Adsorption of Reactive Red 195 from polluted water upon Na₂CO₃ Modified Jute Fibre.

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Abstract- **Sorption of Reactive Red 195 upon Na2CO3 modified Jute Fibre was studied for different concentrations of dye solutions (50, 100, 150 and 200 mg/L). Experiments were done considering parameters such as agitation time range, solution pH (4-12), adsorbent dose (10 gm/L - 20 gm/L) and temperature (293, 303 and 313 K). The adsorption was highly supported at pH 6-7 and lower temperatures. Adsorption phenomena is better explained by Langmuir isotherm, the process of adsorption was best described by the second order pseudo-kinetic model. The maximum sorption ability (q_{max}) is found to be 22.47 mg/g. it was suggested that adsorption is atypical chemical process, exothermic and spontaneous, and in nature, the equilibrium sorption occurred at pH 7.0,. Absorption effects was studied and optimum adsorption was obtained at a jute dose of 15gm/L**

Keywords - Na₂CO₃ Modified Jute Fibre (NaMJF), Reactive Red 195, Isotherm.

I.   INTRODUCTION

In human world, color is very essential aspect. In our daily life whatever commodity we use consist of different colors. Eventually various studies are there for the production of color. More than ten thousand dyes available commercially now a days and annually seven lakh tons of dyes are produced [1]. There are various kinds of dyes available commercially like some of them are acidic, while some are basic and so on. The largest consumer of dye stuffs are the textile industries. During the coloring process of textiles a substantial portion of dyes does not bind with the cotton/synthetics and tend to get loose in open streams [2]. During dyeing process, a large portion of dye comes in contact with open water bodies and tend to make them toxic and hazardous. In coloring process,the companies which uses dyes for their product manufacturing, releases huge amount of effluents which contains large amount of dyes and additives [3]. With the available normal wastewater treatment process, it is practically impossible to remove all the dyes from the effluents and because some dyes are readily mixable with the water, they possesses high risk of flowing into water distribution systems and rivers. And if they undergo simplification then they become highly toxic and carcinogenic [3]. Thus for living organisms, dyes are threat. Thus it is important to save the water bodies from such spoliation. For prevention of spoliation of waterbodies it is necessary to identify particular dye availability in a particular waterbody. Numerous physico, chemico treatment techniques are in use for the treatment process. (e.g.,adsorption, coagulation, biodegradation flocculation, , chemical oxidation, ion-exchange, reverse osmosis, ozonation, membrane filtration and electrochemical methods) have been subjected to remove dye molecules from effluents. But, these differ in their efficiency, cost and environmental impact[3].In this work we have attempted to use an agricultural product, Na₂CO₃ modified jute fibre (NaMJF) for the adsorption of RR from wastewater.

Reactive Red is a commercial azo dye with Color Index Generic Name Reactive Red 195 (Trade name: Tri-active Red 3BS 150%, C27H18O16N7S5ClNa4 FW = 983.5).The dye molecule contains specific functional groups, which can undergo addition or substitution reactions with the -OH, -SH and -NH2 groups present in the fibres.

The azo dyes are among the most important group of dyes for coloring of textiles because of quickness for the substrate process. Thus it is important to remove RR before its transformation. To design adsorption treatment systems, knowledge of kinetic and mass transfer process is essential. In this study the emphasis is on to use of simple pretreated jute fibers as sorbent, as the number of work done with simple jute fibers are very less compared to work done with carbonized powder produced from jute fibers.

The reason behind using simple pretreated jute fibre is because dyes have a strong affinity towards cellulose and jute fiber contains high percentage of cellulose when compared with other bio sorbents (87.4% cellulose). Secondly it is to be studied whether simple pretreated jute fibers produces a competitive result with that of carbonized powder which is very costly.In this article, we analysis the usability of kinetic and mass-transfer models for the sorption of Reactive Red 195 onto NaMJF.

II.   MATERIALS AND METHODS

It is known that components high in cellulose and hemi cellulose composition are good in removing dye from aqueous solution. Composition of Jute fibre consists of Cellulose (65.2 %), Hemi-cellulose (22.2 %), Lignin (12.5 %), waxy materials (0.6 %) and Water soluble matter (1.5 %).

Sun dried jute fibres obtained from market and cut into sizes of 1 mm size and washed with distilled water and dried at 60 °C thus raw jute was obtained. The sample processed with 0.01 M Na_2CO_3 at 27°C for 4 hours, than distilled washed so as to remove excess chemicals in fibers and pH was reduced to 7, than dried at 100 °C for one day and was kept in container. Thus we get the pretreated Na_2CO_3 Modified Jute Fibre (NaMJF).

An azo dye Reactive red 195, havinghaving molecular formula $C_{27}H_{18}O_{16}N_7S_5ClNa_4$; FW = 983.5, was chosen as adsorbate. The molecular structure of the same can be seeing in Fig. 1.
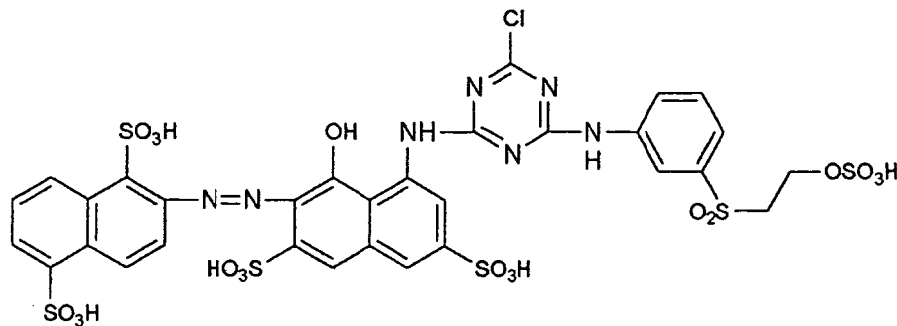

Fig. 1. RR 195

Fig.1. The dye is collected from Himedia. An initial dye solution (1000 mg/L; pH 7) was prepared using doubly distilled water.
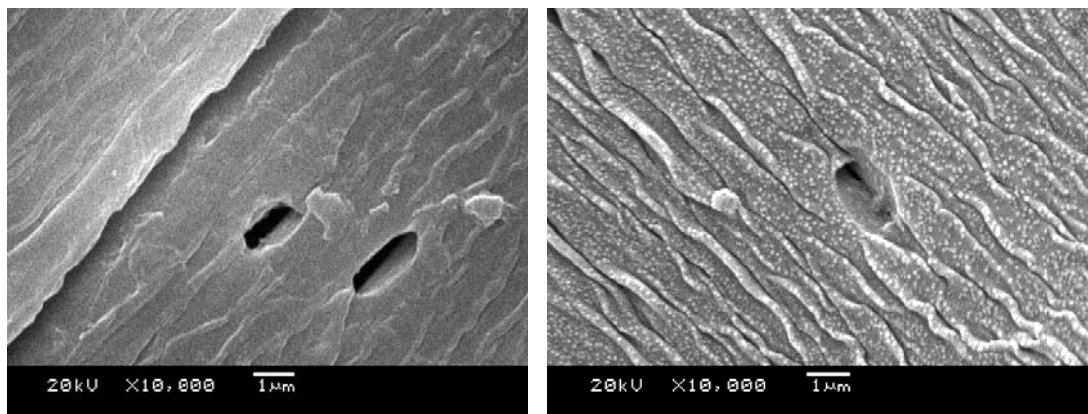

Fig. 2. SEM micrographs: (a) Distilled washed Jute; (b) RR adsorbed jute onto NaMJF.

III.   HARMFUL EFFECTS OF RR 195

Complex azo dye are stubborn to simple aerobic decomposition by bacteria. These aromatic pollutants are stabilized by the strong electron-withdrawing nature and prevent conversions by oxygenase and obstructs the susceptibility of dye compounds to oxidative processes. With normal aerobic decomposition circumstances micro-organisms with special ability to decompose complex azo group can decompose the RR 195. Thus RR 195 and similar kind of complex dyes are subject to anaerobic decomposition treatment system. The anaerobic reduction means depolarization as the azo dyes are converted to usually colorless but potentially harmful, mutagens and carcinogenic componentsthose are hazardous to environment

IV.   EXPERIMENTS AND EQUILIBRIUM STUDIES

Batch adsorption studies were done and at first impact of pH variation onto the reduction of RR by NaMJF was studied and it was studied that the equilibriumsorption obtained at pH 7.0. From the original solutionof 1000 mg/L, different combinations of dye solutions were prepared for solutions of different initial concentrations viz. 50, 100, 150 and 200 mg/L. Initial NaMJF dose was taken as 10g/L and similar rate of dose was mixed with each of the prepared solutions, agitated mechanically with the help of rotary shaker at 303 *K* at 150 rpm until the equilibrium was reached. For time *t* = 0 minute, 5 minute, 10 minute and so on, until equilibrium, the dye concentrations were measured by UV/VIS spectroscopy (Perkin Elmer, Lambda 45). The data's obtained were used to measure the adsorption capacity,*q* (mg/g). Effect of NaMJF dose was analyzed upon the absorption of

RR dye by varying NaMJF dose at 10, 15 and 20 g/L. Experiments are done for different pH values ranging from 4 to 12. A fixed amount of NaMJF (1 gm) was added to the 100 ml of 50 mg/L of RR solution at different pH values (4 - 12) and agitated for 3 h to assess the impact of initial pH on RR concentration, by taking and measuring the samples after each five minute of agitation. Experiments were also done to check for sorption of Reactive Red 195 by the container walls in the absence of jute. Studied revealed that there was no degradation or sorption of Reactive Red 195 by container walls.

Variation of temperature affect was evaluated for 293, 303 and 313 K. Similar analysis was done three times and mean values were taken. The unit adsorption capacity (mg dye per gm adsorbent) was calculated according to a mass balance using the given equation:

$$q_e = \frac{(C_i - C_e)V}{m}$$

V.   THEORY

A. Adsorption Isotherm

The optimumadsorption modelling is fundamental in describing the interactive behavior between sorbates and sorbent and also essential for design and analysis of sorption systems. Adsorption equilibrium data are widely evaluated by different isotherm models. In the present investigation the isotherm study of RR was conducted at different temperatures by keeping the initial RR concentration fixed at 50 mg/L. And the overall study was done including the Freundlich [5,6], Langmuir [5.7], Temkin [5] and Dubinin–Radushkevich [5.8] isotherm models, as they are used for bio-sorption data for this report and for further reports for future. Similarly the case with kinetic modelling studies.

Langmuir: $q_e = \frac{Q_O b C_e}{1 + bCe}$

Where, q_e = No of moles for solute adsorbed per unit wt. of adsorbent at concentration C_e.

Q_o= No of moles for solute adsorbed per unit wt. of adsorbent in forming monolayer coverage, it is independent of temperature.

b=Constant related to energy, it is temperature dependent

C_e=Measured conc. of solute in solution at equilibrium.

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

Where, K_f and 1/n are constant.

C_e = Concentration at equilibrium

q_e= equilibrium sorption capacity

Temkin: $q_e = B_T ln K_T + B_T ln C_e$

Where, K_T is Temkin adsorption potential and B_T is Temkin constant.

D-R isotherm- $ln q_e = ln q_s - \beta \varepsilon^2$

Where q_s = theoretical isotherm saturation capacity (mg/g);

β = Dubinin–Radushkevich isotherm constant

ε = RT ln (1+ 1/ C_e)

B. Kinetic modelling

The pseudo-first-order [9] and pseudo-second-order [10] kinetic models are used for obtaining the rate constants and equilibrium adsorption capacity at different temperatures.

Pseudo-first order: $log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}t$

Pseudo-second order: $\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe} t$

The above models has a limiting factor that they cannot define the diffusion mechanism, so the intra-particle diffusion model (weber & Morris, 1963) was also analyzedfor mechanism process findings.

Intra-particle diffusion: $q_t = k_i t^{0.5}$

C. Activation energy and thermodynamic parameters

E_a(activation energy) for RR adsorption onto NaMJF was calculated by the following equation [11]:

$$ln\, k = ln\, A - \frac{E_a}{RT}$$

Where, activation energy E_a can be achieved by plotting a graph of ln k versus $1/T$.

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Thermodynamic behavior of RR adsorption on NaMJF was analyzed with following thermodynamic parameters – ΔG° (Gibbs free energy change), ΔH° (enthalpy) and ΔS° (entropy). This parameters were then found out by using below equations:

$$\Delta G = -RT \ln K_C$$
$$K_C = \frac{C_a}{C_e}$$
$$\Delta G° = \Delta H° - T\Delta S°$$

VI.   RESULT AND DISCUSSION

A. Effect of pH

It is well known that the pH of a system exhibits significant influence on the adsorptive capacity of adsorbate because of the impact of pH on the surface characteristics of the sorbent and thereby change in the affinity of attraction adsorbate molecules onto sorbent [10]. Therefore the sorption behavior of RR onto NaMJF was studied for a pH range of 4-12 for a volume of 100 ml, agitated for 3 hours at 303 K, with jute dose 10 g/L, rotated at 150 rpm. The analysis shows that rate reduction of RR increases with enhancement of pH of the solution significantly upto 6, after this value of pH further increment of the same doesn't show same rate of increment of RR adsorption onto NaMJF. But since maximum adsorption obtained for pH 7.0, all the further analysis were done at the same pH, Which can be depicted from Fig. 3. Similar trend of pH effect was previously studied for the sorption of CV on rice husk [11]. This variation of adsorption due to change in pH is because that at low pH values surface properties changes and steady the sorbent surfaces tends to get positively charged, and this decreases the sorption of similarly charged dye ions through electrostatic repulsion. As the pH value of solution steadily increases, increment of sorption processoccursbecause of deprotonation of similarly charged adsorbent surface converting the sites into negatively charged, thereby increasing the attraction affinity among the sorbent and the positively charged adsorbate.

B. Effect of CMJ dose

Sorption system of dye also depends upon the sorbent dose which is an essential factor that strongly affects the process adsorption capacity. The sorption of Reactive Red 195 onto NaMJFwere analyzed by changing the dose concentration from 10 gm/L to 20 gm/L for different RR dye concentrations (50, 100, 150 and 200 mg/L) at pH 7.0.The percent sorption increasees with shorter equilibrium time when the jute dose concentration increased from 48 %, 43 %, 36 % and 30 % to 94 % for all the corresponding dye concentrations, i.e. for 50, 100, 150 and 200 mg/L respectively. This occurrence is due the increased jute surface area and thereby increase in creation of larger active sites for adsorption. Fig. 4 shows the conclusion for the same.

C. Effect of temperature and contact time

Investigation showsthe removal of dye decreased with increasing temperature. Fig. 5 represents the sorption of Reactive Red 195 at different temperatures as a parameter dependent on agitation time. This because of the loosening of the bonds between the dye compounds and the attaching surface locations of the adsorbents [5]. The investigation pattern shows in the study thatdecrease in dye removaloccurs with increased temperature which concludes that sorption of Reactive Red 195 by NaMJF is essentially an exothermic one. Moreover, there is high rate of RR adsorption onto NaMJF during the first 90 min of the dye sorbent contact. This quick sorption of dyeis because of the larger amount of active sites/surface area for adsorption of adsorbate molecules. As the contact time gradually keep on increasing, the sorption rate also decreases, and finally proceeds towards adsorption equilibrium. This reduction in sorption of Reactive Red 195 onto NaMJF is because of decrease in total active sites available for adsorption and hence less available binding sites [5]. The equilibrium time for optimum sorption of dyeis found out as 120 min. After 120 minutes, adsorptionof dye does not depend upon increase in time [12] [13].

D. Adsorption Isotherm

From the values obtained from experimental studies, a case of adsorption isotherm data (at T = 293 K) fitted using the two isotherm models which can be depicted from Fig. 6. From the analysis, the equilibrium sorption of NaMJF for RR is determined from the Langmuir isotherm at 22.47 mg/g at 293 K.
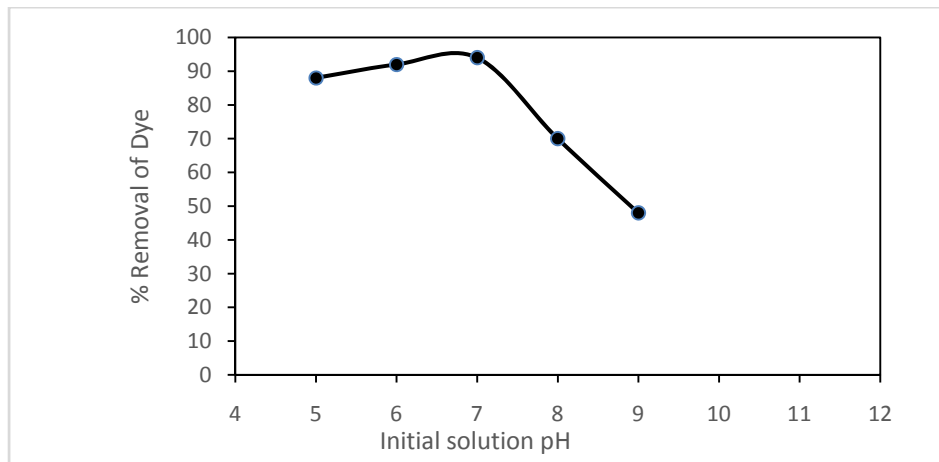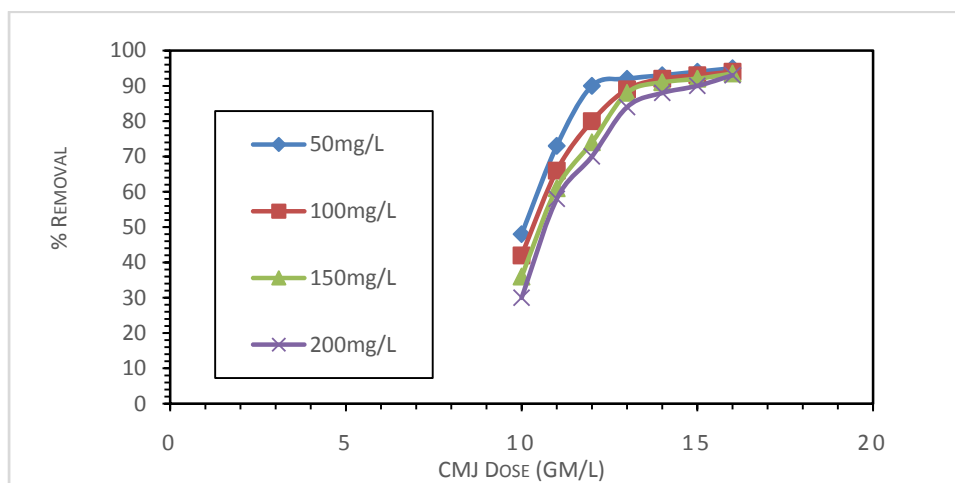
Fig. 3. Effect of pH on adsorption of RR

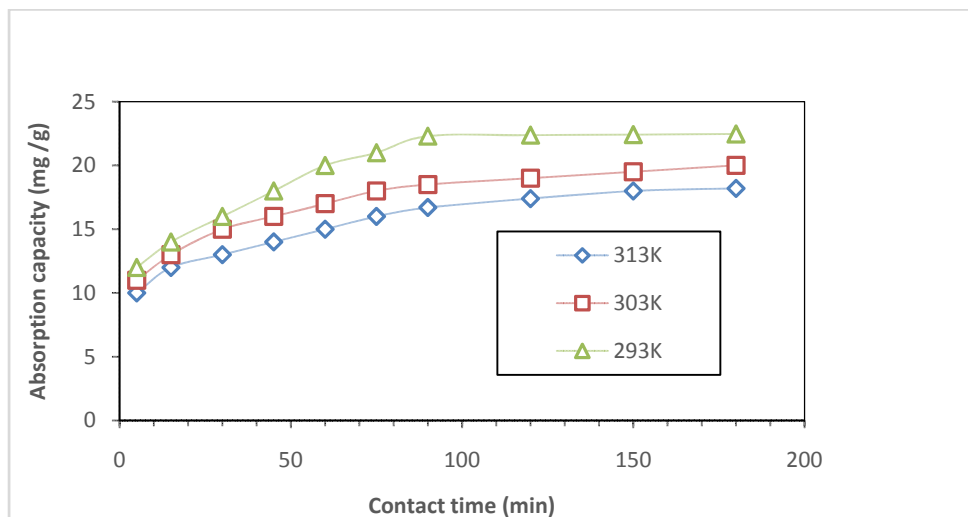Fig. 4. Effect of NaMJF dose on RR removalonto NaMJF

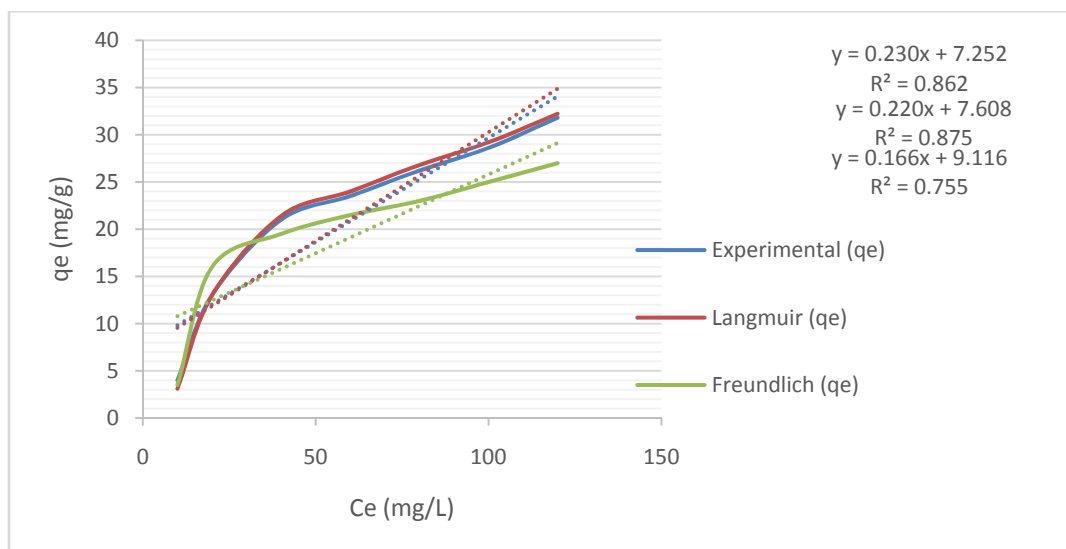Fig. 5. Adsorption of RR at different temperature vs contact time

Fig. 6. Comparison among the experimented and modelled isotherm profiles for the adsorption of RR onto NaMJF.

VII.   CONCLUSION

Na_2CO_3 modified jute fibre (NaMJF) obtained from treating the distilled wash jute with Na_2CO_3 was successfully used as an adsorbent for the quantitative removal of RR 195 from wastewater system. Analysis reveals that equilibrium results is best explained with the Langmuir's isotherm model. The maximum sorption was found out as 22.47 mg/g. The suitable pH for the sorption was favored at 7.0. The inter-particle diffusion played the significant role in the sorption system. Optimum jute dose was calculated at 16gm/L.

It can be commented that the kinetic studies achieved by analysis will be helpful for the understanding to use NaMJF for the reduction of other type of dyes.

REFERENCE

[1]   H. Zollinger,.Colour Chemistry – Synthesis, Properties of Organic Dyes and Pigments. VCH Publishers, New York. (1987) 92-100.
[2]   E.J. Weber, R.L. Adams, Chemical and sediment mediated reduction of the azo dye Disperse Blue 79. Environmental Science & Technology, 29 (1995) 1163-1170.
[3]   C. Wang, A. Yediler, D. Linert, Z. Wang, A. Kettrup, Toxicity evaluation of reactive dye stuff, auxiliaries and selected effluents in textile finishing industry to luminescent bacteria vibrio fisheri. Chemosphere, 46 (2002) 339-344.
[4]   E. Rindle, W.J. Troll, Metabolic reduction of benzidine azo dyes to benzidine in the Rhesus monkey. Journal of National Cancer Institute, 55 (1975) 181.
[5]   S. Chowdhury, P. Saha, Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, Kinetic and thermodynamic studies. Chemical Engineering Journal, 164 (2010) 168-177.
[6]   H.M.F. Freundlich, Over the adsorption in solution. Journal of Physical Chemistry, 57 (1906) 385-471.
[7]   I. Langmuir, The constitution and fundamnetal properties of solids and liquids. Journal of American Chemical Society, 38 (1916) 2221-2295.
[8]   M.M. Dubinin, L.V. Radushkevich, The equation of the charecterics curve of the activated charcoal. Proceedings of the USSR Academy of Sciences, 55 (1947) 331-337.
[9]   S. Lagergren, About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens Handlingar, 24 (1898) 1-39.
[10] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes. Process Biochemistry, 34 (1999) 451-465.
[11] T.S. Anirudhan, P. G. Radhakrishnan, Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solution onto a new cation exchanger derived from tamarind fruit shell. Journal of Chemical Thermodynamics, 40 (2008) 702-709.
[12] S. Chakraborty, P.D. Saha, Adsorption of crystal violet from aqueous solution onto NaOH-modified rice hask. Journal of Carbohydrate Polymers, 86 (2011) 1533-1541.
[13] R. Ahmed, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). Journal of Hazardous Materials, 171 (2009) 767-773.