

MIXING KINETICS IN BATCH ADSORPTION OF CHROMIUM (VI) BY *EMBLICA OFFICINALIS* LEAF POWDER

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ABSTRACT

Mixing in batch adsorption tests is necessary to distribute the solute components uniformly on the adsorbent surface as well as in the whole volume of solution mixture. The degree of homogeneity achieved is dependent on the mixing speed at which contents are mixed together. Batch adsorption experiments were performed for removal of Cr(VI) at different constant agitation speeds by many researchers, but no attention is paid towards the evaluation of the kinetics of mixing so far in batch adsorption experiments. The present paper addresses on the evaluation of kinetics of mixing in batch adsorption of Cr(VI) from aqueous solution using raw *Embllica officinalis* leaf powder (EOLP) as an adsorbent. Experimental results of batch adsorption of Cr(VI) at different agitation speeds viz. 0, 50, 100, 150, 170 and 195 rpm were used to explore the kinetics. A kinetic model based on dimensionless approach and pseudo second order adsorption kinetics has been developed and is best fitted by exponential decay curves with R^2 values of 0.99 and above for different mixing speeds. From the results, it is inferred that the proposed mixing kinetic model describes well the present experimental results but need to be verified in future studies on other batch adsorption tests. This equation can also be used to optimize the mixing speed for achieving a desired degree of removal of Cr(VI) in batch adsorption tests.

Keywords: Batch adsorption, Chromium (VI), *Embllica officinalis* leaf powder, Kinetics, Mixing

I. INTRODUCTION

Agitation is a classic parameter in sorption phenomenon. It influences the distribution of the solute in bulk solution and can also act on the formation of the external boundary film. Mixing in batch adsorption operations is necessary to distribute the solute components uniformly on the adsorbent surface as well as in the whole volume of solution mixture. The degree of homogeneity achieved is dependent on the mixing speed at which contents are mixed together. It has been postulated by [1] that the rate of mixing in a non-segregating particles system is proportional to the difference between the instantaneous homogeneity and its equilibrium value. The homogeneity spontaneously decreases due to segregation.

Mixing of adsorbent with metal solution is also recommended in the literature to enhance the contact opportunity. The effect of mixing process on chemical reaction kinetics for axial flow was studied by [2] assuming that the transformation of the reactants from the bulk state to a distribution at molecular diffusion distance follows an exponential decay curve. The effect of mixing was also studied by [3] and they observed that the uptake of the metal ions Cr(VI) and Cu(II) increased with the increasing agitation rate from 50 to 150 rpm; thereafter the effect was minimal. The increase in agitation rate decreases the film resistance to mass transfer surrounding the sorbent particles. The authors further mentioned that increasing the agitation rate reduces the boundary layer surrounding the surface and hence increases the driving force for metal ions. The minimal effect of agitation on the sorption rate and the adsorption capacity beyond 150 rpm implies that external mass transfer is not the sole rate-limiting factor. Batch adsorption experiments were performed for removal of Cr(VI) at different agitation speeds by many researchers ([4] at 200 rpm, [5] at 250rpm, [6] at 160rpm, [7] at 120 rpm, [8] at 250 rpm, [9] at 120 rpm) on various adsorbents.

Though several investigators have performed batch adsorption experiments for removal of heavy metals by adopting a constant speed of mixing probably based upon the past experiences of previous researchers. So far, no attention is paid towards the understanding of the rate of mixing and mixing kinetics modeling of batch adsorption experiments especially in case of removal of Cr(VI) by different adsorbents.

In the present work, the role of mixing on Cr(VI) adsorption by raw *Emblica officinalis* leaf powder (EOLP) has been studied and a model describing the kinetics of mixing has been developed based on the experimental results.

II. MATERIALS AND METHODS

Aqueous solution of chromium (500 mg/L) was prepared by dissolving 1.414 g AR grade anhydrous potassium dichromate ($K_2Cr_2O_7$) in distilled water and diluted to 1000ml, which corresponds to 1ml = 500 μ g Cr(VI). The aqueous solution was diluted with distilled water to obtain the Cr(VI) synthetic wastewater of desired concentrations. A fresh stock chromium solution was prepared before starting each set of experiments. The pH of the solutions was adjusted using 0.01 M HCl or 0.01 M NaOH. pH of the solutions was measured using pH meter (Elico India, model LI-127), calibrated with buffers of pH 4.0, 7.0 and 9.2. The standard curves were prepared by varying the Cr(VI) concentration from 0 to 20 mg/L. 2.5ml diphenylcarbazide reagent was added to 50ml sample or an aliquot diluted to 50ml with chromium free distilled water. The absorbance was measured at 540nm using UV-Visible Spectrophotometer (Hitachi, model 3210). The regression equation of standard curve was used to determine the Cr(VI) concentrations is given by: $ABS = 0.027 \times C$; $R^2 = 0.999$, where ABS is the absorbance value and C is the Cr(VI) concentration in mg/L.

Mature *Emblica officinalis* leaves were collected from the Institute's campus (MNNIT, Allahabad, India). Leaves were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry first at room temperature in shade and then in an oven at 333 K for 10 hours till the leaves became crisp, which were crushed into a fine powder in a mechanical grinder. The *Emblica officinalis* leaf powder (EOLP) was sieved and the fractions having geometric mean sizes of 460.98 μ m was separated out and washed a number of times with distilled water till

the adsorbent became free from fines and turbidity. After drying for several hours in sunlight, the *Emblica officinalis* leaf powder (EOLP) was stored into poly bags for its use in experiments.

III. MIXING KINETICS : EXPERIMENTAL RESULTS

In batch adsorption system, it is necessary to make proper contact of adsorbent sites with surrounding adsorbate in aqueous solution. In order to evaluate the role of mixing speed on adsorption of Cr(VI), experiments were conducted at different mixing speeds of 50, 100, 150, 170 and 195 rpm (speed limited to available experimental facility at IIT Kanpur, India) and without mixing (zero speed) for Cr(VI) concentration of 10.31 mg/L at pH 3 with EOLP loading of 0.5 g/l. The experimental results are shown in table 1. The role of the mixing and the mixing kinetics of Cr(VI) adsorption by EOLP are analyzed.

Table: 1. Experimental results of mixing kinetics at different mixing speeds for Cr(VI) concentration of 10.31 mg/l and EOLP dose of 0.5 g/L

Time, min	Residual Cr(VI) Concentration at various mixing speeds in rpm					
	No mixing	50.00	100.00	150.00	170.00	195.00
2.5	8.04	7.82	7.64	7.46	7.24	7.30
5	7.04	6.20	6.16	6.10	6.02	6.04
10	6.08	5.40	5.26	5.18	5.13	5.16
20	5.62	4.86	4.76	4.70	4.63	4.68
30	4.23	3.88	3.78	3.70	3.64	3.68
45	4.01	3.72	3.60	3.52	3.40	3.44
60	3.78	3.56	3.50	3.44	3.36	3.40
90	3.78	3.56	3.50	3.42	3.36	3.40
120	3.78	3.56	3.50	3.44	3.36	3.40
180	3.78	3.56	3.50	3.44	3.36	3.40
240	3.78	3.56	3.50	3.44	3.36	3.40

IV. EVALUATION OF ROLE OF MIXING

Agitation is one of the important parameter governing an adsorption process since it influences the distribution of the solute in the bulk solution and the formation of external boundary film. No information in the literature is available so far on this aspect especially for mixing kinetics in batch adsorption tests.

The experimental results of Table 1 are used to assess the role of mixing in present study. The mixing speed of batch test solutions was varied as 0, 50, 100, 150, 170 and 195 rpm due to the speed limitations of equipment. The variation of percent Cr(VI) removal with time of run is plotted for initial Cr(VI) concentration of 10.31 mg/L at all mixing speeds and presented in Fig.1. From this figure, it is evident that percent removal is observed increasing though slightly but steadily up to 170 rpm. Thereafter, the increase of percent Cr(VI) removal is gradual. This shows that the optimal mixing speed for solution-EOLP mixture is around 170 rpm. The possible reason for gradual increase in percent removal with increasing mixing speed may be due to more rigorous contact opportunity between

Cr(VI) ions and EOLP surface. With further, increase in mixing speed beyond 170 rpm, the percent increase in Cr(VI) removal slows down which may be due to non-availability of vacant sites onto the surface of EOLP. Further, it has been noted that even if the solution mixture is not agitated there is still some removal of Cr(VI) on EOLP (Table 1) during contact period of 4 hours. But, with increase in agitation speed the percent Cr(VI) removal is certainly increased. Thus, mixing speed does play an important role in batch adsorption studies.

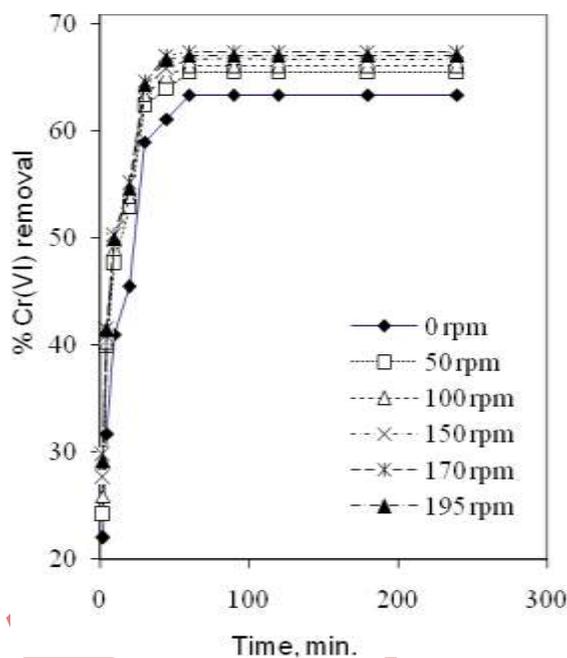


Fig. 1: Effect of mixing speed on Cr(VI) removal [$C_0=10.31$ mg/l, $M = 0.5$ g/l, pH=3, T=298 K]

The effect of agitation on the adsorption of metal ion by $\text{Ca}(\text{OH})_2$ treated fly ash was studied by [10] at different agitation speeds ranging from 100 to 400 rpm. They observed that the amount of dye adsorbed per unit mass of sorbent at equilibrium, increased from 3.99 to 4.98 mg/g with increasing agitation speed from 100 to 200 rpm, which may be due to the fact that increasing the agitation speed reduces the film boundary layer surrounding particles, thereby increasing the external film transfer coefficient and, hence, the adsorption capacity. The degree of agitation reduced the boundary layer resistance and increased the mobility of the system [11]. However, with further increase in the agitation speed (beyond 200 rpm); the adsorption capacity was found to decrease. The decrease in equilibrium adsorption capacity with increase in agitation speed was mainly because at higher agitation speeds, adsorbed dye molecules experienced a strong centrifugal force as a result of which the bound dye molecules were desorbed from the surface of the adsorbent [10]. Therefore, it can be inferred that agitation speed changed the kinetics but not the equilibrium adsorption capacity by a significant amount.

V. PROPOSED MODEL FOR EVALUATION OF MIXING KINETICS

To explore the kinetics of mixing in batch adsorption test for Cr(VI) removal, a kinetic model is developed based on dimensionless approach. From the literature review, it is evident that rate of metal adsorption $\left(\frac{dq}{dt}\right)$ is dependent on variables like initial metal concentration (C_0), concentration of adsorbent (M), residual metal concentrations at different time (C), equilibrium metal concentration (C_e), mixing speed (N) and contact times for adsorbent with metal solution (t_0) and time intervals Δt ($t_{i+1}-t_i$) between sampling can be expressed as:

$$\frac{dq}{dt} = f(C_0, M, C, C_e, N, t_0, \Delta t) \quad (1)$$

Using Buckingham's π -theorem, the dimensionless groups formed are:

$$\Delta t \cdot \frac{dq}{dt}, \frac{C}{M}, \frac{C_e}{C_0} \text{ and } Nt_0$$

Hence,

$$\Delta t \cdot \frac{dq}{dt} = f\left(\frac{C}{M}, \frac{C_e}{C_0}, Nt_0\right) \quad (2)$$

Using a multiplier power function of R.H.S. of (2) can be written as:

$$\Delta t \cdot \frac{dq}{dt} = \left(\frac{C}{M} \cdot \frac{C_e}{C_0}\right)^a \cdot (Nt_0)^b \quad (3)$$

Where a and b are exponents in R.H.S. terms of model (3)

For accounting no mixing conditions, N is replaced by $N+1$ in (3). Therefore, (3) can be re-written as:

$$\Delta t \cdot \frac{dq}{dt} = \left(\frac{C}{M} \cdot \frac{C_e}{C_0}\right)^a \cdot [(N+1)t_0]^b \quad (4)$$

From batch kinetic study, the rate of adsorption can be well described by proposed kinetic model expressed as:

$$\frac{dq}{dt} = k_3 q_e (q_e - q)^2 \quad (5)$$

Where, k_3 is the reaction rate constant obtained from proposed kinetic model at different mixing speeds and are presented in Table 2 obtained from the linear fitting of the (5) at different speeds. Substituting in (5), we get:

$$\Delta t \cdot k_3 q_e (q_e - q)^2 = \left(\frac{C}{M} \cdot \frac{C_e}{C_0}\right)^a \cdot [(N+1)t_0]^b \quad (6)$$

On rearranging,

$$(t_2 - t_1) \cdot k_3 q_e (q_e - q)^2 = \left(\frac{C}{M} \cdot \frac{C_e}{C_0} \right)^a \cdot [(N+1)t_0]^b \quad (7)$$

(7) can be used to fit the experimental results of Table 1 and k_3 values from Table 2 to evaluate the mixing kinetics in batch adsorption of Cr(VI) on EOLP. The L.H.S. of (7) are plotted against R.H.S. term and the curves obtained are shown in Fig. 2 to 7 respectively for mixing speeds 0, 50, 100, 150, 170 and 195 rpm.

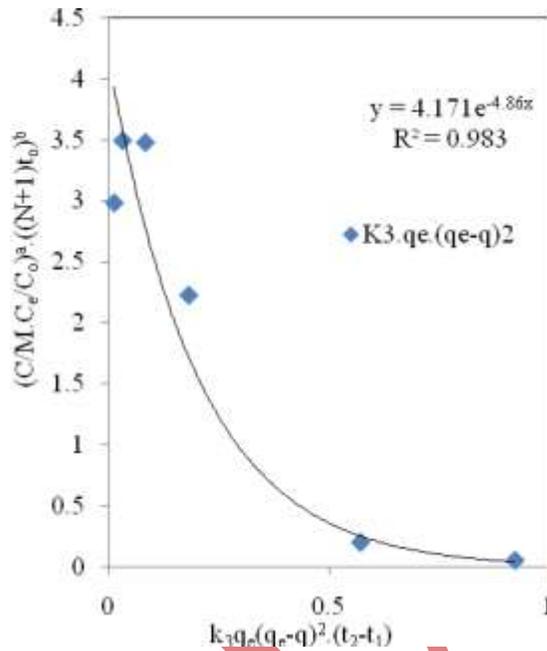


Fig. 2: Fitting of proposed mixing kinetic model for no mixing. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, $pH=3$, $T=298$ K]

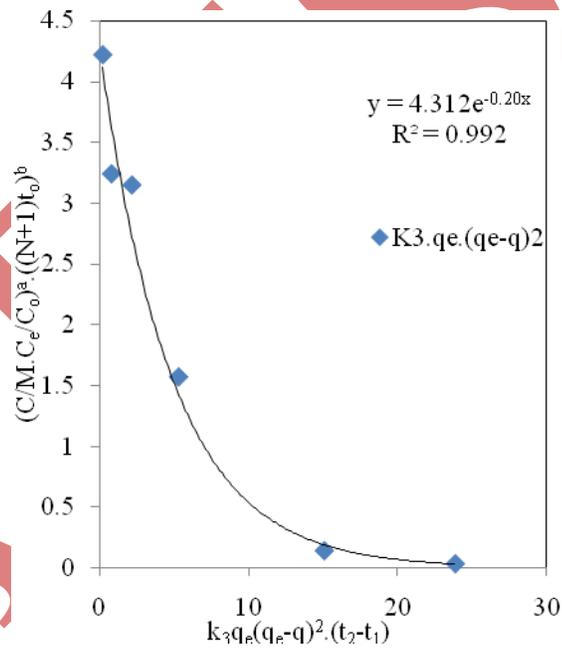


Fig. 3: Fitting of proposed mixing kinetic model at 50 rpm. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, $pH=3$, $T=298$ K]

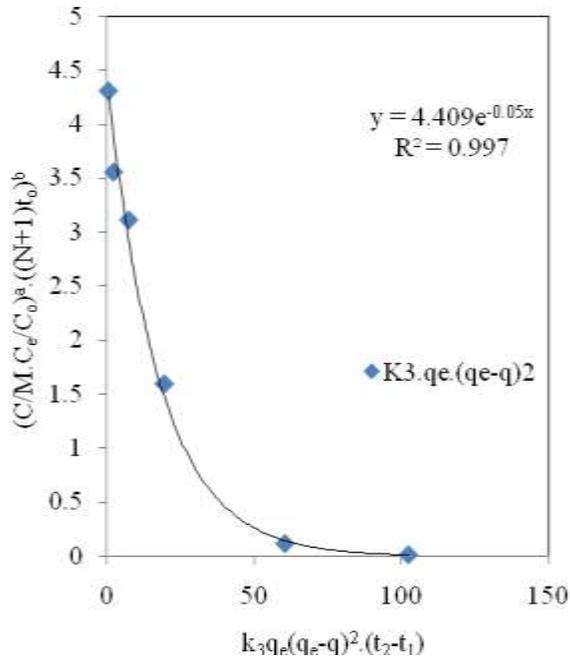


Fig. 4: Fitting of proposed mixing kinetic model at 100 rpm. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, pH=3, $T=298$ K]

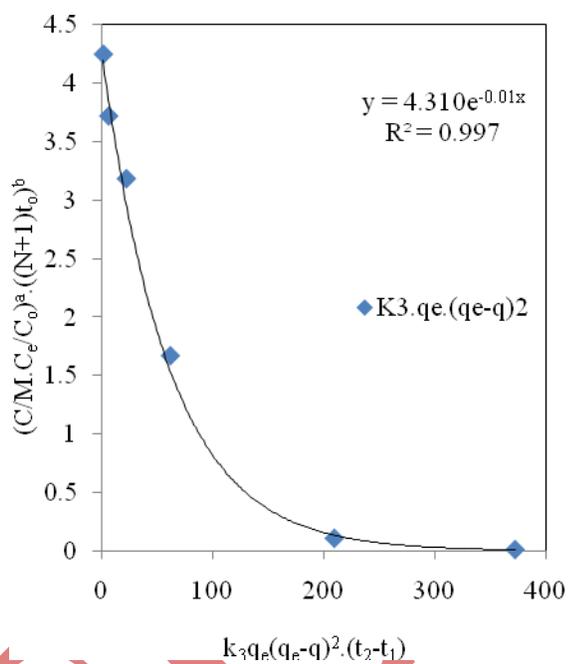


Fig. 5: Fitting of proposed mixing kinetic model at 150 rpm. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, pH=3, $T=298$ K]

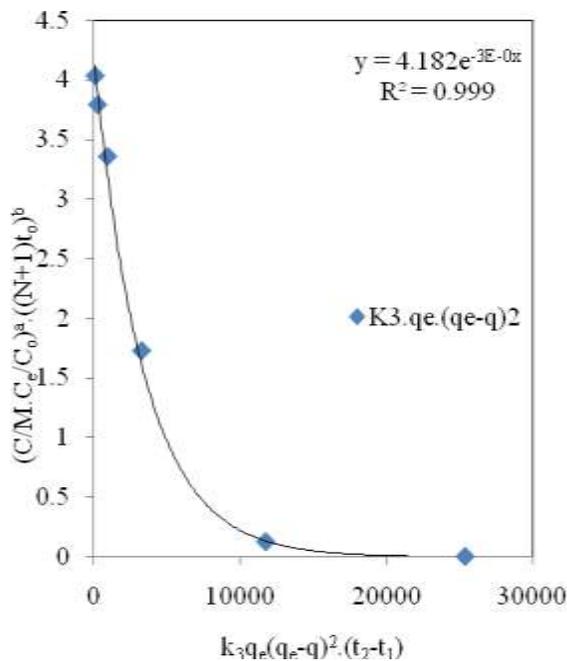


Fig.6: Fitting of proposed mixing kinetic model at 170 rpm. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, pH=3, $T=298$ K]

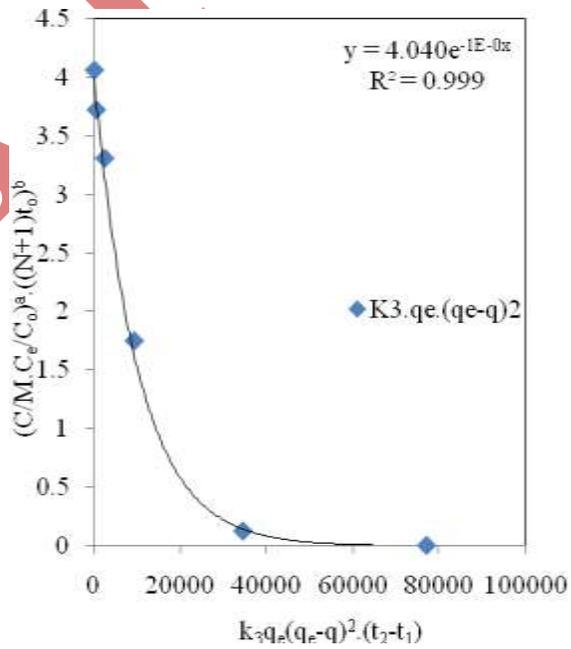


Fig. 7: Fitting of proposed mixing kinetic model at 195 rpm. [$C_0=10.31$ mg/l, $M = 0.5$ g/l, pH=3, $T=298$ K]

Table 2: Proposed kinetic model rate constant (k_3) at different mixing speeds [$C_0=10.31$ mg/L, $M=1.5$ mg/L, $pH=3$ and $T=298K$] obtained from linear fitting of kinetic data at different speeds.

Mixing Speed (N, rpm)	k_3 (mg/g) ⁻² , min ⁻¹	q_e , mg/g
0	1.2569×10^{-3}	13.06
50	1.7238×10^{-3}	13.50
100	1.847×10^{-3}	13.62
150	1.915×10^{-3}	13.74
170	1.93×10^{-3}	13.90
195	1.932×10^{-3}	13.82

The curves in these figures are best fitted by exponential decay curves with R^2 values 0.99 and above. This shows that the function represented by R.H.S. term simulates well the experimental results on mixing kinetics. (7) can also be used to optimize the mixing speed for achieving a desired removal of Cr(VI) in batch adsorption tests.

VI. CONCLUSION

From the results presented on the role of mixing and mixing kinetics, it is evident that the mixing of solution mixture in batch adsorption tests plays an important role in metal removal. A model for mixing kinetics is developed and the experimental data on Cr(VI) removal by EOLP were simulated well. It is inferred that, the proposed mixing kinetics model describes well the experimental results but need to be verified in future studies.

VII. ACKNOWLEDGEMENTS

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REFERENCES

- [1] J. Gyenis, Segregation-free particle mixing, Proceedings of IInd Israel Conference for Conveying and Handling of Particulate Solids, Jerusalem, 1997.
- [2] G. Czerlinski, R. Levin and T. Ypma, The effect of the mixing process on reaction kinetics, Wiley, Periodicals, Inc., 2003.
- [3] P.L. Tang, C.K. Lee, K.S. Lowand, Z. Zainal, Sorption of Cr(VI) and Cu(II) in aqueous solution by ethylene diamine modified rice hull, Environ. Technol., 24(9), 1243-1251, 2003.
- [4] M. Kobya, Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: Kinetic and equilibrium studies, Bioresour. Technol., 91, 317-321, 2004.

- [5] U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, *J. Hazard.Mater.*, 140, 60-68, 2007.
- [6] P. Venkateswarlu, M.V. Ratnam, D.S. Rao and M.V. Rao, Removal of chromium from an aqueous solution using *Azadirachtaindica* (neem) leaf powder as an adsorbent, *Int. J. Physic. Sci.*, 2(8), 188-195, 2007.
- [7] S. Danakumar, G. Solaraj, R. Mohanraj and S. Pattabhi, Removal of Cr(VI) from aqueous solution by adsorption using cooked tea dust, *Ind. J. Sci. Technol.*, 1(2), 576-583, 2007.
- [8] M. Nameni, M.R.A. Moghadam and M. Arami, Adsorption of hexavalent chromium from aqueous solutions wheat bran, *Int. J. Environ. Sci. Technol.*, 5(2), 161-168, 2008.
- [9] B. Kiran and A. Kaushik, Chromium binding capacity of *Lyngbya putealis* exopolysaccharides, *Biochem. Engrg. J.*, 38, 47-54, 2008.
- [10] P. Saha and S. Datta, Assessment on thermodynamics and kinetics parameters on reduction of methylene blue dye using flyash, *Desalination and Water Treatment*, 12, 1-3, 2009.
- [11] G. Crini, H.N. Peindy, F. Gimbertand C. Robert, Removal of C.I. Basic Green-4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies, *Separation and Purification Technology*, 53(1), 97-110, 2007.

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