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ORIGINAL ARTICLE

Removal of Methylene blue from Aqueous solution by adsorption on to $AlPO_4$- tridymit

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ABSTRACT
Porous molecules such as aluminophosphate zeolites have been proven to be effective adsorbent molecules for polluted water containing soluble dyes released from various industries such as paper, textile, paints and varnishes etc. In the current work initial dye concentration, pH, adsorption dosage , contact time and kinetic studies were carried out to evaluate adsorption capacity of $AlPO_4$-tridymite for the removal of methylene blue from aqueous solution. The results showed that $AlPO_4$-tridymite zeolites could be used as an effective alternative adsorbent for the removal of dyes and colours from aqueous solution
Keywords: *Adsorption, Methylene Blue, Aluminophosphate zeolites, Microwave, Water treatment*

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INTRODUCTION

Growing Awareness among the global population towards environment, pollution and prevention is one of the guiding forces for the development of cleaner and effective processes with respect to restoring our natural resources. Most Common methods for wastewater treatments include physicochemical and biological methods such as adsorption, flocculation, precipitation, coagulation, ozonation, photo degradation, membrane filtration [1] etc. But it has been found difficult to remove organic dyes and pigments using conventional methods owing to their complex aromatic structures and stability towards action of light or oxidizing agents and is especially resistant to aerobic digestion. Adsorption is one of the promising options for removing water soluble dyes from waste water[2].

Industries, specifically paper, pulp, leather, textile, paints and varnishes etc., use many organic dyes and pigments as coluring agents. Dyes for example, Methylene Blue, Crystal Violet, Malachite Green, Indigo, Azo dyes, Sulphur dyes, Tyrian Blue etc are extensively used in most of the above said industries and are among the major causes for the deteriorating quality of our natural water resources. Presence of dye in water raises Chemical Oxygen Demand (COD) and Biological Oxygen Demand(BOD) [3], leading to many health problems in both aquatic and terrestrial life. Health hazards range from allergic reactions in humans to death of aquatic organisms[4, 5].

Various molecules including Activated Charcoal[6], Chitin and Chitosan derivatives[7,8], clay materials [9-11], biosorbent molecules such as bagasse[12], rice husk[13] are being studied in order to obtain efficient adsorbents for effective removal of dyes from industrial effluents. Aluminophosphate zeolites are expected to be potential candidates for adsorption removal of organic dyes owing to the presence of bifunctional sites in their framework. Aluminum with slight positive charge acts as an acidic site, while phosphorus in the framework will show slight basic nature. The molecules are insoluble in water and less reactive hence can be easily removed from the system after adsorption. Adsorption in case of aluminophosphate zeolites has been found to be a physical phenomenon. This gives an opportunity for recycling and reusing of adsorbents[14-17].

Methylene Blue is a basic dye which apart from being used as dye in various industries also finds application in Medicine, Chemistry and Biology. Being a phenothiazine derivative it can act as an oxidizing agent in larger quantities and at lower dosages it is a reducing agent. It has adverse effect on cardiovascular system, gastrointestinal system, skin. In the current work we have synthesized aluminophosphate zeolite $AlPO_4$- tridymit and used the same as adsorbent for the removal of water

soluble dye Methylene Blue. Effectiveness of $AlPO_4$- tridymit as adsorbent for the removal of Methylene Blue dye is evaluated using Batch sorption techniques.

MATERIAL AND METHODS

Synthesis and Characterization:

Synthesis of AlPO4- tridymit:

$AlPO_4$- tridymit was prepared by the following procedure. 3.9g of Aluminium hydroxide was dispersed in to minimum amount of distilled water at 60^0C.To this suspension 3.47ml of tri ethyl amine is added drop wise with constant stirring followed by 5.32ml phosphoric acid [Al:P:TEA:: 1:1.9:0.5]. The suspension was kept for aging for 2 hours and then transferred in to Teflon liners. The reaction mixture was then subjected to microwave irradiation at 600W for 300seconds. It is then allowed to cool to room temperature and the product was thoroughly washed with distilled water in an ultrasonic cleaner and finally filtered and dried at 250^oCfor 2 hours in hot air oven. Crystallisation occured in acidic conditions as initial and final pH of the reactive gel and product was found to be around 3.

The product is characterized using FTIR, XRD, EDAX, SEM and BET.

Adsorption Studies:

Preparation of basic dye solution:

Methylene Blue used was of analytical reagent grade(MW=319.86g) .Stock solutions of the test reagent were made by dissolving Methylene Blue, (3,9-bis dimethyl- aminophenazo thionium chloride), in distilled water. 20mg of methylene blue solution was dissolved in distilled water and the solution was made up to 1000ml. Methylene Blue solution was then diluted accordingly to prepare solutions of concentration 4mg/L, 6mg/L, 8mg/L and 10mg/L and used for batch experiments.

Batch experiments were performed to evaluate the effect of adsorbent dosage, pH of the dye solution, contact time and initial concentration of dye solution on to aluminium phosphates.

The adsorption was performed by batch experiments. Kinetic experiments were carried out by stirring 100ml of dye solution of known initial dye concentration with 10mg of $AlPO_4$-tridymite at room temperature at 500 rpm. At different time intervals, samples have been drawn out and then centrifuged at 10,000r/min. The concentration in the supernatant solution was analyzed using a UV spectrophotometer SHIMADZU 1800 by measuring absorbance at λ max = 665 nm and pH = 5.

Effect of adsorbent dosage was studied by adding 2 to 10mg of adsorbent to 20mL of dye solution of known concentration. The solution was stirred for 10 min and centrifuged. Absorbance of the supernatant is measured and the amount of dye adsorbed per unit weight of the adsorbent q_t $mg.g^{-1}$ is calculated using the equation

$$\mathrm{qt} = \frac{(Co - Ct)V}{\mathrm{m}}$$

where, C_0 (mg/l) is the initial dye concentration, C liquid phase concentrations of dye at any time, V is the volume of the solution and m is the mass of dry adsorbent used (g).

Effect of pH on adsorption of methylene blue was studied by adjusting the pH of dye solution to 2, 4, 6, 8 and 10 by the addition of 0.1M HCl or 0.1M NaOH. 2mg of adsorbent was then added to 20mL of dye solution of initial concentration 4mg/L at different pH for 10 min. The solution was then centrifuged and absorbance of the supernatant was read at 665nm.

Effect of contact time on adsorption was evaluated by 20mL of dye solution of known initial concentration with 2mg of adsorbent for different time intervals of 5,10,20,30,40 50 and 60min. The solution was then centrifuged and absorbance was read at 665nm.

Adsorption isotherms were studied by stirring 10g of $AlPO_4$-tridymite in 100mL of dye solution of concentration ranging over 4 to 10mg/L. 1.5mL of dye solution was withdrawn at regular interval of time and absorbance was measured at 665nm.

RESULTS AND DISCUSSION

Characterization of $AlPO_4$-tridymite:

Synthesized $AlPO_4$-tridymite was characterized by FTIR, XRD, SEM and BET analysis.

Infrared spectroscopy:

IR studies was carried out using Brucker Alpha FTIR Spectrophotometer and the results show (**Fig-1**) a sharp and characteristic peak at $1111cm^{-1}$ corresponding to the unsymmetrical stretching frequency of P-O bond. Also we can see weak but definite peaks at $466cm^{-1}$ and $710cm^{-1}$ corresponding to bending vibrations of P-O bond. Weak peak at $1630cm^{-1}$ corresponds to symmetric stretch of P-O bond. Weak band around 600 cm^{-1} corresponds to Al tetrahedron with Al^{3+} [18]. Absence of any peaks around

3000cm^{-1} show that there are no occluded organic moieties or water molecules in the zeolite framework. That ensures the essential porosity of the molecule.

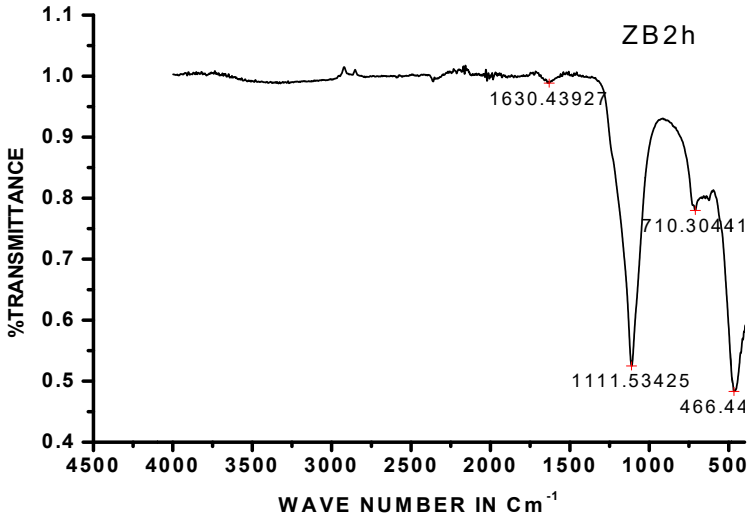

Fig 1: FTIR spectrum of $AlPO_4$- tridymit.

X-Ray Diffraction Spectroscopy:

Powder X-ray diffraction studies were done using PAN analytical X'pert PRO X-RAY diffractometer with graphite monochromatized Cu Ka radiation source (λ-1.541Å). The XRD patterns of the samples (**Fig 2**) confirm that the products have crystallized in $AlPO_4$- tridymit framework [19, 20] and possess high crystallinity.

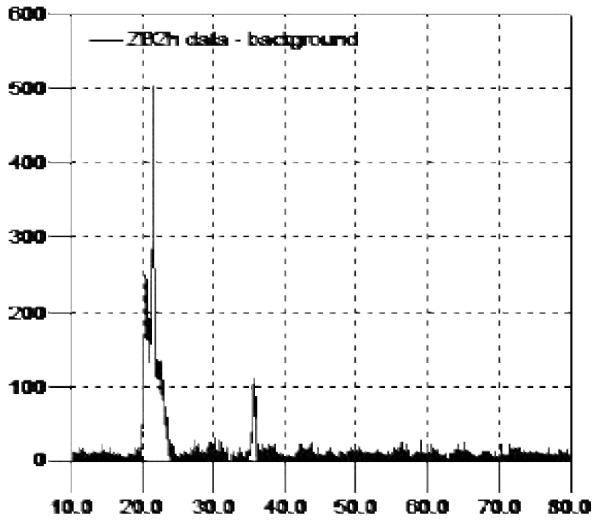

Fig 2: XRD of $AlPO_4$- tridymit

Scanning Electron Microscope- Energy Dispersive X-Ray diffraction:

Morphology of the synthesized adsorbent is studied using JEOL-JSM–6490LV Scanning Electron Microscope (SEM). SEM images (**Fig-3**) of the synthesized molecule shows a rough, agglomerated surface with average particle size ranging around 40-80nm.

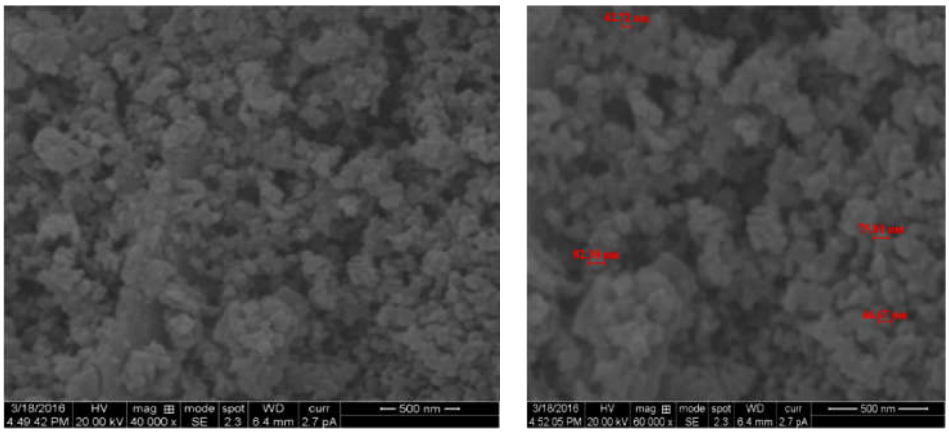

Fig-3: SEM images of $AlPO_4$- tridymit

BET analysis:

BET analysis carried to evaluate surface properties, pore volume, pore diameter using NOVA-1000, VERSION=3.70 instrument and Nitrogen adsorption desorption experiments were carried out. Adsorbent is first degassed at 400°C for 4 hours. It is then subjected to Nitrogen gas adsorption desorption experiments. The results show that total surface area of the zeolite is 16.05m^2/g, average pore diameter was found to be 90.05Å and pore volume was found to be 3.585m^2/g [21].

Effect of contact time and initial dye concentration:

Initial concentration has been found to have negligible effect on adsorption process as can be seen in **fig-4**. Adsorption reaches equilibrium with in first 20 minutes irrespective of the initial dye concentrations. Adsorption is fast in the initial stages of the reaction as the availability of adsorption sites will be maximum almost 70-80% of adsorption is complete within the first 10 minutes.

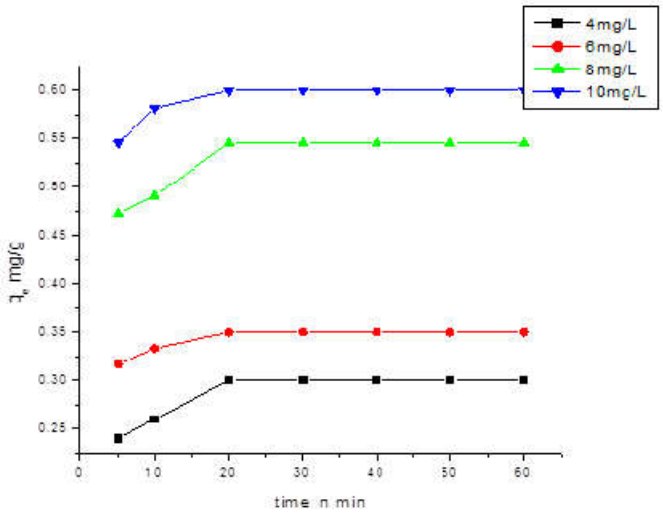

Fig-4: Effect of contact time and initial dye concentration on adsorption

Effect of pH:

One of the key factors that have enormous effect on the process of adsorption is pH of the solution. Higher conditions such as pH 2, pH 12 and pH 14 were found to degrade the molecule and adsorption was found to be maximum at pH -5 as given in **fig-5.**

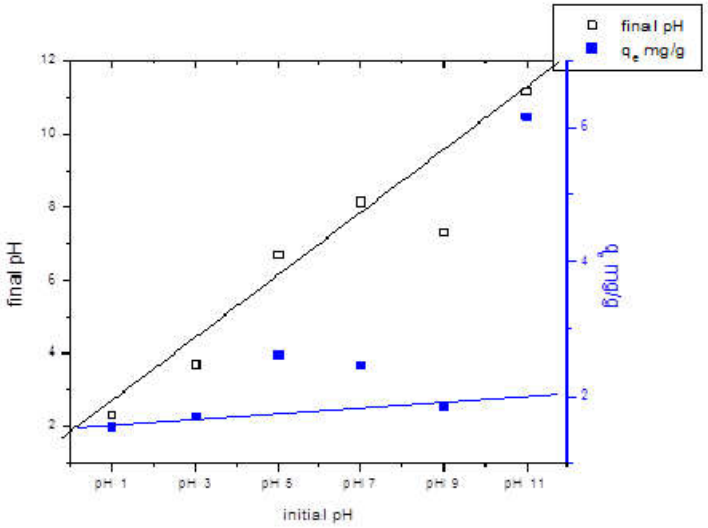

Fig-5: Effect of pH on adsorption

Effect of adsorbent Dosage:

Effect of adsorbent dosage on adsorption is given in **fig-6**. It can be understood from the graph that adsorption efficiency is high at lower dosages. Efficiency of adsorption decreases with increasing adsorbent conditions. Adsorption being surface phenomenon increasing dosage results in agglomeration of molecules which would reduce the available surface area and number of open pores will reduce hence resulting in adsorption efficiency.

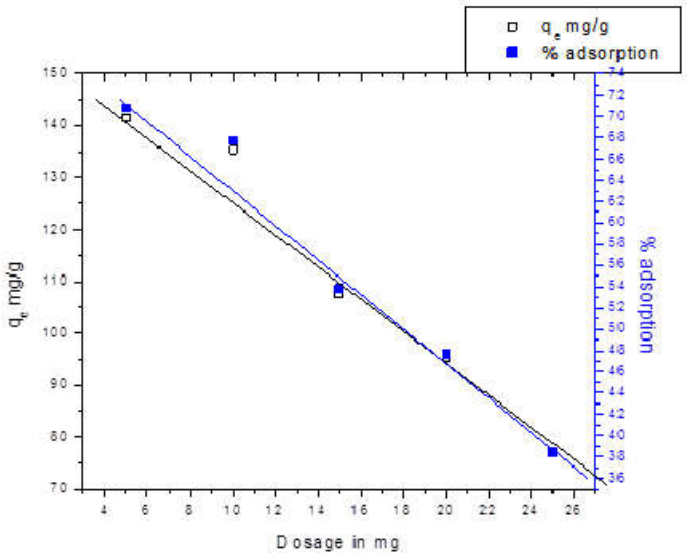

Fig-6: Effect of adsorbent dosage

Adsorption kinetics:

The behavior of the batch sorption process at different initial dye concentrations was analyzed using lagergren pseudo-first order kinetic model and Ho Mc Kay's pseudo second order model. A graph of t/q_t vs time in minutes gives a straight line graph with respect to all initial dye concentrations **(fig 7)** with a calculated correlation coefficient value 0.99 confirms that the adsorption process follows pseudo second order mechanism. Parameters for different kinetic models are as given in Table 1. Average K value for pseudo second order model was found to be 4.0247 x 10^{-3} mg g^{-1} min^{-1}.

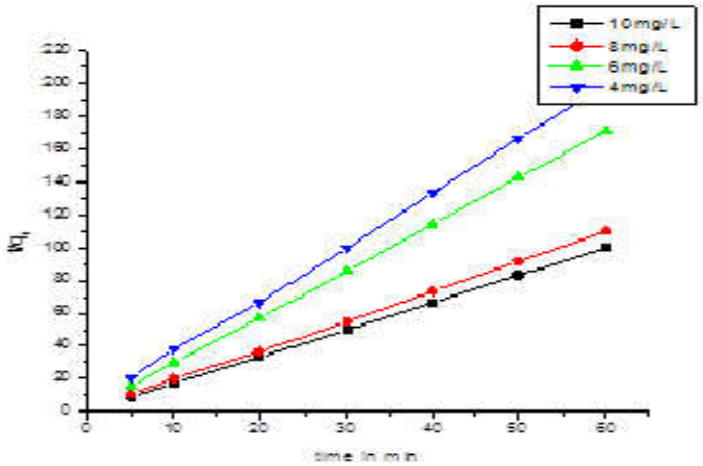

Fig-7: Plot of t/q_t vs time in min for pseudo bi molecular reaction

Table 1: Kinetic constantans for adsorption of methylene blue onto ZB2h:

Initial dye concentration	Pseudo first order		Pseudo second order	
	K_1	R_1^2	K_2	R_2^2
4mg/L	0.1372	0.591	6.4328	0.9995
6mg/L	0.1644	0.583	2.6902	0.9999
8mg/L	0.1278	0.593	2.2505	0.9998
10mg/L	0.1579	0.5809	4.7255	1

Adsorption Isotherms:

Parameters for different isotherms are as given in table 2. From the parameters it is evident that methylene blue forms a monolayer on the surface of adsorbate. Freundlich's Isotherm, Temkin isotherm, Harkins- Jura isotherm and Halsey isotherms can be used to explain the adsorption phenomenon. Harkins –Jura isotherms have highest R2 values.

Table 2: Equilibrium Isotherm parameters for adsorption of methylene blue onto ZB2h

Isotherms	Langmuir's Isotherm		Freundlich's isotherm		Temkin's Isotherm		Harkins –Jura isotherm		Halsey Isothem		Redlich-peterson isotherm	
Parameters	b_o	1.0816	1/n	0.7462	K_T	0.7939	A	0.1971	N	-0.2353	β_{bR}	1.7211
	Q_o	1.7969	K_f	0.9324	b_T	-0.8756	B	0.0552	K	3.2772	R^2	0.4716
	R^2	0.3216	R^2	0.882	R^2	0.842	R^2	0.9159	R^2	0.8832		

CONCLUSIONS

From this study the ability of Aluminophosphate zeolite $AlPO_4$- tridymit synthesized by microwave irradiation to remove of methylene blue was investigated. Adsorption efficiency was high with lower dosages of adsorbents and initial dye concentration was found to have negligible effect on adsorption phenomenon. Adsorption was maximum at pH 5 and Adsorption reaction was found to follow pseudo second order kinetics. Equilibrium isotherm follows Haarkin –Jura isotherm suggesting that adsorption of methylene blue onto $AlPO_4$- tridymit is a physical phenomenon.

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