmin, S. Yingzhi, C; Huijun, L.; Chao, Y. "Effect of chemical modification on dye adsorption capacity of peanut hull". Dyes Pigm.vol, 67, PP. 175–181, 2005.
[13] Z. Aksu, Z.; Tezer, S. "Equilibrium and kinetics modeling of biosorption of remazol black B by rhizopus arrhizus in a batch system: effect of Temperature", Process Biochem,vol, 36, PP. 431–439,2000.
[14] G. Walker,. M.; Hansen, L.; Hana, J. A.; Allen, S. "Kinetics of a reactive dye adsorption onto dolomite sorbent *". J, Water Res*., vol37, PP. 2081–2089, 2003.
[15] M. Karthikeyan, Kumar, K.. S.; Elango, K. P. "Conducting polymer/ alumina composites as viable ions from aqueous solution adsorbents for the removal of fluoride*". J. Fluorine Chem*. vol 130, PP.894–901, 2009.
[16] P. S Kumar, S. Ramalingam, C. Senthamarai, M.Niranjanaa, P Vijayalakshmi, et al. " Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm kinetics and thermodynamics of interactions ". Desalination, PP. 261: 52-60, 2010.
[17] H. Freundlich, Over the adsorption in solution. Z *Phys Chem* A 57, 1906, PP.385-470.
[18] N.K Amin "Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics". *J,Hazard Mater*, vol 165: pp 52-62,2009.
[19] I. Langmuir "The adsorption of gases on plane surfaces of glass, mica and platinum. ", *J Am Chem Soc*, vol 40, PP 1361-1403,1918
[20] M. A. Salem " the role of polyaniline salts in the removal of direct blue 78 from aqueous solution A kinetic study", *J.Reaactive & Functional polymers*,vol 70, pp707-714, 2010.
[21] C.L.Mack, B,Wilhelmi,J.R. Duncan, J.E.Burgess, " Akinetic study of the recovery of platinum ions from an artifical aqueous solution by immobilized Saccharomyces biomass ", *Minerals Eng*, vol 21, pp 31-37, 2008.
[22] S.V. Mohan, Rajkumar, P.N.Sarma, "Removal of Fluoride form aqueous phase by biosorpation onto algal biosorbent spirogyra sp-102; sorption mechanism elucidation", *Hazard. Mater*,vol 141,pp 465-474, 2007.