APPLICATION OF PANI/Al_2O_3 COMPOSITE TOWARDS THE REMOVAL OF TARTRAZINE DYE FROM AQUEOUS SOLUTION

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***ABSTRACT**: Polyaniline/Al_2O_3 composite was prepared via chemical polymerization aniline in aqueous media containing suspended Al_2O_3 particles. Prepared composite used as adsorbent for the removal of tartrazine dye from aqueous solution. Different factors like agitation time, initial concentration of dye, dose of adsorbent, pH of solution and temperature, affecting the removal efficiency of adsorbent, were investigated. From experimental data it was appeared that up to 99% removal of the dye was occurred within contact time of 15 minutes. The ideal pH and temperature for the maximum removal of dye from aqueous solution was 2-4 and 70-80 ^oC respectively. Kinetic study of adsorption process was well described by pseudo-second order model. Freundlich and Langmuir isotherm were well fitted with experimental data. Nature of adsorption process was investigated through thermodynamics study. Positive value for ΔH^0indicates the endothermic process of adsorption.*

Key Words: Polyaniline, Composite, Organic dye, Dye Adsorption, Freundlich isotherm, Tartrazine

INTRODUCTION

Economy of a country largely depends upon its industry. Wide variety of dyes is extensively used in different industries, such as paper, textile, cosmetic, leather and food industries [1].Tartrazine, IUPAC name trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfon -atophenylazo)-H-pyrazole-3-carboxylate, has an azo group which is very toxic to living organism. It is used in food product, confectionary product, cosmetics, drugs, pharmaceuticals, textiles and electroplating due to its low price then β-carotene [2]. Tartrazine is a water soluble organic anionic dye with formula $C_{16}H_9N_4Na_3O_9S_2$.It has molecular weight of 534.36 g/mol. It is also known as food yellow and acid yellow. It is employed to produce yellow color and gives green shade when mixed with brilliant blue [3].Some of the harmful effect of tatrazine dye reported in the literature such as purpura and vasculitis [4]. It is also known to cause some allergic reaction like asthma and urticaria [5].A most recent study shows the potential interaction between the tartrazine and bovine hemoglobin at the molecular level causes the change in conformation, so effect the secondary structure of bovine hemoglobin [6].Removal of dyes from the waste coming out from different industries is very important. Different techniques, such as membrane filtration, coagulation, oxidation, precipitation, ion exchange and adsorption are employed for the removal of dyes[7].Different adsorbent have been used for the removal of dyes like, activated charcoal [8], clay[9], banana pith [10], and rice husk [11]. Now a days conducting polymer, polyaniline, is used as adsorbent for the removal of dyes and heavy metal. Now a day organic inorganic composite are extensively used in adsorption process like polyaniline silica composite [12]. In this paper, adsorption of tartrazine on polyaniline alumina composite is studied. Kinetics and the adsorption isotherm were investigated.

MATERIALS AND METHOD

Material

Tartrazine (Scharlau Chemicals) Aniline (Aldrich), Potassium iodate (Merck), Sodium salt of dodecyl benzene sulfonic acid (Merck), Sulfuric acid (Fischer Chemicals), alumina (Aldrich), Ammonia (Merck) and Distilled water. All chemicals were used without further purification. Distilled water was used throughout the experimental work.

Preparation of Polyaniline

Polyaniline was prepared by following a typical polyaniline preparation in which 0.8g KIO_3 and 0.5 g of sodium salt of dodecyl benzene sulfonic acid was mixed in 100 mL of sulfuric acid (1M) and stirred the solution until the solution become uniform. Then, 1 mL aniline was added to stirred aqueous solution. The reaction was carried out for 20 hours at room temperature. Resultant polymer was filter and washed with distilled water and then dried at room temperature [13].

Preparation of PANI/Al_2O_3 Composite

Polyaniline alumina composite was simply prepared by oxidative polymerization of aniline in aqueous solution containing 0.1g of alumina suspended in it.

Adsorption Studies

Batch experiment technique was employed to study the adsorption process. A series of 100 ml Erlenmeyer flask covered with aluminum foil were used for shaking.The effect of dose, contact time, pH, concentration and temperature was studied. After experimentation, composite were separated by filtration.

The concentration of tartrazine was determined in filtrate using UV-visible spectrophotometer at maximum absorbance (λ_{max} = 429nm).

Adsorption Isotherms

The adsorption data obtained was fitted to both Freundlich and Langmuir isotherm. Freundlich isotherm mostly used to study the adsorption process. Its exponential form is represented as

$$q_e = K_f C_e^{1/n}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where q_e, is the equilibrium amount which is adsorbed (mg g^{-1}), C_e is adsorbate equilibrium concentration (mg L^{-1}) and K_f is constant parameter related directly to adsorption capacity of the adsorbent (mg g^{-1}). Parameter n in the Freundlich isotherm is constant having values between 0-1. The slope and intercept gives value for n and K_f respectively.

The coverage fraction θ, on adsorbent at constant temperature is investigated by Langmuir isotherm. The arranged Langmuir isotherm is given below:

$$\frac{1}{q_e} = \frac{1}{b.q_{max}\,C_e} + \frac{1}{q_{max}}$$

Where $C_e$the equilibrium concentration of dye in mg L^{-1} is, $q_e$is the equilibrium amount which is adsorbed (mg g^{-1}), q_{max} is maximum amount of dye that can be adsorbed on the adsorbent per unit weight of adsorbent and b is Langmuir adsorption constant [14] related to free energy of adsorption.

Adsorption Kinetics

Rate of adsorption of dye on the polyaniline and the rate constant studied by using Pseudo first order and Pseudo second order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$

Where q_e, is the equilibrium amount which is adsorbed and q_t is the amount of dye adsorbed at any time t (both in mg g^{-1}). K is rate constant for the adsorption rate.

Adsorption Thermodynamics

Thermodynamic study is done by using the adsorption data, as the adsorption phenomenon is regarded as equilibrium process. Thermodynamic parameters like change in Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) evaluated by using following relation:

$$\Delta G^0 = -RT\ln K_d$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

RESULTS AND DISCUSSION

FTIR Characterization

FTIR spectra were recorded from 4000 cm^{-1} to 400 cm^{-1} wave number. Spectra of pure polyaniline and alumina loaded polyaniline composite are shown in figure 1 & figure 2.

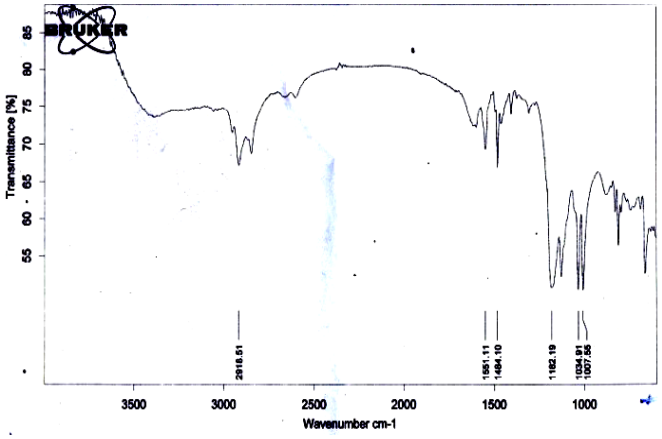

Fig. 1 Spectra of Pure Polyaniline

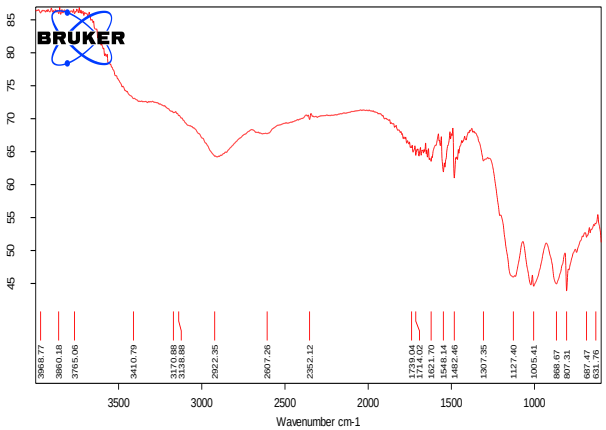

Fig. 2 Spectra of PANI/Alumina Composite

The peak appeared at 2918.51 cm^{-1} due to N-H stretching frequency of benzenoid ring was transformed into a broad band in PANI/Al_2O_3 composite. Peak boroadening of sharp peaks of polyaniline was also seen below 1200 cm^{-1} due to Al_2O_3 adsorption. The C-N stretching was shifted to 1307.99 cm^{-1}. A strong band of Al-O-Al was appeared at 868.67 cm^{-1} which indicates the presence of Al_2O_3 in the polyaniline polymer. Slight shifting of peaks is due to the adhesively attached Al_2O_3 with polyaniline polymer.

Effect of Adsorbent Dose

The effect of amount of adsorbent for the %age removal of dye from aqueous solution was studied through 0.1 to 0.5 g range of adsorbent, keeping all other parameters constant. Stirring was done for 5 minute for each experiment. Initial concentration (C_0) and initial absorbance was 50 mg/dm^3 and 1.950 respectively.

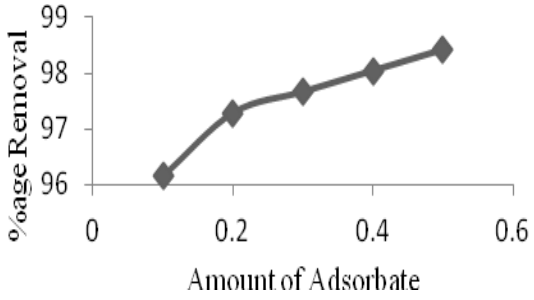

Fig.3 Effect of Adsorbate

Percentage removal increases with increase in adsorbent dose which reaches maximum 98.414 at 0.5g of adsorbent dose as shown in figure 3. This increase in %age removal of the dye from the solution is due to the increase in number of available active site for adsorption.

Effect of Contact Time

50 mg/dm^3 of dye solution was taken in separate flasks along with 0.1g of the adsorbent dose to study the effect of contact time.

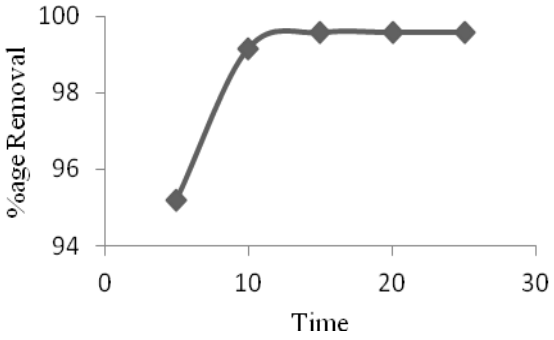

Fig. 4 Effect of Contact Time

Effect of time on %age removal was studied from 5 minute to 25 minute with interval of 5 minute. Maximum percentage removal achieved was 99.57 against 0.1g of adsorbent within 15 minutes. After 15 minute the percentage removal was remained constant for further time.

Effect of Adsorbate Concentration

Impact of initial dye concentration on dye removal is shown in figure 5. Effect of concentration of adsorbate on the percentage removal was also investigated by changing the concentration from 5 mg/dm^3 to 50 mg/dm^3, keeping all other parameters constant. Time

of agitation given was 5 minute for each batch experiment. At 50 mg/dm^3 dye concentration, maximum percentage removal was 95.84.

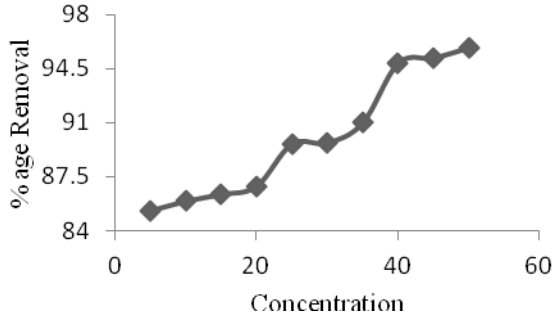

Fig. 5 Effect of Concentration

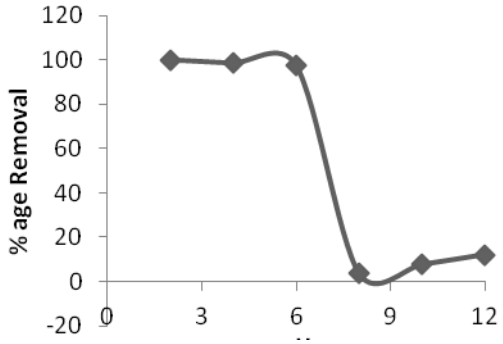

Fig. 6 Effect of pH

Effect of pH

Amount of adsorbate adsorb at the adsorbent highly dependent on the pH of the solution. At high pH, the extent of adsorption was found much lower which increases with increase in hydrogen ion concentration which reaches maximum 99.90 at pH of 2. During the study of effect of pH on the amount adsorb all other parameters were kept constant. Initial concentration of dye taken was 50 mg/dm^3. This increase in concentration is due to the fact of existence of polyaniline in doped form in acidic media, form where negatively charged species is exchanged by negatively charged tartrazine

Effect of Temperature

To study the effect temperature on the %age removal, experiments were performed on different temperature ranging from 20 ^{0}C to 80 ^{0}C. Other parameters like, pH, initial concentration of the adsorbate, amount of adsorbent and time of agitation for each experiment were kept constant. The optimum temperature for the maximum removal was found about 80 ^{0}C, % age removal was found 99.97. Increase in %age removal with increase in temperature was due to the more solubility of the dye and mobility of ion.

Adsorption Isotherm

Equilibrium data obtained by varying the initial concentration of adsorbate against fixed amount of adsorbent was applied to Langmuir and Freundlich isotherm model.

Langmuir Adsorption Isotherm

Figure 8 represent Langmuir adsorption isotherm obtained by plotting $1/q_e$ against $1/C_e$. A straight line graph was obtained with correlation coefficient R^2 equal to 0.975 almost approaching to 1, indicating the more fitted experimental data with Langmuir isotherm.

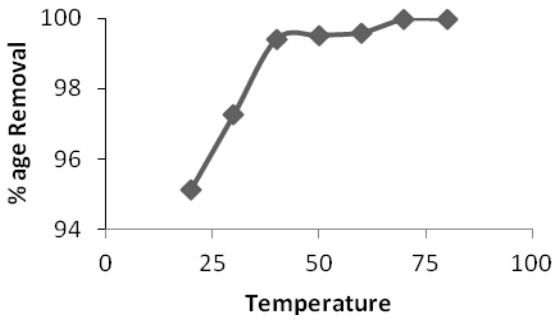

Fig. 7 Effect of Temperature

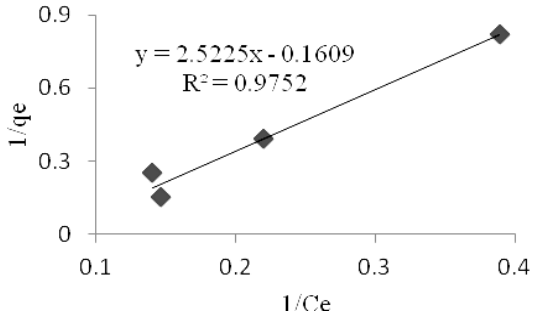

Fig. 8 Langmuir Adsorption Isotherm

Freundlich Adsorption Isotherm

Equilibrium data obtained by varying the dose of adsorbent and concentration of dye was applied to the Freundlich model as given below:

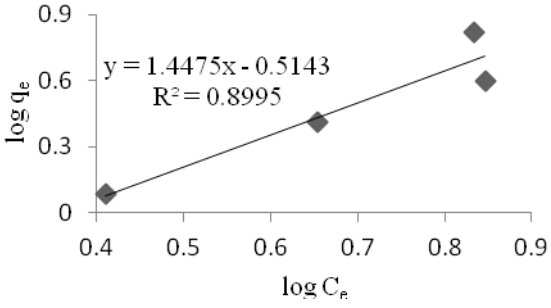

Fig. 9 Freundlich Adsorption Isotherm

Figure 8 represents Freundlich adsorption isotherm, shows correlation coefficient R^2 equal to 0.899. Freundlich constant "n" known as heterogeneous dimensionless constant coming from slope is equal to 0.691. For heterogeneous favorable adsorption process its value should be between 0-1. Its value is slightly greater than one, showing unfavorable adsorption process. Relative values of correlation coefficient R^2 indicating the more linear Langmuir isotherm curve compared to Freundlich isotherm curve, so experimental data was more fitted with Langmuir isotherm. "b" is Langmuir constant having units of dm^3 mg^{-1}, whose value should be less than 1 for favorable monolayer homogeneous adsorption process, as is in this work it was 0.063 dm^3 mg^{-1}.

Table 1 Adsorption capacity comparison between various adsorbent with PANI/Al_2O_3

Type of Adsorbent	Adsorption Capacity (q_{max})
Bottom ash [15]	1.1×10^{-5}
Hen feather [16]	6.4×10^{-5}
Activated carbon [17]	18.58×10^{3}
Polyaniline [18]	2.47
Chitin [19]	30
Chitosan [19]	350
PANI/Al_2O_3 composite	6.25 [This study]

Where K_L is Langmuir equilibrium characteristics related to affinity of adsorbent toward adsorbate. Based on Langmuir constant "b" another dimensionless constant "R_L" indicates the adsorption affinity. For favorable adsorption process its value should be between 0-1 whereas its value greater than 1 shows the unfavorable adsorption process. In this work its value coming out to be 0.048, which is very small and indicating the greater affinity or interaction between the adsorbent and adsorbate as previously reported in the literature [15]. On the basis of R^2 value it is clear that adsorption of tartrazine onto the PANI/Alumina composite follows monolayer adsorption process. One of the most important parameter obtained from Langmuir isotherm is q_{max} (mg g^{-1}) which shows the maximum adsorption capacity of adsorbent, from this work its value coming out to be 6.25 for tartrazine dye.

Adsorption Kinetics

Chemical reaction and mass transfer mechanism was investigated by applying basic kinetic model to the experimental data.

Pseudo-first Order Kinetics

Figure 3.9 represents Pseudo-first order kinetics from which correlation coefficient (R^2 = 0.493) clearly shows the incompatibility of adsorption process of tartrazine on to the composite. Pseudo-first order rate constant for adsorption process comes out to be 1.0×10^{-3} min^{-1}.

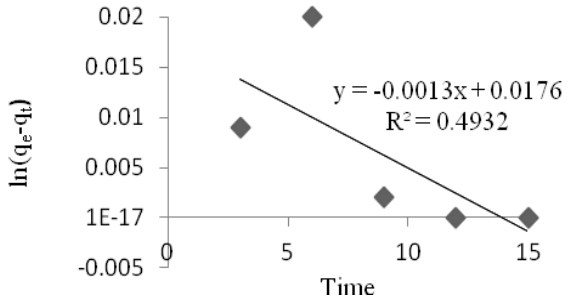

Fig. 10 Pseudo-first Order Model

Pseudo-second Order Model

Figure 10 represent Pseudo-second order kinetics from which correlation coefficient (R^2 = 0.984) obtained shows that the adsorption process of tartrazine on to the PANI/Alumina composite well fitted with Pseudo-second order kinetics. Pseudo-second order rate constant for adsorption process comes out to be 4 g mg^{-1} min^{-1}. Results from the kinetic data, it is clear that adsorption process follows the pseudo-second order. As indicated by the value of R^2, Pseudo-second order kinetics is more strongly followed by the adsorption process as compared to Pseudo-first order kinetics. It was predicted from above results that adsorption process occurred by chemisorption [16].

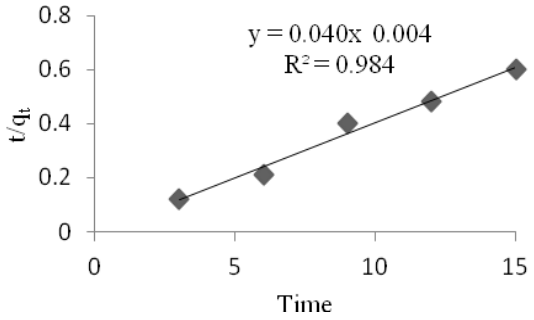

Fig. 11 Pseudo-Second Order Model

Table 2 Kinetics Parameters

Pseudo-first Order		Pseudo-second Order	
R^2	0.493	R^2	0.984
K_1	1.0×10^{-3} min^{-1}	K_2	4 $gmg^{-1}min^{-1}$
q_e	1.01mgg^{-1}	q_e	25.0 mgg^{-1}

Thermodynamic Study

Thermodynamic parameters like enthalpy, entropy and free energy determined by using Gibbs free energy equation. Change in entropy and enthalpy determined from the slope and intercept of the above equation: Value of slope coming from graph is 20482 J/K indicates spontaneous nature of adsorption whereas positive value of enthalpy 6×10^6 KJ/mol shows the endothermic nature of the adsorption process.

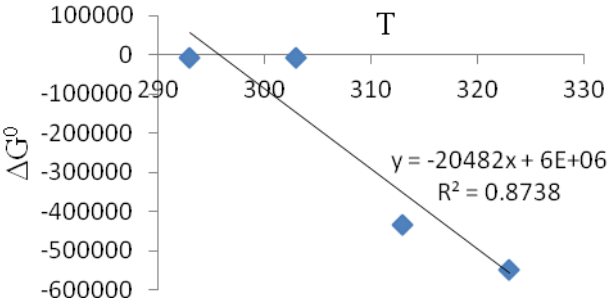

Fig. 12 Thermodynamic study

CONCLUSION

The PANI/Al_2O_3 composite was prepared from polyaniline polymer in the presence of an oxidizing agent via in situ polymerization method. This composite shows better adsorption properties. Adsorption of dye increases with increasing amount of composite, contact time & temperature, and by decreasing pH of medium. Prepared composite could be promised adsorbent for removal of tartrazine from polluted water.

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REFERENCES

1. Jeon, Y. S., Lei, J. and Kim, J, Dye adsorption characteristics of alignate/polyaspartate hydrogels. J. Ind. Eng. Chem, 14: 726-731 (2008).
2. Wan, W. S., Ariff, N. F., Hanafiah, M. A. K. M, Preparation, characterization and environmental

application of cross linked chitosan/coated bentonite for tartrazine adsorption from aqueous solution. Water, air, soil pollution. 206: 25-36 (2010)

3. Scientific opinion on the re-evaluation on tartrazine (E 102) on request from the European Commission. EFSA journal. 7(11): 1331-1383 (2009).
4. Robinson, G. Tartrazine-the story so far. Food. Chem. Toxicol. 26: 73-76 (1988).
5. Moutinho, I. L. D. and Bertges, L. C. Prolonged use of the food dye tartrazine (FD & C yellow n^o 5) and its effects on the gastric mucosa of wister rats. Brazilian journal of biology. 67 (1): 141-145 (2007).
6. Li, Y., Wei, H, and Liu, R. A probe to study the toxic interaction of tartrazine with bovine hemoglobin at the molecular level: Luminescence. 2(29): 195-200 (2014).
7. Chiou, M, and Chuang, G: Competitive adsorption of dye metanil yellow and RB15 in acid solution on chemically cross-linked chitosan beads. Chemosphere: 62: 731-740 (2006).
8. Sharma, C. Y., Uma, S. N. Upadhyay, F. J. Applied sciences in environmental sanitation 4: 21 (2009).
9. K.R. Ramkrishna, T. Viaraghavan, Water Science and Technology 36 (1997) 189.
10. C. Namasivayam, D. Prabha, M. Kumutha, Bioresource Technology 64 (1998) 77.
11. G. McKay, G. Ramprasad, P.P. Mowli, Water, Air, and Soil Pollution 29 (1986) 273.
12. Muhamad, M. A, and El-Nasr, A. A, Kinetics and isotherm studies of methylene blue adsorption onto polyaniline nanotubes base/silica composite, J. Ind. Eng. Chem. 18: 1964-1969 (2012).
13. Hossein, E., Hamid, R. K. Production of polyaniline composite containing Fe_2O_3 and CoO with nanometer size using hydroxypropylcellulose as a surfactant, J. Eng. Sci and Tech., 5(2), 146-152 (2008).
14. Hall, K., Eagleton, L., Acrivos, A., Vermeulen, T., "Pore- and solid diffusion kinetics in fixed-bed adsorption under constant-pattern condition", Ind. Eng. Chem. Fund., 5 (2), 212-223 (1996).
15. Mittal, A., Mittal, J., Kurup, L. Adsorption isotherm, kinetics and column operation for the removal of hazardous dye Tartrazine from aqueous solution using waste materials bottom ash and deoiled soya, as adsorbent. J, Hazard, Mater., B136, 567 (2006)
16. Mittal, A., Mittal, J., Kurup, L. Freundlich and Langmuir adsorption isotherm and kinetic for removal of tartrazine from aqueous solution using hen feathers. J, Hazard, Mater., 146, 243 (2007).
17. Gupta, V.K., Jain, R., Shrivastava, M., Nayak, A. Equilibrium and thermodynamic studies on the adsorption of the dye Tartrazine onto waste "coconut husk" carbon and activated carbon. J. Chem. Eng. Data, 55, 5080 (2010)
18. Ansari, R., Keivani, M.B., Delavar, A.F. Application of polyaniline nanolayer composite for removal of tartrazine dye from aqueous solution. J. Polym. Res. 18, 1931 (2011)
19. Dotto, G.L., Vieira, M.L.G., Pinto, L.A.A. Kinetics and mechanism of Tartrazine adsorption onto chitin and chitosan. Ind. Eng. Chem. Res, 51, 6599 (2012).