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ADSORPTIVE REMOVAL OF METHYLENE BLUE FROM WASTEWATER USING ZEOLITE-IRON OXIDE MAGNETIC NANOCOMPOSITE

M.K.Dwivedi[1], Rashmi Agrawal[2], Pragati Sharma[3]

[1, 2, 3]*Department of Chemistry, Govt.(Autonomous) Holkar Science College Indore (MP)India)*

ABSTRACT

Zeolite synthesized from coal fly ash was mixed with magnetite nanoparticles in suspension to produce Zeolite-iron oxide magnetic nanocomposite and was used for the removal of methylene blue from aqueous solution. Batch study revealed that the adsorption of methylene blue was strongly pH dependent, and maximum methylene blue removal was found to occur at equilibrium pH of 8. Optimum adsorbent dose, contact time and temperature were found 5g/L, 15 minutes and 30^{0}C respectively. Initial methylene blue concentration was also investigated as a function of methylene blue removal efficiency of adsorbent. The Langmuir and Freundlich isotherm models were tested for their applicability but the former isotherm fitted the data better. According to Langmuir isotherm maximum adsorption capacity is 4.93 mg/g.

Keywords: Nanocomposite, adsorption, methylene blue

I. INTRODUCTION

Water pollution is a very burning problem not only in India but all over the world. Due to industrialization and urbanization it is increasing leaps and bounds. Most of the industries such as paper, printing, textile, food, cosmetics use dyes to colour the product synthesize in the particular industry.

Dyes are highly coloured polymers and low biodegradable. Dyes being one of the important recalcitrant, permit for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolve oxygen and also decrease the recreation value of stream [1].

Several physicochemical methods i.e. coagulation and flocculation, oxidation or ozonation and membrane separationhave been proposed to treat contaminated water containing dyes. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used [2].A number of agricultural and industrial waste havebeen studied for their capacity to remove dyes from aqueous solutions, such as rice husk[3],flyash [4], sludge[5],flower waste[6], zeolite [7], bottom ash[8], clay[9], graphene composite [10].

The application of nanomaterials to solve the environmental problem has received the great attention in current years. Magnetic composites can be used to adsorb contaminants from aqueous or gaseous effluents and after adsorption can be separated from the medium by a simple magnetic process [11] .Commercially available magnetic material are rather expensive and cannot be used for large scale processes. Materials obtained from magnetic modification of low cost adsorbents have many environmental applications.

Zeolite synthesized from coal fly ash has been found as a good material for nanoparticles support and hosting [12,13].Zeolite from coal fly ash –iron oxide nanocomposite was used as an adsorbent for the removal of anionic dyes and heavy metal ions from aqueous solution [14,15].

The purpose of this study is to know the feasibility of magnetic nanocomposite material for the removal of methylene blue from water. Nanocomposite material was obtained by mixing magnetite nanoparticles in suspension with zeolite synthesised from coal fly ash. Batch experiments were designed for the sorption process and the effects of temperature, pH value, initial concentrations of methylene blue and adsorbent dosages on adsorption were evaluated. The optimum condition was also discussed for methylene blue removal.

II. MATERIALS AND METHODS

Coal fly ash that was collected from H.E.G. Thermal Power Station, Mandideep (Bhopal). Methylene blue of Anal grade supplied by Merck, India used as an adsorbate.

The stock solution was prepared in deionized water. The standard calibration curve of known concentrations of methylene blue was plotted by finding out the absorbance at the characteristic wavelength of λmax665 nm.

2.1 Preparation of Zeolite from Fly Ash:

Hydrothermal treatment method was used to convert coal fly ash for zeolite synthesis. 20 g of fly ash was heated to 100^{o}C in an oven for 24 h with 160 ml of 3.5 mol L^{-1}NaOH solution. It was repeatedly washed with deionized water till the pH reached to 11 and dried at 50^{o}C for12 h [16].

2.2 Preparation of Magnetic Nanocomposite from Zeolite:

In the first step, magnetite particles were prepared by adding of 2 M NaOH solution drop by drop in a 100ml solution of ferrous sulfate (1.8 g) with agitation until the pH reached 11. The slurry was heated on a water bath. After that, the magnetite was washed with distilled water and dried at room temperature. Magnetite particles were redispersed in aqueous solution and zeolite synthesized from fly ash was added slowly with agitation. The obtained zeolite from fly ash-iron oxide magnetic composite was washed with distilled water, dried at room temperature and milled.

2.3 Adsorption Studies

The adsorption was performed using the batch method. The equilibrium adsorption uptake and percentage removal of methylene blue from the aqueous solution q_e (mg/g) was calculated using the following relationship:

Amount adsorbed $q_e = \frac{(Co-Ce)V}{W}$ (mgg^{-1}) …………(1)

% removal $q_e = \frac{100\,(Co-Ce)}{Co}$ …......… (2)

Where C_o is initial adsorbate concentration (mg L^{-1}),Ce is equilibrium adsorbate concentration (mg L^{-1}),V is the volume of solution (L), W is the mass of adsorbent (g).

2.4 Adsorption Isotherms

The equilibrium data obtained in the present study were analyzed using Langmuir and Freundlich isotherm models. The rearranged Langmuir and Freundlich isotherm equations can be described as:

$1/q_e = 1/q_m + (1/bq_m)(1/c_e)$ .... (3)

$\log q_e = \log K_f + \frac{1}{n} \text{Log } Ce$ . ... (4)

Where q_m and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively .K_f is a freundlich constant related to the adsorption capacity (mg/g) and n is an empirical constant.

III. RESULTS AND DISCUSSION

3.1Characerization of adsorbent

3.11 XRF Analysis:

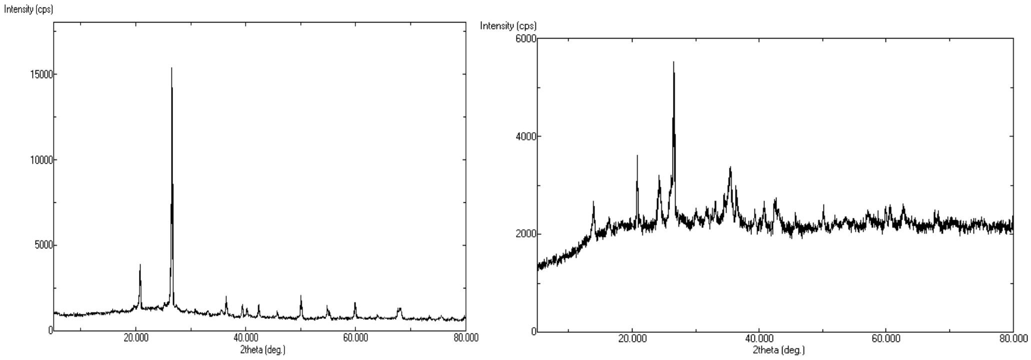
The chemical composition of coal fly ash determined by X-ray fluorescence spectrometer is shown in Table 1. The result shows that the mineralogy of this CFA is very rich and it is class F fly ash. The sum of SiO_2, Al_2O_3 and Fe_2O_3 content in the CFA was found to be greater than 70%, while its CaO content was lower than 5%. Minor elements within the CFA were also identified by the XRF and the results reveal that trace elements like Sc, Ni, Cu, Sr, Rb, Zr, Nb are also present.

Table 1:Chemical constituents of the fly ash

Constituents	Weight %	Constituents	Weight %
SiO_2	55.26	V_2O_5	0.11
Al_2O_3	22.75	BaO	0.08
Fe_2O_3	7.12	MnO	0.08
CaO	4.10	Sc_2O_3	0.05
TiO_2	2.95	SrO	0.04
K_2O	2.14	ZnO	0.04
P_2O_5	1.65	NiO	0.03
SO_3	1.58	RbO_2	0.02
Na_2O	1.23	CuO	0.02
MgO	0.63	Nb_2O	0.01
ZrO_2	0.11		

3.12 XRD analysis

The identification of the mineralogical constituents and phase properties of nanocomposite was examined by X-ray diffracter on a model Bruker D-8 advance X-ray diffractometer and is shown in fig. 2.



(a) (b)

Fig. 2 X-ray diffraction pattern of (a) CFA and (b)nanocomposite

It can be observed from fig. 2 that the nanocomposite consists mostly of mullite, quartz, a small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO_2). The intensity of quartz is very strong with mullite forming a chemically stable and dense glassy surface layer. XRD pattern of nanocomposite material illustrates the incorporation of magnetite in zeolite structure.

3.2 Batch Studies

3.2.1 Effect of contact time

The Influence of contact time was studied at methylene blue concentrations of 4 and 8 ppm with a fixed adsorbent dose of 5 g/l at 30$\pm$1^{o}C at natural pH 6.7.From the Fig.3 it is clear that adsorption of methylene blue uptake was found to occur in the first rapid phase (15 min) and thereafter the adsorption rate was found to decrease. It is also observed that at higher concentration of Methylene Blue (8 mg/l), the absorption efficiency is high (80.5 %) as compare to the maximum efficiency of 74.25% for 4 mg/l after 15min of contact time. The higher adsorption rate may be due to an increased number of vacant sites on the adsorbent available at the initial stage.

3.2.2 Influence of pH:

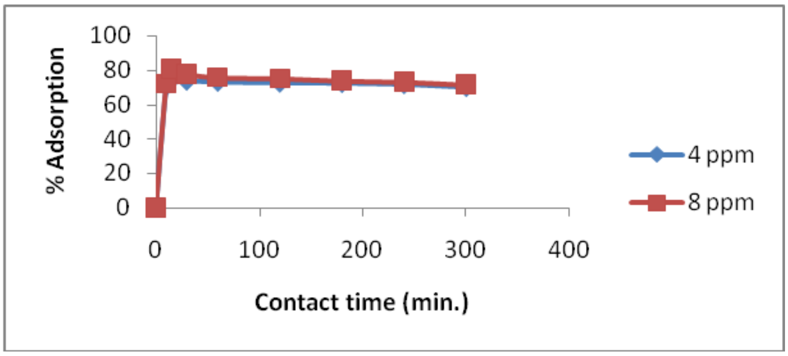


Fig. 3 Effect of contact time

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The effect of pH on the adsorption of methylene blue was evaluated at 30^{o}C at different pH values in the range of 2–10. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH. Fig.4 suggests that adsorbed amount decreased with increasing pH value, an appreciable amount of adsorption occurred at pH 8.

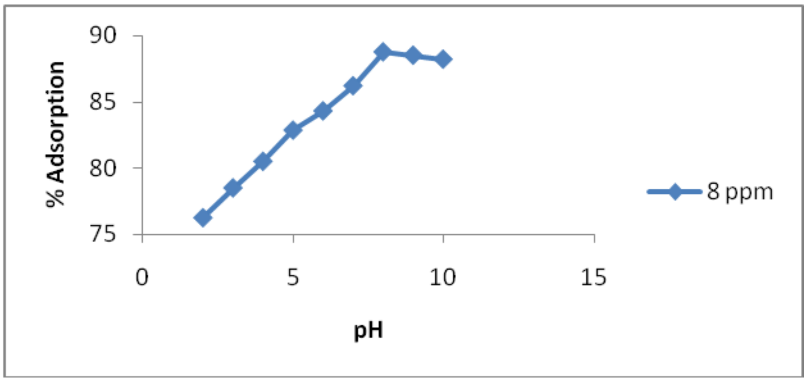


Fig. 4 Influence of pH

3.2.3 Influence of adsorbent dosage

In order to investigate the effect of mass of adsorbent on the adsorption of methylene blue, a series of adsorption experiments was carried out with different adsorbent dosage at an initial methylene blue concentration of 8 ppm. Fig. 5 shows the effect of adsorbent dosage on the removal of methylene blue.

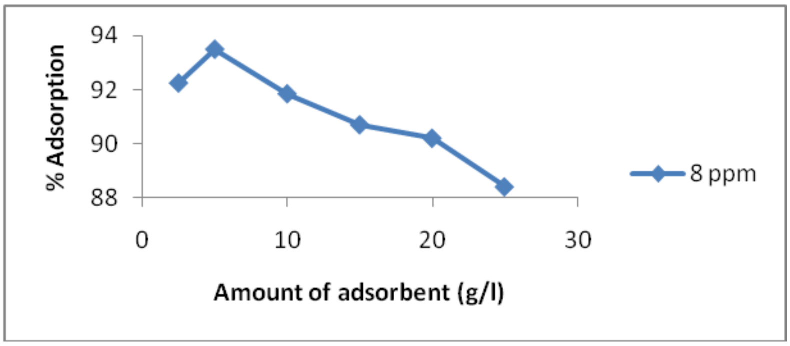


Fig. 5 Influence of adsorbent dosage

The percentage removal of methylene blue increased with the increase in adsorbent initially from 0.05 to 0.1 g. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. With the increase in the amount of adsorbent, the sites for adsorption increase initially. But on increasing it further the adsorption efficiency is reduced. It may be due to the overcrowding of adsorbate molecules which prevent the diffusion through the actual adsorption sites.

3.2.4 Influence of initial concentration and temperature

The effect of initial concentration and temperature on the removal efficiency was investigated in the temperature of 30^0,40^0 and 50^0C. The experiments were carried out with fixed adsorbent dose of 5 g/l of nanocomposite and initial methylene blue concentration of 8 ppm at pH 8.0.Results indicating that methylene blue uptake were favoured at lower temperature (fig.6). The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

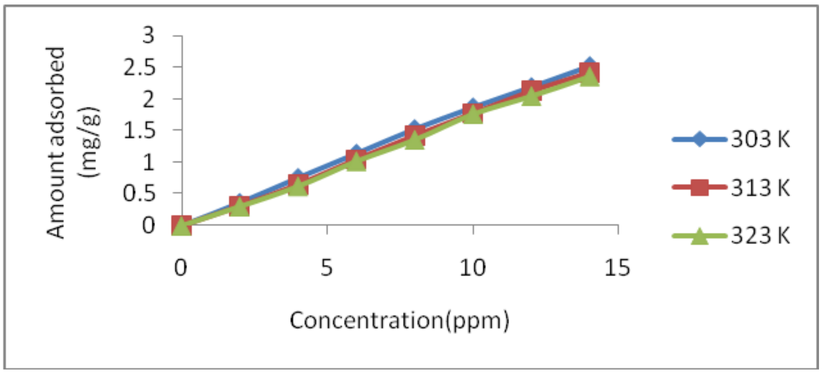


Fig. 6 Influence of initial concentration and temperature

3.2.5 Adsorption Isotherms

Langmuir and freundlich isotherm models have been used to evaluate the adsorption data for Methylene blue. Langmuir isotherm is based on the assumption of uniform adsorption energy throughout the surface of the adsorbent. The experimental data on the uptake of Methylene blue at 30^0 c have been fitted in the rearranged Langmuir equation and the plot obtained is shown in fig.7which suggests the applicability of Langmuir adsorption model.

Freundlich isotherm has been used for determining the adsorption capacity of adsorbents. The plot of log qe against log Ce, shown in fig 8 is linear. The 1/n value is less than 1 which suggests the favourable adsorption of methylene blue onto adsorbent. The values of Langmuir and Freundlich constant are given in the Table2.The Langmuir isotherm was found to fits the experimental data better than the Freundlich isotherm.The best fit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of methylene blue onto adsorbent with the maximum sorption capacity as 4.9358 mg/g.

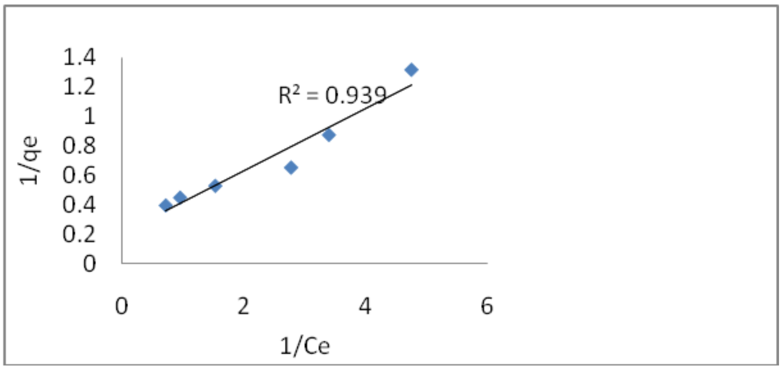


Fig. 7 Langmuir isotherm plot of Methylene blue at 303 K

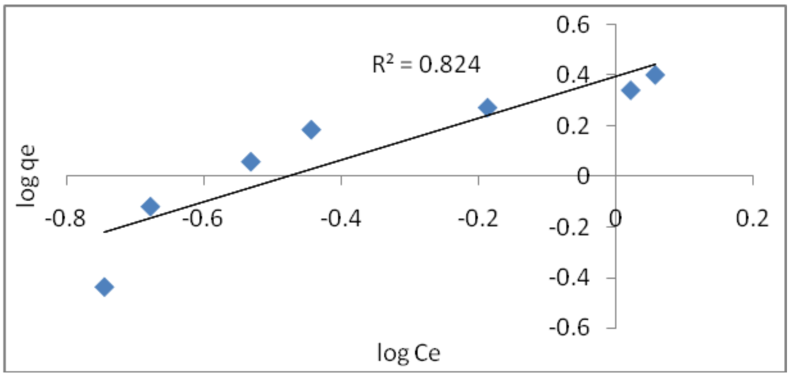


Fig. 8 Freundlich isotherm plot of Methylene blue at 303 K

Table 2:Freundlich and Langmuir isotherm parameters at 303 K

Freundlich parameters			Langmuir parameters		
K_f	1/n	R^2	Qm (mg/g)	b	R^2
2.4831	0.8269	0.8248	4.9358	0.9512	0.9399

IV. CONCLUSION

This study revealed that nanocomposite material prepared from coal fly ash can be successfully employed as adsorbent for the removal of Methylene Blue dye. The pH was found to be significant factor which affects the adsorption capacity of Methylene Blue. The removal of Methylene Blue, a cataionic dye is about 95.5 % at 8mg/l with a dose of adsorbent of 5 g/l and pH 8.0 at 303 K. The optimum contact time was found to be 15 min. The adsorption process was found to be exothermic in nature. The adsorption data was analyzed by Langmuir and Freundlich models and fitted well. The fitness of Langmuir isotherm model suggested a monolayer adsorption of methylene Blue on the surface of adsorbent.

V. ACKNOWLEDGMENT

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