

**CATIONIC DYE (METHYLENE BLUE) REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON ALUMINOPHOSPHATE ZEOLITES****Nirmala B^{*1}, Suresh Kumar B.V², Chethan B.S³, Srilakshmi B.P³, Sudha A.G³, Suresha E³**¹*Assistant Professor, Department of Chemistry, University College of Science, Tumkur University, Tumkur-572 103*²*Assistant Professor, Department of studies and research in geology, University of Mysore, Mysore- 560006*³*UG students, University College of Science, Tumkur University, Tumkur-572 103****Corresponding Author Email: nirmala2528@gmail.com****ABSTRACT:**

Removal of dyes from waste water is a major ecological problem. Color impurity in industrial effluents poses a significant risk to human health and the environment. Much effort has been expended to degrade them using various methods. The objective of this work is to study the adsorption of dye solution, methylene blue on microwave assisted synthesis of isopropyl amine templated aluminophosphate zeolites. The effectiveness of the aluminophosphate zeolites was evaluated at different adsorption dosage and contact time. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. The surface morphology of the adsorbents have been analysed using the scanning electron microscope (SEM). This work shows aluminophosphate zeolites could be utilized as an effective adsorbent for treating dye waste water.

KEYWORDS:

Aluminophosphate zeolites, adsorption, methylene blue, waste water, dye removal

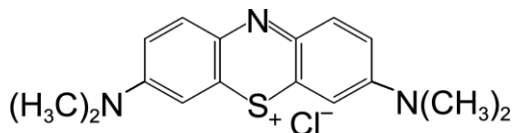
INTRODUCTION

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solids [1]. Dyes in surface waters are of barrier effect on the sun light penetration and aeration of water body, and thus reduce photosynthetic activity. The toxic nature of the dye effluents causes to death of soil microorganisms when they are used for irrigation purposes and this affects agricultural productivity. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by their mutagenic and carcinogenic effect. The discharge of such effluents is worrying for both toxicological and environmental reasons [2, 3]. Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation [4],

adsorption [5], ozonation [6], electrochemical techniques [7], and fungal decolonization [8]. Further these methods are inefficient and incompetent because these dyes are stable towards light, oxidizing agents and aerobic digestion and are also highly soluble in aqueous media. A comprehensive investigation shows that adsorption technique is considered to be most effective, simple method to remove water soluble dyes [9]. Different types of adsorbents such as metal oxides, agrowaste etc., are used [1]. Of which activated carbon is considered to be very effective, unfortunately it is expensive [10]. On the other hands, zeolite was found very effective in reducing ammoniacal nitrogen and COD [11-14] since it have high cationic exchange capacities, large surface areas and high residual carbon contents. The objective of the present study was to investigate the ability of aluminophosphate zeolites for the removal of methylene blue from an aqueous solution by adsorption. Methylene blue (MB) is the

cationic dye that is most commonly used for coloring. It is generally used for dyeing cotton, wool, and silk. MB can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if

ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea [15]. Therefore, decolorization of dyes is important aspects of wastewater treatment before discharge.



Structure of methylene blue

MATERIALS AND METHODS

Preparation of adsorbents:

The adsorbent isopropyl amine templated Aluminophosphate zeolites crystallization carried out using a domestic microwave oven. The reactants were phosphoric acid, aluminium hydroxide, Isopropyl amine. Aluminium hydroxide was first hydrolysed in deionized water and then phosphoric acid and IPA added to the mixture dropwise into the reaction mixture while stirring and heating at 60°C. IPA is a structure directing agent. After the addition of IPA, the gel was aged at room temperature for 2 h. The

suspension was transferred into a teflon liner and tightly covered with a lid and placed in a microwave oven and exposed to microwave for 60 seconds at 900w. After the synthesis, the liner was cooled to room temperature. The products were first cleaned in ultrasonic cleaner after recording the final pH, filtered, washed with distilled water several times and dried followed by calcination for 2 hours. The crystallinity of the samples was analyzed by powder X-ray diffractometer (Figure 1) and the surface morphology studied through SEM (Figure 2).

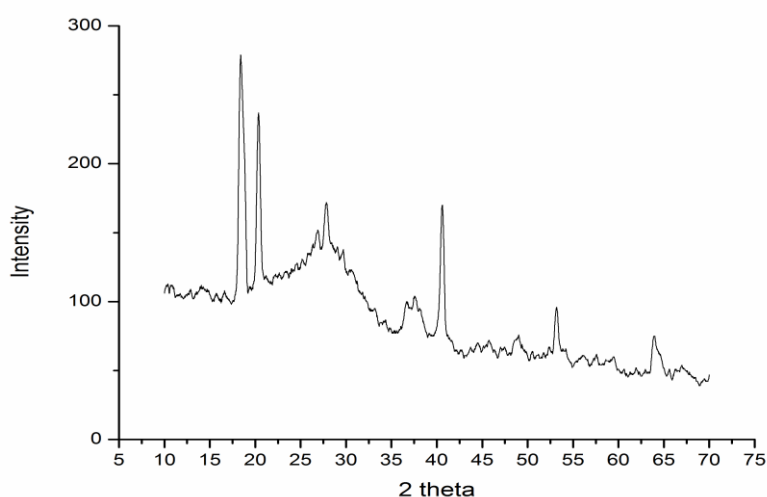


Fig.1: XRD analysis of aluminophosphate zeolite

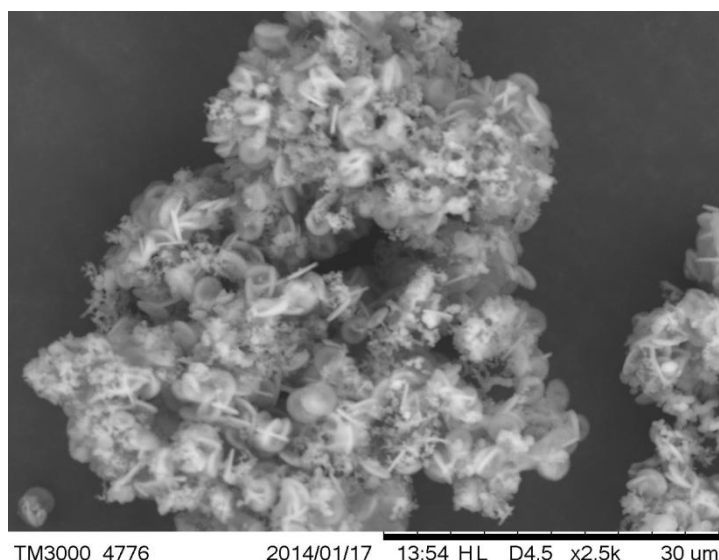


Figure 2: SEM micrograph of IPA templated Aluminophosphate zeolite

Preparation of stock solution of Methylene blue dye

Methylene blue dye is widely used in textile, paper and carpet industries. It is a basic cationic dye. Methylene blue dye [C.I. =52015 B, chemical formula= $C_{16}H_{18}ClN_3S$; molecular weight= 373.91g; melting point =100–110°C (and λ_{max} =660 nm (reported) and 670 nm (experimentally obtained) was obtained from s. d. Fine Chemicals, Mumbai, India. An accurately 0.02 gm. weighed quantity of the dye was dissolved in 500 ml distilled water to prepare stock solution. The solution is blue in colour. Experimental solutions of the desired concentration were obtained by dilutions of stock solution in 100 ml of distilled water.

a. Estimation of optimum amount of adsorbent

In order to find out the optimum amount of adsorbent at which maximum adsorption takes place, 1.7×10^{-5} mg/L of methylene blue dye solution was taken in a series of flasks with different quantity of adsorbents; 0.1, 0.2, 0.3, 0.4 and 0.5 gm. of aluminophosphate zeolites. The solution of dye was kept on a shaking magnetic stirrer for 15-20 min at 120 rpm for shaking. Dye concentration estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max} using a spectrophotometer. The samples to be withdrawn from the magnetic stirrer at predetermined time intervals and the dye solution

should be separated from the adsorbent by the help of a Centrifuge. The absorbance of solution is then measured.

b. Estimation of optimum concentration of dye solution

For the determination of optimum concentration of dyes, solutions of different concentrations of dye were prepared. From 1.7×10^{-5} mg/L to 3.5×10^{-5} mg/L of dye solution was placed in respective flasks with optimum amount of adsorbents for 15-20 min. The samples withdrawn from the magnetic stirrer at predetermined time intervals and the dye solution separated from the adsorbent with the help of a Centrifuge. The absorbance of solution is then measured. Dye concentration estimated spectro photometrically at the wavelength corresponding to maximum absorbance, λ_{max} , using a spectrophotometer.

c. Effect of pH on Methylene blue uptake:

The pH is one of the most important factors controlling the adsorption of dye onto adsorbent presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Adsorption of MB onto aluminophosphate zeolites was carried out for the examination of the effect of pH at a range of 2.00-8.00 and it was found that the adsorption capacity increased with increase in

pH (Figure 3). The pH of the dye solutions were adjusted with dilute HCl (0.1N) or NaOH (0.1N) solution by using a pH meter. The effect of pH on the adsorption of methylene blue on aluminophosphate zeolites studied at RT, adsorbent dosage 0.1g and contact time 1 h for the dye concentration 3.5×10^{-5} mg/L. Final % absorbances of dye solutions were measured using UV spectrophotometer ($\lambda_{max}=670\text{nm}$). Figure 3 showed that at low pH value, the adsorption was decreased. When solution pH increased from 2.00 to 9.00, the adsorption increased.

The maximum dye uptake was observed in the pH range of 6.00. The basic dyes give positively charged ions when dissolved in water. Thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species. When the pH of dye solution is increased the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent [16]

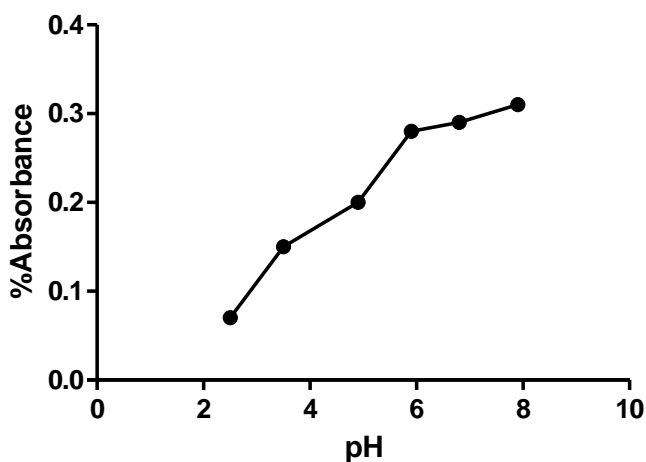


Figure 3: Effect of initial pH on the adsorption of MB onto aluminophosphate zeolites

d. Effect of contact time and initial Methylene blue concentration

Experiments were carried out at fixed adsorbent dose (0.1 g/100 mL) in the test solution at room temperature (27 ± 2 °C), pH 7 and at different initial concentrations

of MB (1.7×10^{-5} to 3.6×10^{-5} mgL⁻¹) for 60 minutes. Figure 4 shows that the percentage of adsorption efficiency of aluminophosphate zeolites decreased with the increase of initial MB concentration in the solution.

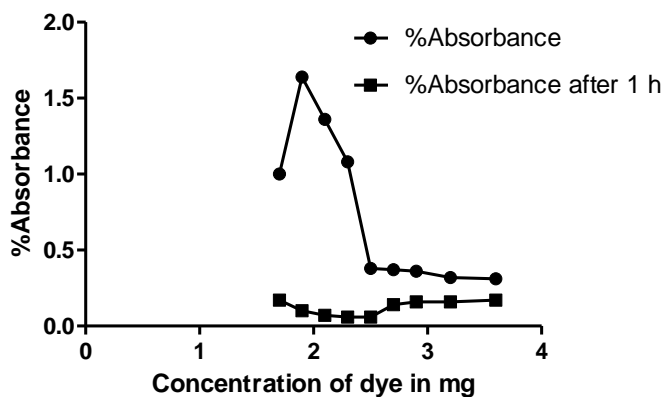


Figure 4: Effect of contact time and initial Methylene blue concentration

e. Effect of adsorbent mass on MB adsorption with contact time

The relation between removal of MB and reaction time were studied to see the rate of dye removal. It was found that more than 50% removal of MB concentration occurred in the first 50 min, and thereafter the rate of adsorption of the MB onto aluminophosphate zeolites was found to be slow. The rapid adsorption at the initial contact time is due to the highly negatively charged surface of the aluminophosphates for adsorption of cationic MB in the solution at pH 7. Later slow rate of MB adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species onto the surface of

Aluminophosphate zeolites and the available cationic adsorbate species in the solution as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent.

The experiments were studied by changing the quantity of adsorbent (0.1, 0.15, 0.2g/100ml) in the test solution while keeping the initial MB concentration (3.6×10^{-5} mgL⁻¹), temperature (27 ± 2 °C) and pH (7.0) constant at contact times for 100 min (Fig. 5). The adsorption increased as the adsorbent dose increased from 0.1 g to 0.2 g/100 mL at equilibrium time (100 min). Maximum MB removal was achieved within 25–50 min after which MB concentration in the reaction solution was almost constant.

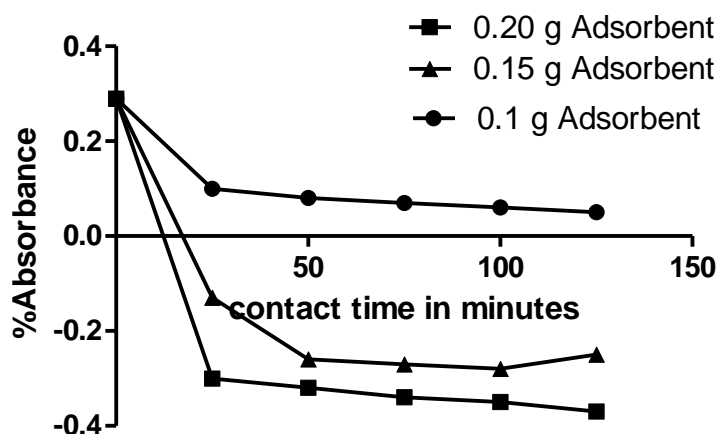


Figure 5: Effect of adsorbent mass on MB adsorption with contact time

CONCLUSION

From the of present study, it may be concluded that Isopropylamine templated aluminophosphate zeolites could be used as an effective adsorbent for the removal of methylene blue from aqueous solution. The amount of dye adsorbed varied with initial dye concentration, pH, contact time and adsorbent dose. Maximum adsorption observed at pH =6 and maximum dye removed at 50 to 100 minutes. With this environment friendly adsorbent, considerable dye removal can be achieved. So it can be substituting other expensive bio-adsorbents. With the experimental data obtained in this

study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents.

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REFERENCES

[1] Crini, G.; 2006. Non-Conventional low-cost adsorbents for dye removal: A Review, *Bioresource Tecnology*, 97,1061.

- [2] Robinson, T.; McMullan, G.; Marchant R.; Nigam, P.; 2001. *Bioresour. Technol.*, 77, 247.
- [3] Aksu, Z.; 2005. *Process Biochem.*, 40, 997.
- [4] Han, R. P.; Zhang, J. H.; Zou, W. H ; Shi, J.; Liu, H. M.; 2005. *J. Hazard. Mater.*, 125, 266.
- [5] Gupta, V. K.; Ali, I.; Suhas D.; Mohan, 2003. *J. Colloid Interface Sci.*, 265, 257.
- [6] Ho, Y. S.; Chiu, W. T.; Wang, C. C., 2005. *Bioresour. Technol.*, 96, 1285.
- [7] Kumar, K. V.; 2006. *J. Hazard. Mater.*, 136, 197.
- [8] Ho, Y. S.; 2006. *Water Res.*, 40, 119.
- [9] A.Dabrowski, 2001. Adsorption-From Theory to Practice, *Advances in colloids and Interface Science*, 93, 135-224.
- [10] X.Y.Yang, B.Al-Duri, 2001. Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon, *Journal of Chemical Engineering*, 83,15.
- [11] Lee, J. H., Kim, D. S., Lee, S. O., & Shin, B. S. 1996. Treatment of municipal landfill leachates using artificial zeolite. *Chawon Risaikring*, 5, 34-41.
- [12] Chang, W., Hong, S., & Park, J., 2001. Effect of zeolite media for the treatment of textile wastewater in abiological aerated filter. *Process Biochemistry*, 37, 693–698. [http://dx.doi.org/10.1016/S0032-9592\(01\)00258-8](http://dx.doi.org/10.1016/S0032-9592(01)00258-8)
- [13] Jung, J., Chung, Y. C., Shin, H. S., & Son, D. H., 2004. Enhanced ammonia nitrogen removal using existent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research*, 38, 347–354. <http://dx.doi.org/10.1016/j.watres.2003.09.025>
- [14] Otal, E., Vilches, L. F., Moreno, N., Querol, X., Vale, J., & Fernández Pereira, C.; 2005. Application of zeolitised coal fly ashes to the depuration of liquid wastes. *Fuel*, 84, 1440-1446. <http://dx.doi.org/10.1016/j.fuel.2004.08.030>
- [15] Senthilkumaar, S.; Varadarajan, P. R.; Porkodi, K.; Subbhuraam, C.V.; 2005. *J. Colloid Interface Sci.*, 284, 78.
- [16] Özdemir, Y.; Do an, M.; Alkan, M., 2006. *Micropor. Mesopor. Mat.*, 96, 419



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