Removal of Malachite Green from Aqueous Solution by Zeolite-Iron Oxide Magnetic Nanocomposite

Neeraj Jain[1*], M.K. Dwivedi[2], Rashmi Agarwal[3] and Pragati Sharma[4]
[1]CSIR-Central Building Research Institute, Roorkee-247667, U.K., India
[2-4]Department of Chemistry, Govt. Holkar Science College, Indore-452001, M.P., India

Abstract: *Discharge of dye effluents into the natural streams may be toxic to the aquatic lives as well as human being. In the present studies, zeolite was synthesized from coal fly ash by alkaline hydrothermal treatment and mixed with magnetite nanoparticles in suspension to produce zeolite-iron oxide magnetic nanocomposite. It was used as adsorbent for the removal of malachite green dye from aqueous solution. Magnetite nanoparticles in suspension were synthesized by precipitating iron ions in a NaOH solution. The morphology of nanocomposite was characterized by XRD, EDX and SEM. The effect of various experimental parameters such as contact time, pH, adsorbent dose and temperature were investigated. Batch study revealed that the adsorption of malachite green (MG) was strongly pH dependent and maximum dye removal was found to occur at an equilibrium pH of 8.0. Optimum adsorbent dose, contact time and temperature were found 5 g/l, 60 minutes and 303 K respectively. Effect of varying initial malachite green concentration was also investigated to study the removal efficiency of adsorbent. Kinetic studies were performed to have an idea of the mechanistic aspects and to obtain the thermodynamic parameters of the process. The adsorption of malachite green onto nanocomposite followed pseudo-first-order kinetics. Adsorption data were also correlated with both Langmuir and Freundlich isotherm models. Results indicated that according to the Langmuir and Freundlich isotherms, the maximum sorption capacities are 21.05 and 5.01 mg·g/1 for malachite green respectively. Thermodynamic parameters ΔG^o, ΔH^o and ΔS^o were calculated as -3.1913 kJ/mol, -14.13 kJ/mol and -0.038 kJ/mol/K respectively indicating that process of adsorption is exothermic and spontaneous in nature. The results indicated that zeolite from fly ash-iron oxide magnetic nanocomposite, was a potential adsorbent for field application in removal of contaminants from aqueous solution.*

***Keywords:*** *Adsorption, nanocomposite, malachite green, fly ash, zeolite, kinetic, Langmuir, Freundlich*

I.   Introduction

A growing number of organic and inorganic pollutants in water system are being identified as potentially harmful to health of aquatic life and human beings. Among the different pollutants of aquatic system, dyes are a large and important group of industrial chemicals. Dyes are used in almost every industry from textile to food industries to colour their products. Disposal of dyeing industry wastewater pose one of the major problems, because such effluents contain number of contaminants, odour and colour. Out of these, colour is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents. Further, dyes are non biodegradable due to their complex molecular structures making them more stable and hard to biodegrade [1-2]. Possible methods of colour removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Among these, adsorption currently appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste tyres, baggasse, blast furnace slag, fly ash, zeolites and lignin to agricultural products such as wool, rice husk, coconut husk, saw dust, peat moss etc. [3-12]. A number of low-cost adsorbents such as activated carbon prepared from various wastes [13-16], diatomaceous earth [17], industrial waste products [18], bagasse fly ash [19], clay mineral [20], biodegradable waste [21], hydrotalcite [22], coffee grounds [23], metal hydroxide sludge [24], agricultural waste [25], dolomitic sorbents [26], charcoal from extracted residue of coffee beans [27], bentonite and polyaluminum hydroxide [28] have been studied for adsorption of different dyes from solutions.

Adsorption of dyes by zeolites has evolved into one of the most effective physical process for the decolorization of textile wastewater. Although the adsorption of dyes over zeolite has been extensively investigated [29-31], only a few studies have been reported on adsorption of dye onto fly ash based zeolite [32-35]. The adsorbents combining magnetic separation technology with adsorption process have been widely used in environmental purification [36-38]. Zeolite from fly ash/iron oxide composites were used as adsorbents for the removal of metal ions of Zn^{2+}, Cd^{2+} and Pb^{2+} from water [39-43].

Malachite green (MG) is a water soluble basic triphenylmethane dye which is used to colour the material like silk, wool, jute, leather, cotton, paper and other industries. In aquaculture, it acts as an anti-fungal, anti-bacterial and antiparasitical agent. It has been classified as Class II health hazard, but is still used in some countries because of its low cost. It is difficult to biodegrade and removes it from water. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, and respiratory toxicity [43].
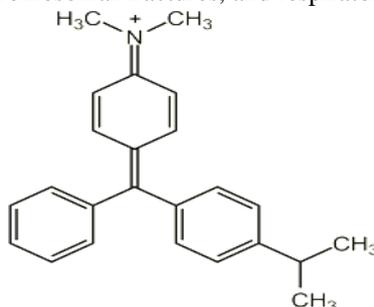
Scheme 1: Structural formula of Malachite Green

The objective of this study was to assess the feasibility of using zeolite-iron oxide magnetic nanocomposite for removing malachite green dye from aqueous solutions. Nanocomposite material was obtained by mixing magnetite nanoparticles in suspension with zeolite synthesized from coal fly ash. The adsorption studies such as effect of contact time, pH, adsorbent dose, initial concentration and temperature were explored in batch experiments. The adsorption isotherm and kinetic analysis studies were used to elucidate the adsorption mechanism.

II.   Materials and Methods

2.1 Materials
Coal fly ash was collected from H.E.G. Thermal Power Station, Mandideep (India). Sieved fly ash (100 mesh down) was used without any pretreatment. Malachite green (MG) of analytical grade supplied by Merck, India was used as an adsorbate. The stock solution (1 g/l) was prepared in deionized water. The standard calibration curve of known concentrations of malachite green was plotted by finding out the absorbance at the characteristic wavelength of λ_{max} at 620 nm.

2.2 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 NaOH solution. The zeolitic material was repeatedly washed with deionized water until pH 11 and dried at $50^{o}C$ for 12 h [22].

2.3 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 zeolite/magnetite ratio was 3:1 (w/w). The obtained zeolite from fly ash-iron oxide magnetic composite was washed with distilled water, dried at room temperature, milled and used as adsorbent for malachite green [41]**.**

2.4 Characterization of fly ash and zeolite-magnetite nanocomposite
The pH measurements were made using a pH meter (model CT Cl-46, Toshniwal Instruments, Delhi, India). The chemical constituents of fly ash were analyzed using Bruker S-8 Tiger WDXRF. The surface area was measured with a model QS-7 Quantasorb surface area analyzer. The specific gravity was determined using specific gravity bottles. The Scanning Electron Microscopy (SEM) was carried out using model LEO 438 VP, UK to study micro structure and qualitative characteristics of the ash of the fly ash. The identification of the mineralogical constituents and phase properties of fly ash was examined by Bruker D-8 advance X-ray diffractometer with a Cu-anode. The diffractometer was operated at 40 kV and 40 mA for 1 h over the range of 2θ from 0° to 80°. The infrared spectrum of the adsorbent was recorded in potassium bromide and Nujol mull in the range of 500-4000 cm^{-1} using a Perkin Elmer spectrophotometer. All color measurements were made on a Spectronic 20D+ Thermospectronic spectrophotometer in the visible range at 620 nm in absorbance mode.

2.4 Sorption procedure

Adsorption of malachite green was carried out by a batch technique in aqueous suspensions using zeolite-magnetite nanocomposite as adsorbent and experiments were conducted to observe the effect of various parameters such as pH, temperature, amount of adsorbent, initial adsorbate concentration, and contact time. Adsorption isotherms were recorded at equilibrium conditions for concentration of dyes over the range 10-90 mg/l at a fixed pH (8.0) and temperature (303 K). The selected concentration range was ascertained after a good deal of preliminary examination. Adsorption study was made in a mechanically agitated 100-ml Erlenmeyer flask filled with 20 ml of dye solution of desired concentration along with a known amount of adsorbent. When the equilibrium was thought to be established, supernatant was carefully filtered through Whatmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at λ_{max} of 620 nm. Stock solution of due was diluted to the required volume and concentration. The experiments were performed in duplicate and the average results were reported. The amount of dye adsorbed at time t, q_t (mg/g), was obtained by calculating the difference between the initial and the final malachite green concentration as shown in equation 1:

$$q_e = (C_0-C_e) \times V/W \tag{1}$$

Where q_e (mg/g) is the amount of dyes adsorbed, and C_0 (mg/l) is the initial dye concentration, while C_e (mg/l) is the concentration of dye in solution at equilibrium, V (L) is the volume, and W (g) is the weight of adsorbent. The percentage removal of the dye was computed using the following equation

$$\text{Percentage of removal (\%)} = (C_i-C_e) \times 100/Ci \tag{2}$$

Where C_i and C_e are the initial and equilibrium concentration of dye (mg/l) in solution.

2.5 Adsorption isotherms

The adsorption equilibrium models often provide insight into the sorption mechanism, surface properties and affinity of adsorbent. The most commonly used equilibrium models are Langmuir and Freundlich isotherms [44].

Langmuir isotherm is based on the assumption that maximum adsorption corresponds a saturated moonolayer of solute on homogenous adsorbent surface. It comprised of a finite number of identical sites with homogeneous adsorption energy. A basic assumption states takes sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further transmigration can take place at the same site. The total monolayer capacity of the adsorbent is equal to Q_o, a Langmuir constant. The rearranged Langmuir isotherm is represented by following equation:

$$C_e/q_e = 1/ Q_o \, b + C_e/ Q_o \tag{3}$$

where, C_e is the equilibrium concentration of dye (mg/l), q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_o is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption. Hence, a plot of C_e/q_e versus C_e yields a straight line with Q_o calculated from the slope and the value of b as its intercept.

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface or surface supporting sites of varied affinities it. Due to variation of interactions between the adsorbed molecules sites with of stronger affinity are occupied first, and in this way multilayer setting of adsorbate molecules takes place. The validity of the Freundlich isotherm model was proved by using following relation: Freundlich isotherm is an exponential equation and can be written as:

$$q_e = K_F \, C_e^{1/n} \tag{4}$$
$$\log q_e = \log K_F + 1/n \log (C_e) \tag{5}$$

where, K_F is the constant indicative of the relative adsorption capacity of the adsorbent (m/g), and 1/n is the constant indicative of the intensity of the adsorption.

2.6 Thermodynamic Studies

Linearized Van't Hoff equations (Eqs. 6 and 7), were used to calculate the thermodynamic parameters such as Gibbs's free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) during the process.

$$\log K_c = \Delta S^o/2.303 \, R - \Delta H^o/2.303 \, RT \tag{6}$$
$$\Delta G^o = -RT \log K_c \tag{7}$$

Where K_c is equilibrium constant (amount of adsorbate in adsorbent/amount of adsorbate in solution)

2.7 Kinetic studies

Intraparticle diffusion is the most common technique used for identifying the mechanism involved in adsorption process. In order to investigate the mechanism of the malachite green adsorption onto fly ash based nanocomposite, intraparticle diffusion based mechanism was studied. Kinetic studies were carried out in batch at 60 mg/l of initial dye concentration with a fixed dose of adsorbent dose of 5 g/l at 303 K and pH 8.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to fly ash, K_{ad} has been studied using the Lagergren first order rate equation:

$$\log (q_e - q_t) = \log qe - K_{ad} \, t \, / \, 2.303 \tag{8}$$

where, q_e is the amount of dye adsorbed at equilibrium, and q_t is the amount of dye adsorbed at time t (both in mg/g).

III. Results and Discussion

3.1 Characterization of fly ash

The chemical composition of fly ash determined by WDXRF has been shown in Table 1 which depicts that the major constituent of the fly ash is SiO_2, (55.26 %) followed by Al_2O_3 (22.75 %), Fe_2O_3 (7.12 %), CaO (4.10 %) and MgO (0.63 %). The fly ash predominantly consists of trace metals with the chief constituents being oxides, silicates and aluminosilicates of calcium, iron and other bases. These oxides have a tendency to form metal hydroxide complexes in the solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to the development of a positive or negative charge on the surface. The surface area of fly ash is 2.89 m^2/g and specific gravity is 2.2 g/cm^3.

Table 1: Chemical constituents of the fly ash

Constituents	Weight %
SiO_2	55.26
Al_2O_3	22.75
Fe_2O_3	7.12
CaO	4.10
TiO_2	2.95
K_2O	2.14
P_2O_5	1.65
SO_3	1.58
Na_2O	1.23
MgO	0.63
LOI	4.10

The results of SEM investigation of coal fly ash and nanocomposite are shown in Fig. 1 which reveals typical fly ash morphology and surface texture. Most of the particles present in the fly ash are sub-angular and spherical in shape. The image also reveals that the particles present in the fly ash are covered with relatively smooth grains of quartz, clusters of iron (Fe-oxide). Irregular surface of glass matrix is observed which may be responsible for an increase in adsorbent pore volume.
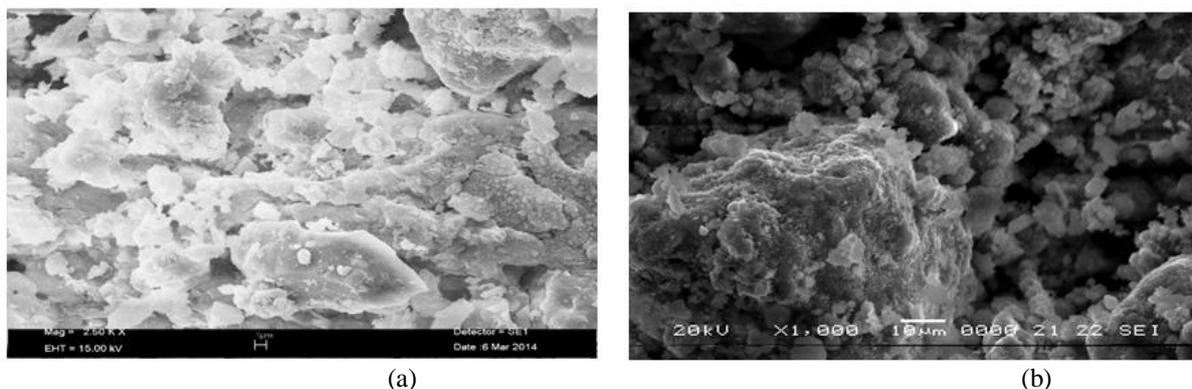

(a)   (b)
Fig. 1: SEM image of (a) Coal fly ash and (b) zeolite-iron oxide Nanocomposite

The diffractogram (Figure 2) shows the X-ray diffraction pattern of fly ash (Fig. 2a) for particle size $\leq$ 45 μm. It is observed that the fly ash consists mostly of mullite, quartz, hematite and 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. The low calcium oxide intensity is characteristic of low-Ca Class-F fly ash. XRD pattern of nanocomposite material illustrates the incorporation of magnetite in zeolite structure (Fig. 2b).
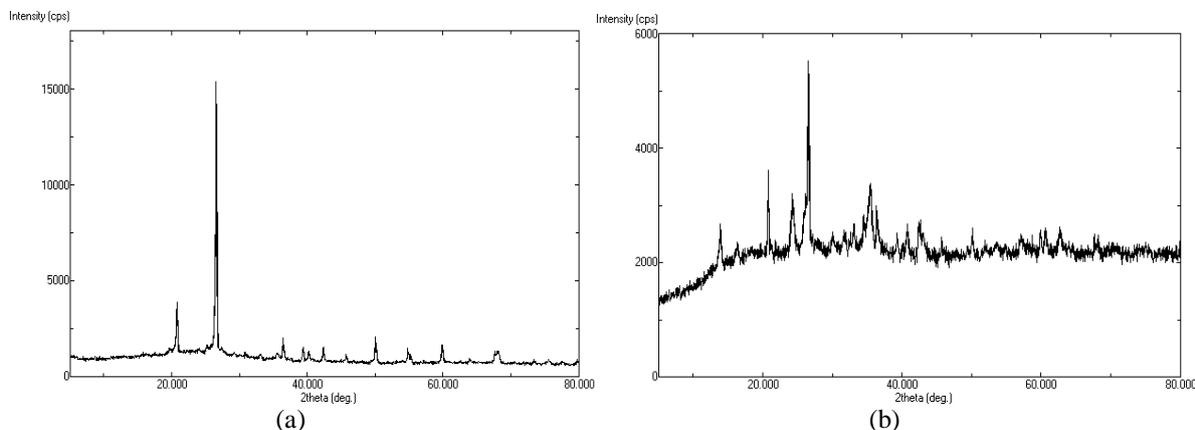
Fig. 2: X-ray diffraction pattern of (a) Coal fly ash and (b) nanocomposite

The infrared spectrum of fly ash (Fig. 3) shows broad and weak peaks in the region of 4000-500 cm^{-1} associated with the functional groups that are on the surface of coal fly ash. The band appearing at 560 cm^{-1} is associated with octahedral aluminium present in mullite. In addition, bands appearing between 800-600 cm^{-1} are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of alumino-silicate system. Band appearing at 2360 cm^{-1} could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at 800-1200 cm^{-1} and 450-550 cm^{-1} assign to asymmetric stretching mode and bending mode of T-O bond respectively. These bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibrations of $Si(Al)O_4$ groupings. Although some interference can be made about surface functional groups from IR spectra, the weak and broad bands do not provide any definitive information about the nature of the surface oxides. The data, however, indicate the presence of some surface groups on the adsorbent material.
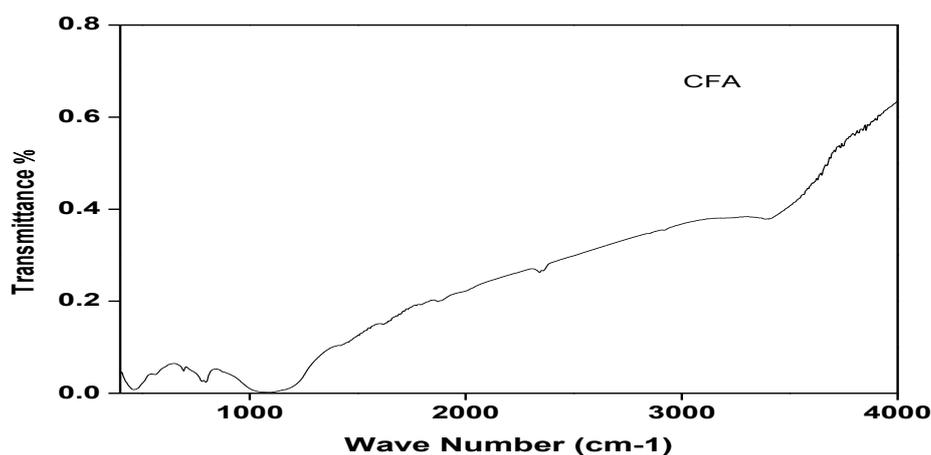
Fig.3: FTIR of coal fly ash

3.1 Effect of contact time

The effect of contact time was studied at malachite green concentrations of 60 and 80 mg/l with a fixed adsorbent dose of 5 g/l at 303 K and natural of pH of 3.7. The contact time was varied from 10 min to 300 min for both the concentrations studied and the percentage efficiency was calculated. The results of contact time on adsorption efficiency have been plotted in Fig. 4. A perusal of Fig. 4 indicates that the efficiency of dye adsorbed is rapid in initial stage up to 60 min and after that remains almost constant due to saturation of the active site which do not allow further adsorption to take place It is also observed that at higher concentration of

malachite green (80 mg/l), the adsorption efficiency is high (83.5 %) as compare to the maximum efficiency of 82.5 % for 60 mg/l after 60 min of contact time. The observed increase in the adsorption of dyestuffs with increasing concentration may be due to sufficient adsorption sites at adsorbent [45]. The optimal contact time to attain equilibrium was experimentally found to be about 60 min.
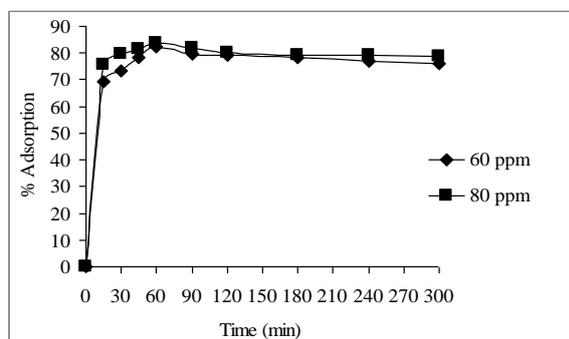

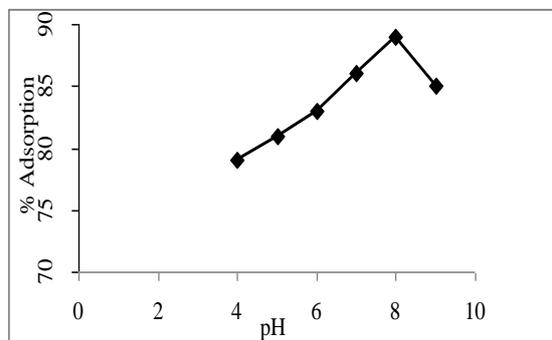**Fig. 4:** Effect of contact time on MG adsorption

Fig. 5: Effect of pH on MG adsorption

3.2 Effect of pH

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The studies were conducted at a fixed concentration of adsorbate (80 mg/l), contact time (60 min) and adsorbent dose 5 g/l at 303 K. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH and the change in adsorption of the dye was studied over a pH range of 4-9. The results obtained are presented in Fig. 5, which show that adsorption of malachite green increases with increase in pH from 4.0 to 8.0 and on further increase in pH the solution become colourless. Malachite green (Pk_a = 10.3) becomes protonated in the acidic medium and deprotonation takes place at higher pH. Consequently, the positive charge density would be more on dye molecules at low pH and these accounts for the higher uptake on the negatively charged surface for adsorbent.

3.3 Effect of adsorbent dose

In order to investigate the effect of mass of adsorbent on the adsorption of malachite green, a series of adsorption experiments was carried with different adsorbent dosage varied from 2.5 to 25 g/l at an initial dye concentration of 80 mg/l at natural pH of 8.0 and temperature 303 K. The contact time was kept 60 min and the results are shown in Fig. 6. It is observed that the percentage removal efficiency of malachite green increases initially with increase in adsorbent dose from 2.5 to 5 g/l and after that a decrease has been observed. The maximum efficiency at a dose of 5 g/l is 90%. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in adsorbent dosage. The decrease in efficiency at higher adsorbent dose may be attributed to the overcrowding of adsorbate molecules which prevent the diffusion through the actual adsorption sites.
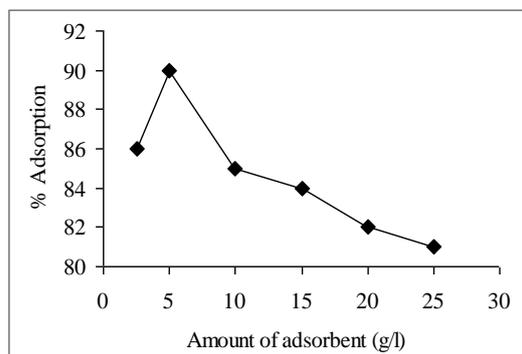

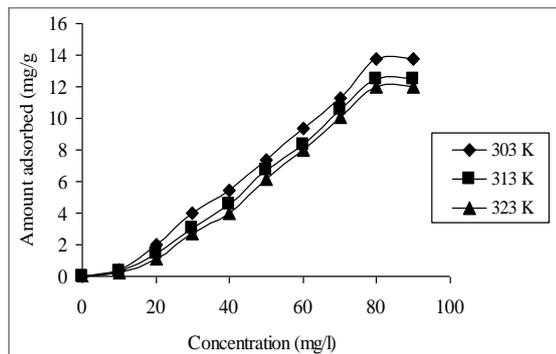**Fig. 6:** Effect of adsorbent dosage on MG adsorption

Fig. 7: Effect of temperature on MG adsorption

3.4 Effect of temperature and initial concentration

The effect of initial concentration of malachite green between the ranges of 10 to 90 mg/l was carried out to observe the absorption efficiency at various temperatures ranges from 303 K to 323 K with fixed adsorbent dosage (5 g/l) and 9.0. The contact time was kept 60 min. The results of the studies are shown in Fig. 7 which depicts that dye uptake increases with increase in initial malachite green concentration from 10 to 80 mg/l and thereafter equilibrium is achieved in dye uptake efficiency at 303, 313 and 323 K. However, the uptake

of dye was higher at 303 K with a dye uptake efficiency of 13.80 mg/g of adsorbent. The increment in sorption capacity may be due to the increase of dye concentration which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity. The rate of uptake of dye was found to be slightly decreased with increase in temperature, thereby indicating the process to be exothermic in nature. This decrease in adsorption efficiency on increase in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

3.5 Adsorption Isotherms
The results obtained on the adsorption of malachite green were analyzed by the well-known models given by Langmuir and Freundlich.

3.5.1 Langmuir isotherm
The adsorption of malachite green at equilibrium with increase in initial dye concentration at 303 K has been fitted in Langmuir model and Freundlich isotherms. In Langmuir isotherm, $1/q_e$ (mg/g) has been plotted against $1/C_e$ (mg/l) and a straight line with slope $1/bQ_o$ is obtained as shown in Fig. 8. A perusal of Fig. 8 shows that the adsorption of malachite green on iron oxide nanocomposite follows the Langmuir isotherm. Langmuir constants Q_o and b are calculated and the values of these constants are given in Table 2 along with coefficient of correlation (R^2). The maximum adsorption capacity (Q_o) was 21.05 mg/g.
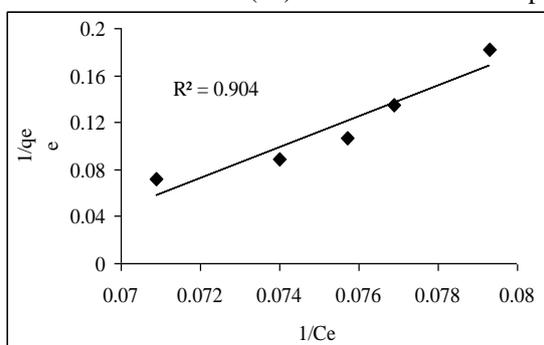

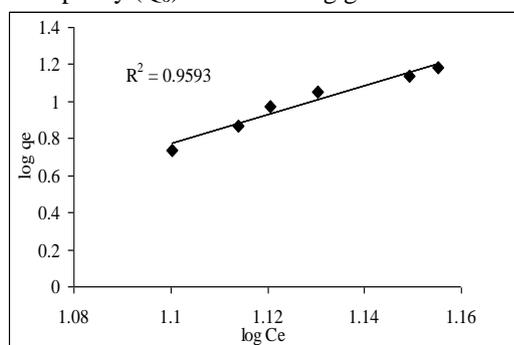**Fig. 8:** Langmuir isotherm plot of MG   **Fig.9:** Freundlich isotherm plot of MG

3.5.2 Freundlich isotherm
The equilibrium adsorption data has also been data fitted in the linear form of Freundlich isotherm model and the plots of log q_e against log C_e shown in Fig. 9 are linear. The values of K_F and n, calculated from intercept and slope of the plot (Figure 9), respectively, are given in Table 2. The values of n are less than 1, which suggest the favorable adsorption of dye onto the fly ash. The values of the regression coefficients indicate that the data satisfactorily follow both Langmuir and Freundlich models but the Langmuir isotherm fits the experimental data better.

Table 2: Freundlich and Langmuir isotherm parameters at 303 K

Freundlich parameters			Langmuir parameters		
K_f (mg/g)	n	R^2	Q_m (mg/g)	b	R^2
5.01	0.1283	0.959	21.05	0.0036	0.904

3.6 Thermodynamic Studies
The values of ΔH^o and ΔS^o were calculated from the slope and intercept respectively of the plot log K_c versus $1/T$. These values were used to calculate value of ΔG^o according to Eqs. 7 and 8. The results are summarized in Table 3. Negative values of ΔGo, ΔH^o and ΔS^o are indicative of feasible, exothermic and spontaneous nature of the process along with free diffusion of adsorbate molecules through bulk phase. Further the value of ΔS^o (<1) indicates that the process is highly reversible.

Table3: Thermodynamic parameters for the adsorption of malachite green on nanocomposite

ΔG^o (kJ/mole)	ΔH^o (kJ/mole)	ΔS^o (kJ/mole/K)
-3.19	-14.13	-0.038

3.7 Kinetic studies
The graph (Fig. 10) obtained for $\log(q_e - q_t)$ versus time (t) in minutes exhibits straight lines and confirm the adsorption process to follow first order rate kinetics in each case. The K_{ad} value calculated from slope of the plot ($K_{ad}/2.303$) is 0.0628 min^{-1}.
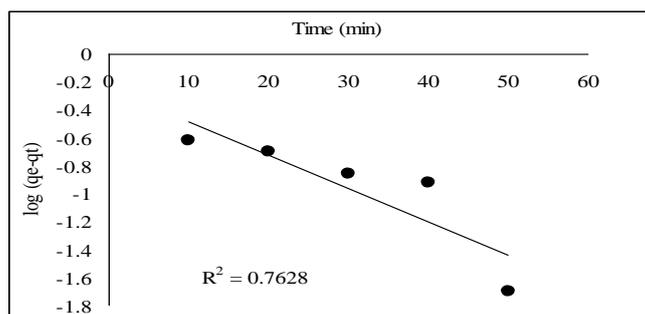
Fig.10: Lagergren plot for the removal of malachite green

IV.   Conclusions

A Zeolite-iron oxide magnetic nanocomposite was synthesized from fly ash based zeolite and iron oxide in suspension and used for the removal of malachite green dye. The prepared adsorbent proved to be more effective than other expensive adsorbents. The optimal contact time value obtained was 60 min and pH was 8. It was observed that dye removal efficiency decreased with increasing initial dye concentration as well as temperature at an optimal adsorbent dose of 5 g/l. The maximum dye removal efficiency was 13.8 mg/g for initial dye concentration of 80 mg/l and temperature 303 K. The adsorption process was of first order and exothermic in nature. The adsorption data was correlated with Langmuir and Freundlich isotherm models. The fitness of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. Thermodynamic parameters were calculated and indicated that each of these adsorption processes was spontaneous and exothermic in nature. The cost of synthesized zeolite was very low as compared to commercial zeolite available in the market as it was prepared from fly ash-a waste from thermal power station. Utilization of fly ash as zeolite for adsorption will solve not only its disposal problems and environmental hazards, but also help as potential adsorbent for removal of dyes from waste waters. Furthermore, supporting of magnetite nanoparticles on zeolitic material from coal fly ashes during the preparation process prevents the coaggregation of the iron oxide nanoparticles and help for their storage and pelletization.

References

[1]. A.K. Goswami, S.J. Kulkarni, S.K. Dharmadhikari, P.E. Patil, Fly ash as low cost adsorbent to remove dyes. International J. Scientific Research and Management, 2(5), 2014, 842-845.

[2]. A. Ahemad, B. Hameed and N. Aziz, Adsorption of deirect dye on palm ash: kinetic and equilibrium modelling, J. Hazardous Material, 141, 2007, 70-76.

[3]. Xiaoying Jin, Ming-qin Jiang, Xaio-quan Shan, Zhi-guo Pei and ZuliangChen, Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite. Journal of Colloid and   Interface Science, 328, 2008, 243-247.

[4]. S. Wang and Z.H. Zhu, Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, Journal of hazardous materials, 136 (3), 2006, 946-952

[5]. S.J. Allen, G. Mckay and K.Y.H. Khader, Intraparticle diffusions of basic dyes during adsorption onto Sphagnum Peat, Environ Pollution, 56, 1989, 39.

[6]. G. Mckay, M.S.Geundi and M.M. Nassar, Equilibrium studies during the removal of dye stuff from aqueous solutions using bagasses pitch, Water Reseasrch, 25, 1991, 271.

[7]. Shakti Das and Sanghamitra Barman, Studfies on removal of sarfranine-T and methyl orange dyes from aqueous solutions using Nax zeolite synthesized from fly ash, International Journal of Science, Environment and Technology, 2(4), 2013, 735-747.

[8]. K. Mittal and C. Venkobachar, Sorption and desorption of dyes by sulphonated coal, J. Environ. Engg. Div. ASCE, 119, 1993, 366.

[9]. R. Liu and H. Tang, Study of the photocatalytic effects of the Ti-doped hydroxyapatite in the degradation of methylene blue solution, Water Research, 34(16), 2000, 4029.

[10]. Y. Subbareddy, V. Jeseentharani, C. Jayakumar, K.S. Nagaraja, and B. Jeyaraj, Adsorptive removal of malachite green (oxalate) by low cost adsorbent, J. Environ. Res. Develop., 7, 2012, 275-284.

[11]. S. Yadav, D.K. Tyagi and O.P. Yadav, Equilibrium and kinetic studies on adsorption of aniline blue from aqueopus solution onto rice husk carbon, International Journal of Chemistry Research, 2(3), 2011, 59.

[12]. Ting-Chu Hsu, Adsorption of an acid dye onto coal fly ash, Fuel, 87, 2008, 3040.

[13]. H. Metivier-Pignon, C. Faur-Brasquet, P. Jaouen and P. Le Cloirec, Coupling ultration with an activated carbon cloth for the treatment of highly colored wastewater: a techno-economic study, Environ Technol, 24, 2003, 735-743.

[14]. V.K. Gupta, and I., Removal of endosulfan and methoxychlor from water on carbon slurry, Environ Sci Technol, 42, 2008, 766-770.

[15]. A. Mittal, V.K. Gupta, A. Malviya and J. Mittal, Process development for removal and recovery of metanil yellow by adsorption on waste materials –bottom ash and de-oiled soya, J. Hazard Materials, 151, 2008, 821-832.

[16]. V.K.Gupta, A. Mittal, V. Gajbe and J. Mittal, Adsorption of basic fuchsin using waste materials –bottom ash and de-oiled soya as adsorbents, J. Colloid Interface Science, 319, 2008, 30-39.

[17]. M.A.Al-Ghouti, M.A. Khrsisheh, S.J. Allen and M.N. Ahmed, The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth, J Environ Manage, 69, 2003, 229-238.

[18]. V.K. Gupta, Suhas, I. Ali and V. K. Saini, Removal of rhodamine B, fast green and methylene blue from wastewater using red mud - an aluminum industry waste, Ind Engg Chem Res, 43, 2004, 740-1747.

[19]. V.K.Gupta, D. Mohan, S. Sharma and M. Sharma, Removal of basic dyes (rhodamine B and methylene 20 blue) from aqueous solutions using bagasse fly ash, Sep Sci Technol, 35, 2003, 2097-2113.

[20]. B. Armagan, O. Ozdemir M. Turan and M.S. Celik, Clay mineral process for colour removal of textile wastewater, J. Environ. Sci. Hlth. Part A Toxic Hazard Subst Environ, 38 (10), 2003, 2251-2258.

[21]. M.P. Elizalde-Gonzalez, A.A. Pelaez- Cid, Removal of textile dyes from aqueous solution by adsorption on biodegradable wastes, Environ Technol, 24, 2003, 821-829.

[22]. N.K. Lazaridis, T.D. Karapantsios and D. Georgantas, Kinetic analysis for the removal of a reactive dye from aqueous onto hydrotalcite by adsorption, Water Research, 37, 2003, 3023-3033.

[23]. M. Hirata, N. Kawasaki, T. Nakamura, K. Motsumoto, M. Kabayama, T. Tamura and S. Tanada, Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment, J Colloid Inter Science, 254, 2002, 7-22.

[24]. S. Netpradit, P. Thiravetyan and S. Towprayoons, Application of waste metal hydroxide sludge for adsorption of azo reactive dyes, Water Research, 37, 2003, 763-772.

[25]. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani and S. Pattabhi, Utilizatuin of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution, Bioresource Technol, 87, 2003, 129-132.

[26]. G. M. Walkar, L. Hansen, J.A. Hanna and S J Allen, Kinetics of a reactive dye adsorption onto Dolomitic Sorbents, Water Research, 37, 2003, 2081-2089.

[27]. T. Nakamura, M. Hirata, N. Kawasaka, S. Tanada, T. Tamura and Y. Nakahon, Decolorization of indigo carmine by charcoal from extracted residue of coffee beans, Environ Sci Technol, 38, 2003, 555-562.

[28]. S. Kacha, Z. Derriche and S. Elmaleh, Equilibrium and kinetics of colour removal from dye solution with bentonite and polyaluminium hydroxide, Water Environ Research, 75, 2003, 15-20.

[29]. S.K. Alpat, O. Ozberak and H. Akey. The adsorption kinetics and removal of cationic dye toluidine blue from aqueous solution from Turkish zeolite, J. Hazard.Mater 151, 2008, 219-230.

[30]. J. Yener and T. Kopac, Adsorption of basic yellow 28 from aqueous solution from clinoptilolite and Amberlite, J. Colloid Interface Sci., 294, 2006, 255-256.

[31]. B. Armagon, M. Turan and M.S. Celik, Equilibrium studies on the adsorption of reactive azo dyes on the zeolite, Desalination, 170, 2006, 33-39.

[32]. S.M. Venkat, D.M. Indra and C.S. Vima, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. of Env. Manage. 74 (3), 2006, 647-652.

[33]. L. Peng and Z. Liuxue, Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents, Separation and Purification Technology 58(1), 2007, 32-39.

[34]. A. Garg, M. Mainrai, V.K. Bulasara and S. Barman, Experimental investigation on adsorption of amido black 10B onto zeolite sysnthesized from fly ash, Chemical Engg. Communications, 202(1), 2015, 123-130,

[35]. S. Das, S. Barman and R. Thakur, Removal of methyl orange and mythelene blue dyes from aqueous solution using low cost adsorbent zeolite synthesized from fly ash, J. Environ Sci Eng. 54(4), 2012, 472-80.

[36]. Q. L. Zhang, Y. C. Lin, X. Chen, and N. Y. Gao, A method for preparing ferric activated carbon composites adsorbents to remove arsenic from drinking water, J. Hazard. Mater. 148, 2007 671-678.

[37]. P. Yuan, M. Fan, D. Yang, H. He, D. Liu, A. Yuan, J. Zhu and T. Chen, Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions, J. Hazard. Mater. 166, 2009, 821-829.

[38]. G. S. Zhang, H. J. Liu, R. P. Liu, and J. H. Qu, Removal of phosphate from water by a Fe–Mn binary oxide adsorbent, J. Colloid Interface Sci., 335, 2009, 168-174.

[39]. D. A. Fungaro and J. E. A. Graciano, Adsorption of Zinc Ions from Water Using Zeolite/Iron Oxide Composites, Adsorpt. Sci. Technol. 25, (2007) 729-740.

[40]. D. A. Fungaro, M. Bruno, L. C. Grosche, Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash, Desalin. Water Treat., 2, 2009, 231-239.

[41]. D. A. Fungaro, M. Yamaura, and T. E. M. Carvalho, Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron o oxide magnetic nanocomposite, J. At. Mol. Sci. 2(4), 2011, 305-316

[42]. D. A. Fungaro, M. Yamaura and R. Gabriel Craesmeyer, Uranium removal from Aqueous solution by zeolite from fly ash –iron oxide magnetic nanocomposite, International Review of Chemical engineering, 4 (3), 2012, 353-357.

[43]. M.K. Dwivedi, I.P. Tripathi and Atul Kumar Dwivedi, Sorption studies on removal of malachite green from wastewater by coal fly ash, Int. J. Scientific Research, 3(11), 2014, 57-60.

[44]. P. Somasundaran, Encyclopedia of Surface and Colloid Science, 2006, 2nd Edition, Taylor & Francis, New York.

[45]. V.J.P. Poots, G. Mckay, and J.J. Healy, The removal of acid dye from effluent using natural adsorbents-I, Peat, Water Research, 10, 1971, 1067-70.