

Methylene Blue adsorption from aqueous solution using polyaniline polymer

Shashi Tiwari,^a and Potsangbam Albino Kumar^{b*}

^a*Department of Civil Engineering, Manav Rachna International Institute of Research and studies, Faridabad -121004, (Haryana), India*

^b*Department of Civil Engineering, National Institute of Technology Manipur- 795004*

*Email: albinoiit@gmail.com

Abstract

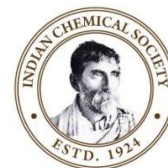
A functionalized amine based polymer was employed in this study for Methylene Blue (MB) dye adsorption present in aqueous solution. Polyaniline polymer was synthesized on top of jute fiber (PANI-jute) as support medium and assess its surface pH (pH_{ZPC}) as 6.6 suggesting positive surface charge below pH 6.6 and negative surface charge above it. Maximum adsorption of MB occurs at neutral pH range through electrostatically binding of cationic MB and deprotonated negative surface charge PANI-jute. Very low removal was observed at acidic pH due to surface protonation of amines ($-NH_3^+$) which repels the cationic MB ions. Surface characterization was carried out with SEM images before and after adsorption and the study parameters include contact time, initial MB concentration, dose of adsorbent, desorption and recycle & reuse of the polymer adsorbent. In kinetic study, the correlation coefficient (R^2) for first order equation is observed to be 0.3267 – 0.6959 for initial MB of 5 – 100 mg/L whereas that of second order is almost 0.99 to unity suggesting second order adsorption and the predominately chemical adsorption nature of MB on PANI-jute. Adsorption isotherm study reveals Langmuir isotherm better fitting than Freundlich, however close correlation value of both the isotherm indicates the adsorption well explainable by both the isotherm. This finding indicates the partly homogeneity as well as the heterogeneity of the surface of PANI-jute. The monolayer coverage or maximum adsorption capacity of polyaniline jute is observed to be 111.11 mg/g. Repeated recycling study suggests the adsorption effective till the 10th cycle and still further amount to total uptake of more than 1.11 g MB per gram of PANI-jute. Such an enormous amount of MB uptake capability is well higher than other reported adsorbents.

Keywords: Methylene blue, polyaniline, adsorption, isotherms, kinetics.

Introduction

The global annual dye production is estimated to be more than 7×10^5 tons consisting of more than 100,000 commercially dyes and 10–15% of the dye discharged in the effluent¹. Even a dye concentration of less than 1 ppm is highly visible, objectionable², toxic, carcinogenic, recalcitrant in nature and is hazardous to human and environmental

health. Above this, dyes are more difficult to degrade due to its complex aromatic structures and xenobiotic properties³. One of the most widely applied dyes is the organic dye, Methylene blue (MB)⁴ though not strongly poisonous, still it persists harmful effects on human. Among the dyes, MB widely serves as a model compound for removing from aqueous solutions due to its strong adsorption capability on



solid adsorbent⁵. Thus removal of dyes from effluents becomes an obligation to necessity. Several adopted methods for the removal since last few decades includes sedimentation/coagulation/flotation, electrokinetic coagulation⁶, precipitation, adsorption⁷ biodegradation (microbiological decomposition)⁶, photochemical treatment, irradiation, photocatalysis, sonication⁸ and membrane filtration such as ion-exchange and ultra-filtration⁹. Amongst these, the most widely practiced method is adsorption due to its high efficiency, simplicity of design, flexibility and capability to separate wide range of chemical compound. Several reported studies have already demonstrated the effectivity of dye adsorption through activated carbon derived from nutshells¹⁰, date pits¹¹, bagasse¹², fir woods and pistachio shells¹³ and oil palm¹⁴. However the issues of generated sludge, ineffective treatment and slow kinetics limits the application of activated carbon. Recently, several authors reported the application of chitosans as well as chitosan coated glass beads for adsorption of dye effectively due to the presence of functionalized group amines^{15,16}. The lone pair of electrons in sp³ hybridized nitrogen in amine bond with cations¹⁷. Therefore there arises a need for approach to synthesis and employ polymer based adsorbent rich in functional group amines for removal of MB. Again amine based functionalized polyaniline was utilized for adsorption of hexavalent chromium from hydrous solution¹⁸. In this study, we employed the same polymer polyaniline (PANI-jute) for effective adsorption and recovery of MB from aqueous solution. The primary target of the examination is to identify binding mechanism, optimum pH, dyes removal capacity, desorption and reuse capacity of PANI-jute through lab-scale investigation in batch mode studies.

Materials and Methods

Adsorbent synthesis

The amalgamation of polyaniline (short chain oligoaniline) adsorbent on the jute fiber surface

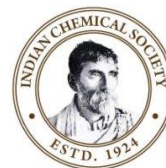
was similar to our previous work¹⁸. Here, aniline (C₆H₅NH₂) was oxidized in an acidic aqueous medium through addition of ammonium peroxydisulfate [(NH₄)₂S₂O₈] as oxidant and 1,4-phenylenediamine as chain terminator agent (Fig.1). Chemicals used for the synthesis were of AR grade and waste jute bags were washed with detergents, dried, cut into fibers (0.5-1.0 cm) for the present study.

Analytical experiment and analysis

Adsorption of MB (MB) by PANI-jute was conducted at various conditional parameters. The sets of experiments conducted are shown in Table 1. Typically, adsorption experiments were conducted in batch mode by contacting 1 L of synthetically MB contaminated solution with the design amount of PANI-jute. To accomplish proper mixing between adsorbate and adsorbent, a paddle stirrer was engaged with rapid mixing of more than 100 r.p.m. Small fluctuations of pH were arrested by adding either HCl or NaOH and extra addition of acid/base never exceeds 2% of the total MB sample volume. A preliminary investigation showed adsorption equilibrium of MB by PANI-jute to be 90 minutes; hence experiments were run for 2 hours to accomplished adsorption equilibrium. The amount of MB adsorbed were analyzes on filtrate solution after the MB contaminated PANI-jute were segregated from the sample through filtration and it's evaluated as

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where, q_t is the measure of MB ion adsorbed per unit weight of PANI-jute (mg/g) at any instant of time t , C_0 and C_t are the initial concentrations and concentration at time t respectively, m is the mass of PANI-jute (g) and V the volume of MB sample (L). In order to cross checked the leakage of any MB on other surface like stirrer, beaker or precipitation, a blank solution without any PANI-jute was always run in parallel. The experimental data were considered for analysis only after 3 similar sets of experiments are



conducted with a maximum average standard deviation of less than 5%. Concentration of MB evaluated at 665 nm wavelength by UV/visible Spectrophotometer, Model: Lambda 25 Perkin Elmer after identifying the maximum wavelength through scanning.

Results and Discussion

Adsorbent Characterization

PANI-jute surface morphology before the MB adsorption and after adsorption is presented in Figure 2(a) and 2(b) respectively. Though virgin PANI-jute surface is homogenous and smooth it becomes heterogeneous and uneven due to the deposition of MB on it.

pH of zero point charge (pH_{ZPC})

In chemical based adsorption, the surface charge of adsorbent does play an important role in adsorbate uptake efficiency. The pH_{ZPC}, which is defined as pH at zero point of charge will help in identifying the mechanism of cationic or anionic adsorbate adsorption at particular solution pH. pH_{ZPC} of PANI-jute was evaluated by conducting the Set 1 experiment and determined by the fast alkalimetric titration method¹⁹. From Figure 3, it can be clearly seen that pH_{ZPC} for PANI-jute was 6.6. Therefore below pH 6.6, the acidic water will donate more proton than hydroxide groups, and so the PANI-jute surface will be positively charged. Conversely, above pH 6.6, the surface of PANI-jute will be negatively charged and will be able to bind cationic ions through electrostatic attraction.

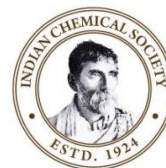
Effect of solution pH

In adsorption process, especially chemical predominant adsorption, pH is a critical parameters since it can reveal the mode of interaction of the ions (adsorbate) and adsorbent. Impact of pH on MB adsorption on PANI-jute was analyzed by conducting set 2 analyses. In order to distinguish any amount of MB against adsorption on PANI-jute, a control experiment of MB without any adsorbent was also run

parallel at pH 2- pH 11 and the observation is shown in Fig 4. Throughout pH 2- pH 11, C/C₀ is close to unity except at extreme pH of 2 and pH 11 with value of 0.8- 0.83. These findings suggest the well solubility of MB at pH 3 to pH 10 and change in the molecular form of MB at extreme pH⁸. Therefore it can be concluded that the removal of MB at pH 3- pH 10 are solely due to adsorption on PANI-jute. Again from Fig. 4, it's clear that for MB experiment with PANI-jute dose, the C/C₀ decrease from 0.85 to almost 0.1 with increase in pH from 3 to pH 6.3 suggesting the increase in MB adsorption at basic pH. Within the pH range of 6.3 to pH 10, almost equal adsorption occurred with C/C₀ of 0.11 to 0.04. At pH in acidic range, the amines (-NH₂) of the polymer adsorbent PANI-jute polymer gets protonated (-NH₃⁺) and electro-statically repels the cationic MB ions resulting in less adsorption at extreme acidic pH. With the increase in solution pH, the surface of PANI-jute gets deprotonated and thereby decreases the repulsion of MB ions. The probable mechanism of MB adsorption on PANI-jute at this neutral pH is through the coordinate bond formation of positively charged MB ion to lone pair of electrons present in sp³ hybridized amine nitrogen of PANI-jute (Fig. 5)²⁰. A similar pattern was observed for adsorption of methylene blue onto *Posidonia oceanica* (L.) fibres²¹. Above this, it's already identified the pH_{ZPC} of PANI-jute and observed to be pH 6.6. Hence the surface of PANI-jute will be positive charge below pH 6.6 and negative above it. This also contributes to electrostatic attraction and binding of more cationic dye MB on PANI-jute above pH 6.6. Hereafter all the experiments for adsorption of MB by PANI-jute were carried out at neutral pH of nearby 7.

Effects of time and adsorption kinetics

Effect of time on MB adsorption and its kinetics was investigated by conducting experiment set 3 and the findings are shown in Figure 6. For initial MB concentration of 5 mg/L, the equilibrium between MB and PANI-jute was achieved before 5 minutes and for all higher MB concentrations, its 20



minutes. Equilibrium time further increased to 90 minutes for almost higher MB concentration up to 100 mg/L and was constant beyond that. It can be observed that with the initial MB concentration of 5 mg/L, 88% removal was achieved whereas for MB concentration up to 100 mg/L, removal decreased to 40%. However, MB uptake increased from 4.4 mg/g to 40 mg/g with an increase in initial MB ion concentration from 5 mg/L to 100 mg/L. With an increase in concentration, the number of MB ions increased and so chances of contact between MB ions and adsorption sites also increased. Above this, at higher MB concentration, overcrowding of ions causes the mass transfer on ions from the bulk solution to the adsorbent. This was responsible for higher MB uptake by unit amount of adsorbent. The data were also fed into Lagergren's pseudo-first order & second order model [Equations 2 and 3] and analyzed for the kinetics details of adsorption [Equations (4) and (5)]²²:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$\text{or, } \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

$$\text{or, } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where, q_e (mg/g) is the MB ions adsorbed at equilibrium time and q_t (mg/g) at any instance of time t , while k_1 and k_2 are first and second-order kinetic rate constant respectively. The fixing of first and second order kinetics is shown in Fig 7 and 8 respectively. The coefficients of second order are also provided in Table 2. With very lesser value of correlation coefficient (R^2) 0.4 to 0.8 for first order against consistent higher value of 0.99 for second order, the adsorption of MB can be well explained by the theory of second order adsorption. This also suggests the predominately chemical adsorption nature of MB on PANI-jute against physical adsorption. However, correlation coefficients can't be the sole criteria for confirming the fitness of the

model²³. For further confirmation of identifying the right kinetic model, data were treated with Chi-square test²⁴:

$$\chi^2 = \sum \frac{(q_t - q_m)^2}{q_m} \quad (6)$$

where q_t and q_m (mg/g) are experimental and the kinetic model predicted MB adsorption capacity at time t , respectively. A Correlation coefficient (R^2) of above 0.99 (Table 2) along with lesser error between calculated and experimental q_t values for second order model (with much less χ^2 value of 0 – 4.68) suggest MB adsorption following second order kinetics²⁵. Confirming the second order MB adsorption on PANI-jute, the data were treated using the Elovich equation [Equation 7]. Elovich equation is used for checking adsorption on highly heterogeneous adsorbents²⁶ like PANI-jute and confirms the chemical adsorption.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (7)$$

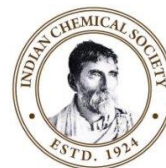
where, α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are the initial adsorption and desorption rate constant respectively during any experiment while q_t is MB adsorbed on PANI-jute at any time t . β is function of the adsorbate structural-chemical characteristics and the diffusion coefficient of the solute. Applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ with assumption of $\alpha\beta t \gg 1$,²⁷ equation (7) becomes

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (8)$$

Plotting q_t vs $\ln(t)$ of initial MB of 5 to 100 mg/L, it yields straight lines and the coefficients were evaluated from the slope and intercepts (Fig. 9). Correlation coefficients (R^2) of 0.953 to 0.993 which are higher than 0.95 for all different initial MB confirms Elovich's equation for explaining MB adsorption on PANI-jute. This study further confirms the predominant chemical adsorption than physical adsorption through diffusion.

Adsorption effects due to adsorbent dose

Effect of adsorbent dose on MB uptake was analyzed by conducting experiment set 4 varying the



adsorbent dose from 0.5 g/L to 8 g/L for three varied initial MB concentration (20, 50 and 100 mg/L). MB removal (%) and uptake with an adsorbent dose for various MB concentrations are shown in Figure 10. It was observed that MB removal (%) for all the MB concentrations increased from 15% to 80% with increase in the adsorbent dose. As we increased the quantity of adsorbent, adsorption sites number or surface area increases and subsequently conclude that high dose of adsorbent result in higher MB removal. However as adsorption dose increased, MB uptakes decreased from 84mg/g to 4mg/g. This is because of system reaches to equilibrium at lower value of “q” suggesting the adsorption sites remained unsaturated.

Adsorption Isotherms

For isotherm study, the data were analyzed with Langmuir and Freundlich’s nonlinear equation (Eq. 9 & 10) and linearised equation for Langmuir and Freundlich adsorption isotherm models [Equations (11 & 12) respectively]^{28,29}.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (9)$$

$$q_w = k_f C_e^{\frac{1}{n}} \quad (10)$$

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}} \quad (11)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (12)$$

where, q_{\max} is the maximum monolayer coverage, b is the energy constant of adsorption, K_f is the Freundlich capacity factor and n is the Freundlich’s intensity factor. For the favorable adsorption, the value of ‘ n ’ should be in the range of 1–10. A dimensionless separation factor (R_L) is also evaluated to indicate the favorability of the adsorption and is given by [Equation 13]³⁰.

$$R_L = \frac{1}{1 + b C_0} \quad (13)$$

The plot of linear equation of Langmuir and Freundlich isotherms are shown in Figure 11 and Figure 12 respectively. The regression data of both Langmuir’s and Freundlich’s linear and nonlinear

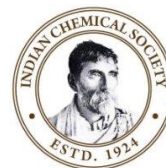
isotherm model are shown in Table 3. Chi-square test was also done to evaluate the better fit isotherm using equation 14²⁴:

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (14)$$

where, q_e and q_{em} (mg/g) are MB adsorbed at equilibrium evaluated from experiment and predicted isotherm models, respectively. The regressions coefficients (R^2) for Langmuir’s linear and nonlinear isotherm are 0.952 and 0.994 respectively against 0.883 and 0.885 for Freundlich’s suggesting the fixing of MB adsorption on PANI-jute on Langmuir’s isotherm. Comparing between linear and Nonlinear Langmuir’s isotherm, lesser λ^2 of 1.45 for nonlinear suggest better fit. The predicted q_e values at different C_e values are plotted (Figure: 13) using the four equations (9-12) clearly indicating the best-fit isotherm for nonlinear Langmuir’s isotherm. Using equation 13, R_L value was evaluated and observed to be in range 0.0427 – 0.4715, which is below unity suggesting favourable adsorption. On economical analysis of the adsorbent, it was observed that the synthesis of 5 g of adsorbent requires chemicals costing Rs. 51.11. As maximum q_e is 111.1 mg/g (Table 3), therefore removal of 100 mg of methylene blue will require Rs. 9.20.

Desorption

Since the adsorption of MB by PANI-jute is due to the chemical bond formation, there is a higher chance of recovery of adsorbed MB ions from the PANI-jute through the introduction of desorbents. The desorbents needs to have higher affinity for MB than amines of PANI-jute. Mineral acids such as HCl, H₂SO₄, HNO₃ are employed as a desorbent with varied strength & the results are mentioned in Table 4. It is observed that, as the strength of mineral acids increases from 0.001 M to 0.01 M, the desorption of MB increases from 80- 87%, 81- 88% and 79- 87% for HCl, HNO₃ and H₂SO₄ respectively. The introduction of more acids or protons (H⁺) replaces the MB ions from the amine surface of PANI-jute and thus recovers more MB ions. However, further



increase of desorbent strength from 0.01 M to 1 M, yields decrease in desorption to 68%, 46%, & 68% for HCl, HNO₃ & H₂SO₄ respectively. Probably, at extreme pH i.e. pH less than 2.5, there may be a complex ions formation with adsorbed MB resulting in non releasing of the MB ions. Another observation during the desorption of MB from PANI-jute was that, the time required for complete desorption was observed to be around 5-10 minutes. For both the mineral; acids of 0.01 M and 0.001 M strength, complete desorption was over within 10 minutes. Such rapid desorption supports the mechanism of unbinding chemical bond formation between the amines of PANI-jute and MB.

Reuse

The investigation on desorption of MB (MB) suggest recovery of more than 87% by the mineral acids. Therefore, the capability of PANI-jute to reuse is explored to evaluate the number of adsorption-desorption cycles. The result of recycling is shown in Table 5 and can be seen that more than 10 cycles can be effectively conducted without a decrease in adsorption as well as desorption of MB effectively. Hence altogether the uptake capacity by PANI-jute is increased by 10 folds i.e. 111mg/g to 1111mg/g and further chances of recycling can still be conducted. A comparative Table of MB with other several adsorbents is shown in Table 6.

Adsorption with industrial wastewater

Adsorption with actual industrial wastewater was conducted with sample collected from dye industries of Delhi. The samples were not collected from inside the industries due to legal issues but from their periphery where discharges untreated effluents. The concentrated dye effluents were observed to be diluted with domestic wastewater in public sewers. The samples of three sites in Delhi, India were given in Table 7. The removal of industrial dye by PANI-jute was observed to be in the range 38-42 %. The presence of co-ions such as total suspended solids (TSS) with high concentration also interferes with the

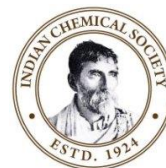
adsorption of MB. However, adsorption after filtration of TSS shows an increase in adsorption with 50% and further removal of turbidity results in 73% MB removal. The presence of other co ions probably inhibits the adsorption^{25,35}.

Conclusions

On study on MB adsorption by PANI-jute, maximum adsorption is 111.11 mg/g. Optimum parameters of the adsorption were observed at neutral pH range and followed second order kinetic model suggesting the predominant chemical adsorption. The probable mechanism of MB adsorption on PANI-jute is through the coordinate bond formation of cationic MB ion to lone pair electrons in *sp*³ hybridized amine nitrogen. Adsorption isotherm study reveals nonlinear Langmuir isotherm fixed better than that of both Linear and nonlinear Freundlich's isotherm equation. Desorption with mineral acids was able to recover more than 80% adsorbed MB and able to reuse of PANI-jute for 10th cycles and amounts to total uptake of more than 1111 g MB per gram of PANI-jute. Such enormous amount of MB uptake capability is well higher than other reported adsorbents.

References

1. A. N. Fernandes, C. A. Almeida, N. A. Debacher and M. M. Souza, *J. Mol. Str.*, 2010, **982**, 62–65.
2. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Hazard Mater.*, 2010, **177**, 70–80.
3. K. M. Parida, *Ind. Eng. Chem. Res*, 2011, **50** (2), 843–848.
4. J. W. Sheng, *App. Clay Sci.*, 2009, **46** (4), 422–424.
5. B. H. Hameed, *Dyes and Pigments*, 2007, **75** (1), 143–149.
6. D. Pokhrel and T. Viraraghavan, *The Sc. of the Total Env.*, 2004, 333.
7. D. Yue, Y. Jing, J. Ma, C. Xia, X. Yin and Y. Jia, *Desalin.*, 2011, **267**, 9-15.



8. J. Ma, Y. Jia, Y. Jing, J. Sun and Y. Yao, *Applied Clay Sc.*, 2009, **46**, 114.
9. N. Hilal, H. Al-Zoubi, N. A. Darwish, A. W. Mohammad and M. Abu, *Desalin.*, 2004, **170**, 281-308.
10. M. Ahmedn, W. E. Marshall, A. A. Hussein, I. Goktepe and R. M. Rao, *J. of Chem. Tech. and Biotech.*, 2004, **79**, 1092-1097.
11. F. Banat, S. Al-Asheh and L. Al-Makhadmeh, *Chem. Eng. and Tech.*, 2004, **27**, 80- 86.
12. W. T. Tsai, C. Y. Chang, M. C. Lin, S. F. Chien, and M. F. Hsieh, *Chemos.*, 2001, **45**, 51-58.
13. F. C. Wu, R. L. Tseng and R. S. Juang, *J. Coll. Inter. Sc.*, 2005, **283**, 49-56.
14. I. A. Tan, B. H. Hameed and A. L. Ahmad, *Chem Engg J.*, 2007, **127**, 111-119.
15. G. L. Dotto, M. L. G. Vieira and L. A. A. Pinto, *Ind. Eng. Chem. Res.*, 2012, **51**, 6862-6868.
16. J. S. Piccin, G. L. Dotto, M. L. G. Vieira, and L. A. A. Pinto, *J. Chem. Eng. Data*, 2011, **56**, 3759-3765.
17. G. P. Kumar, P. A. Kumar, S. Chakraborty and M. Ray, *Sep. and Purif. Technol.*, 2007, **57**, 47-56.
18. P. A. Kumar, S. Chakraborty and M. Ray, *Chem. Engg. J.*, 2008, **141**, 30-140.
19. C. P. Huang and F. B. Ostovic, *J. Env. Engg. Div.*, 1978, **104**, 863-878.
20. B. Yasemin and A. Haluk, *Desalination*, 2006, **194**, 259-267.
21. M. C. Ncibi, B. Mahjou, M. Seffen, *J. Hazard. Mater.*, 2007, **B139**, 280-285.
22. Y. S. Ho, *Water Res.*, 2006, **40**, 119-125.
23. N. Chiron, R. Guilet, E. Deydier, *Water Res.*, 2003, **37**, 3079-3086.
24. Y. S. Ho, W. Chiu and C. Wang, *Biores. Technol.*, 2005, **96**, 1285-1291.
25. M. Ghaedi, D. Ghazanfarkhani, S. Khodadoust, N. Sohrabi and M. Oftade, *J. Indus. Eng. Chem.*, 2013, **20(4)**, 2548-2560
26. Y. S. Ho, J. F. Porter and G. McKay, *Water, Air & Soil Poll.*, 2002, **141**, 1-33.
27. Y. S. Ho and G. McKay, *Trans. IchemE*, 1988, **76B**, 332-340.
28. I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1361-1403.
29. H. M. F. Freundlich, *Zeitschrift für Physikalische Chemie (Leipzig)*, 1906, **57A**, 385-470.
30. R. K. Hall, L. C. Eagleton, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fund.*, 1966, **5**, 212-223.
31. H. Deng, J. Lua, G. Li., G. Zhanga, and X. Wanga, *Chem. Eng. J.*, 2011, **172**, 326- 334.
32. B. H. Hameed and A. A. Ahmad, *J. Hazard. Mater.*, 2009, **164**, 870-875.
33. O. Hamdaoui, *J. Hazard. Mater.*, 2006, **135**, 264-273.
34. Y. Liu, Y. Zheng and A. Wang, *J. of Environ. Sciences*, 2002, **4**, 486-493.
35. D. Ozer, G. Dursun and A. Ozer, *J. Hazard. Mater.*, 2007, **144**, 171-179.

Conflict of interest

The authors hereby declared that there is no conflict of interest for this manuscript.

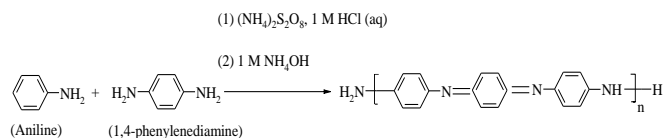


Fig. 1. Synthesis scheme of short chain polyaniline (oligoaniline).

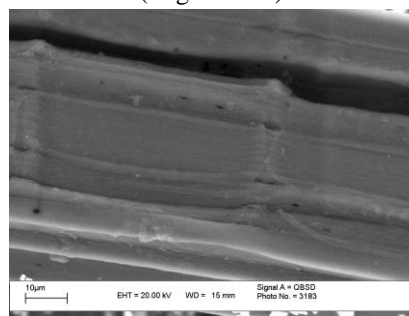


Fig. 2(a). SEM images of PANI-jute before MB adsorption.

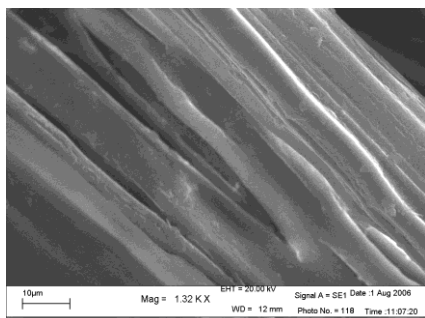


Fig. 2(b). SEM images of PANI-jute after adsorption.

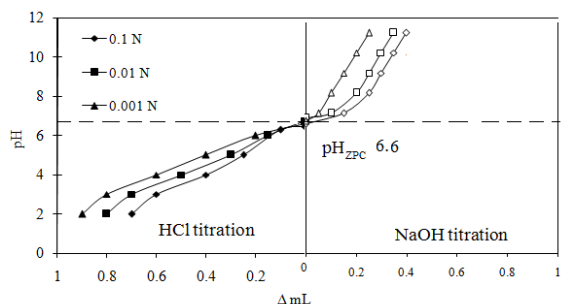


Fig. 3. pH of zero point charge (pH_{ZPC}) of PANI-jute.

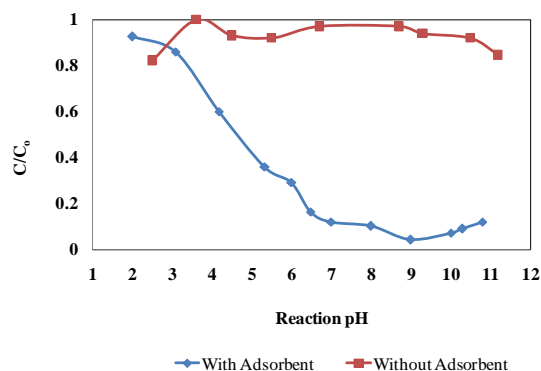


Fig. 4. Effect of pH on MB adsorption by PANI-jute.

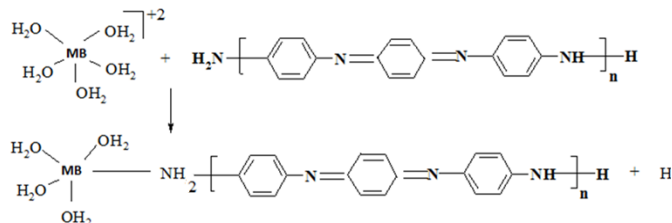


Fig. 5. Proposed mechanism for binding MB by PANI-jute through coordinate bond.

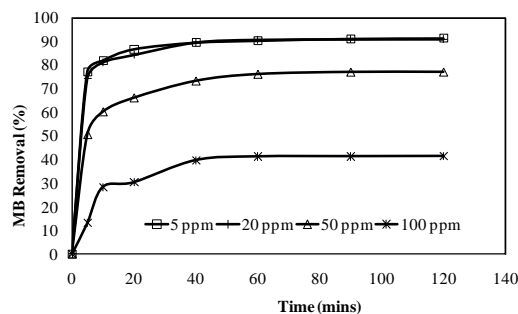


Fig. 6. Effect of time (mins) on adsorption of MB

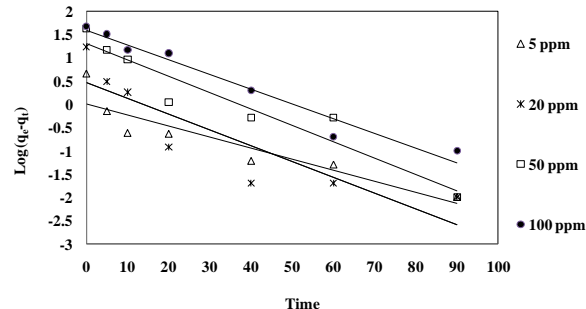


Fig. 7. Lagergren's pseudo-first order model

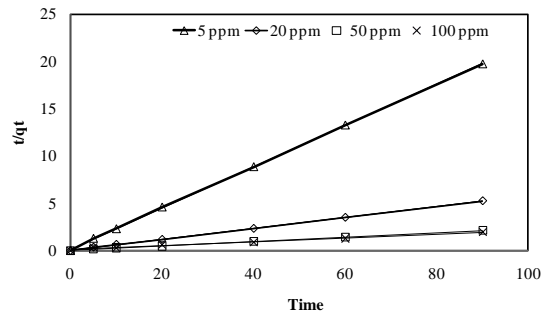


Fig. 8. Lagergren's pseudo-second order model

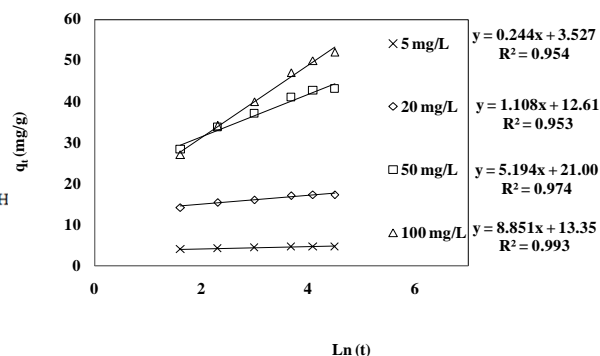


Fig. 9: Elovich Model, for adsorption kinetics

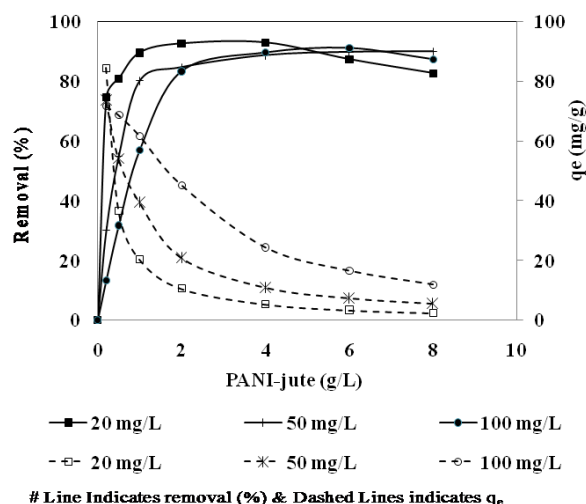


Fig. 10. Effects of PANI-jute dose on adsorption.

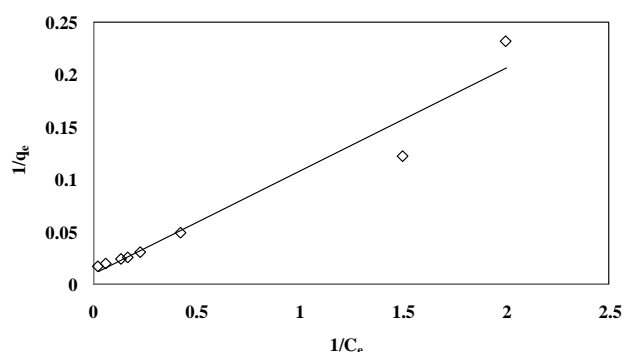


Fig. 11. Plot of Linear Langmuir Isotherm.

Table 1. Sets of experiments conducted.

Experiment No	Variable parameters	Controlled parameters	Purpose
1	Strength of NaCl (10^{-1} , 10^{-2} , 10^{-3} M)	Dose of PANI-jute: 1 g/L	To determine pH_{ZPC} of PANI-jute
2	pH	Initial MB concentration: 5 mg/L, PANI-jute dose: 1 g/L	Effect of solution pH; Identification of binding mechanism
3	Initial MB concentration: 5, 20, 50 & 100 mg/L	PANI-jute dose: 1 g/L; Vol: 1 L; pH 7.	Effect of initial MB concentration effect on adsorption
4	Adsorbent dose: 0.2, 0.5, 1, 2, 4, 6, 8 g/L	Initial MB concentration: 20, 50, 100 mg/L, pH: 7;	Effect of dose and adsorption isotherm
5	HCl, H ₂ SO ₄ , HNO ₃ : 0.01, 0.1, 1	Initial MB concentration: 50 mg/L, pH: 7;	Desorption studies
6	No of Cycles	Initial MB concentration: 50 mg/L, pH 7, Dose: 1 g/L	Reuse

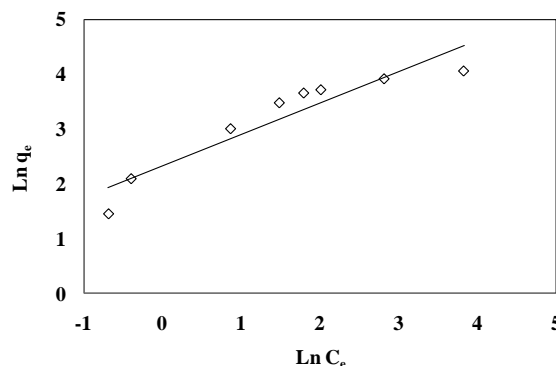


Fig. 12. Plot of Linear Freundlich Isotherm.

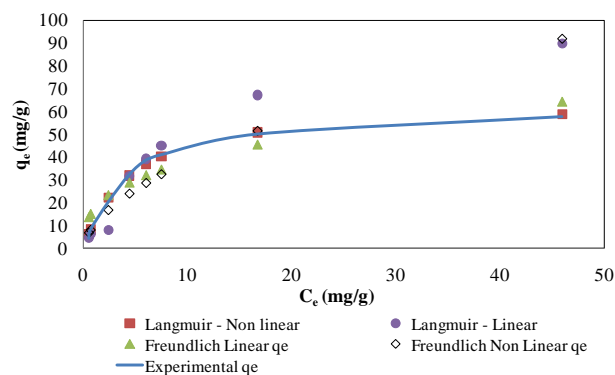
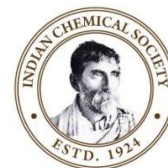


Fig. 13. Plot of Linear & Nonlinear Langmuir's and Freundlich's Isotherms.

**Table 2.** Coefficients of second order model for MB adsorption by PANI-jute.

Initial MB (mg/L)	k_2	q_e (Exp)	q_e (Predicted)	(R^2)	χ^2
5	0.440	4.56	4.58	1	0.00
20	0.112	17.46	17.54	0.99	0.24
50	0.010	44.63	45.45	0.99	0.91
75	0.007	46.45	47.61	0.99	1.47
100	0.002	49.15	52.63	0.99	4.68

Table 3. Coefficients of Langmuir and Freundlich's isotherm.

Isotherm	Langmuir				Freundlich			
	R^2	a (mg/g)	b (L/mg)	λ^2	R^2	K_f	n	λ^2
Linear Model	0.952	111.11	0.092	31.05	0.883	10.37	1.75	28.66
Nonlinear Model	0.994	64.34	0.2242	1.45	0.885	17.53	2.94	31.54

Table 4. Desorption of MB from PANI-jute.

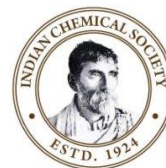
Desorbent	HCl				HNO ₃				H ₂ SO ₄			
	0.001	0.01	0.10	1.00	0.001	0.01	0.10	1.00	0.001	0.01	0.10	1.00
Strength (M)	0.001	0.01	0.10	1.00	0.001	0.01	0.10	1.00	0.001	0.01	0.10	1.00
Desorption (%)	80	87	76	68	81	88	64	46	79	87	76	68

Table 5. Recycling and reuse of PANI-jute for MB adsorption (Initial 55 mg/L).

Cycles	MB effluent (mg/L)	MB removal (%)	Desorption MB Concentration (mg/L)	(%)
1	6.04	89.04	40.06	81.66
2	6.09	88.94	40.95	83.57
3	5.21	90.55	38.99	78.17
4	5.62	89.80	39.70	80.26
5	5.21	90.55	51.24	81.23
6	4.56	91.73	39.47	78.10
7	5.68	89.69	38.11	77.13
8	4.67	91.51	44.20	87.68
9	6.27	88.61	40.95	83.88
10	6.15	88.83	41.78	85.37

Table 6. Comparison of MB maximum adsorption capacities of various adsorbent with PANI-jute.

S. no	Adsorbent	Maximum MB adsorption (mg/g)	References
1	Activated carbon	6.33	[25]
2	Cotton stalk	147.06	[31]
3	Phosphoric Acid treated cotton stalk	222.22	[31]



4	Sulphuric acid treated cotton stalk	555.56	[31]
5	Garlic peel	142.86	[32]
6	Saw Dust	111.97	[33]
7	Crushed Bricks	80.60	[33]
8	Vermiculite hydrogel composites	1685	[34]
9	Dehydrated peanut hull	161.3	[35]
10	PANI-jute	490	Present Studies

Table 7. MB at various sites of Delhi industrial effluent

Sl No	Industrial Sites	pH	Concentration of MB (mg/L) after dilution with sewage	TSS (mg/L)	Removal(%)PANI-jute
1	Badli	6.87	3 mg/L	150	40
2	Shahbad	6.52	4.5 mg/L	160	42
3	Bawana	6.34	5.2 mg/L	140	38