Research Paper

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Sorption Studies on Removal of Malachite Green from Wastewater By Coal fly ash

Chemistry

KEYWORDS : Adsorption, coal fly ash, Freundlich and Langmuir Isotherm, Malachite green

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ABSTRACT

Coal fly ash has been used as a low cost adsorbent for the removal of malachite green from wastewater. Effect of various operating variables, viz., solution pH, adsorbent dose, adsorbate concentration, temperature on the removal of malachite green has been studied. The experimental results indicate that 10 mg L-1 g of coal fly ash was able to remove 99.5% of dye from an initial concentration of 10 mg L-1.Equilibrium was achieved in 60 min. The adsorption of malachite green decreased with increasing temperature indicating exothermic nature of the adsorption process. The material exhibits good adsorption capacity and the adsorption data follow the Freundlich model better than the Langmuir model. Isotherms have been used to determine thermodynamic parameters of the process, viz., free energy change, enthalpy change and entropy change.

INTRODUCTION

Many industries such as textile, leather tanning, paper and pulp, and food consume dyes extensively The presence of dyes and pigments in water, even at very low concentrations, is highly visible and undesirable. It not only affects an esthetic merit, but also inhibits sunlight penetration and reduces photosynthetic action within ecosystem. The disposal of dye wastewater is a big challenge and it causes harm to the aquatic environment (Arul kumar et al., 2011).

The dye under consideration is Malachite Green (MG), which is important water-soluble dye belonging to triphenylmethane family. MG is widely used to dye wool, silk, cotton, and leather materials. In agriculture, commercial fish hatchery and animal husbandry also acts as an antifungal therapeutic agent, while for human it is used as antiseptic. Research has indicated that MG can be toxic to human cells and promotes liver tumor formation. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic .MG has a complicated chemical structure it is resilient to fading on exposure to light and water. Therefore, MG is difficult to be removed from wastewaters by commonly used techniques. However, since it dissociates in aqueous solutions, it is prone to be strongly adsorbed into adsorbent such as coal fly ash.

The potential of fly ash as a natural adsorbent had been investigated by Z. Derakhsha et.al (2013), R. Malarvizhi et.al (2010), Ting-Chu Hsu (2008), S. Kara et al.,(2007), S. Wang et.al.(2004), D. Mohan et al. (2002), S.K. Khare et. al.(1987), A. Khan Tabrez et. al.(2009), Indra Deo Mall et al. (2006). Their work identified the potential for removing dyes from wastewater. However, the work on removal of malachite green by fly ash is very scanty. Therefore studies have been taken to test the effectiveness of fly ash to remove malachite green from aqueous solution.

In this paper, batch experiments were designed for the sorption process, and the effects of temperature, pH value, initial concentrations of malachite green and fly ash dosages on adsorption were evaluated. The optimum condition was also discussed for malachite green removal.

EXPERIMENTAL METHODOLOGY

Materials and Instruments

Fly ash sample was collected from Unchahar Thermal Power Station , Singrauli (MP).It was sieved, and the particle size of 100 mesh was collected and used without pretreatment. All chemicals and reagents used were of analytical grade and were obtained from E. Merck, India. Stock solution of malachite green was prepared using malachite green in deionized water. A pH meter (Systronic) was used for pH measurements. X-ray measurements were made using a PhillipsX-ray diffractometer employing nickel-filtered Cu Ka radiations. The surface area of the adsorbent was measured by a surface area analyser (Quantasorb ModelQS-7). IR spectra of the samples were recorded on an infrared spectrophotometer (FTIR Perkin Elmer Model1600). The density of the adsorbent were determined by mercury porosimeter and specific gravity bottles respectively.

Adsorption studies

Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100 ml capacity covered with Teflon sheets to prevent contamination. The effect of contact time (0–360 min), concentration (10.0-70.0 mg/L), solution pH (2.0–12.0), adsorbent dose (5.0-25.0 g /L), and temperature (303 K, 313 K, and 323 K) were studied. Isotherms were obtained by adsorbing different concentrations of malachite green after prescribed contact time, the solutions were filtered and the concentrations of malachite green were determined by atomic absorption spectrophotometer.

RESULT AND DISCUSSION

Characteristics of Fly Ash

Chemical composition

The chemical composition of coal fly ash was determined by X-ray fluorescence spectrometer .Table 1 shows the results of the chemical analysis of the test sample.

Table 1

Chemical constituents of the fly ash

Constituents	SiO_2	Al_2O_3	C_aO	Fe_2O_3	MgO	Others	LOI
Wt. %	61.10	25.02	1.69	6.92	0.53	4.94	2.6

XRD analysis

The x-ray diffraction pattern of fly ash sample was shown in Figure 1. It can be observed from the figure that fly ash consists mostly of Quartz, mullite, and 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 glossy surface layer. The low calcium oxide intensity is characteristic of low-Ca Class-F flyash

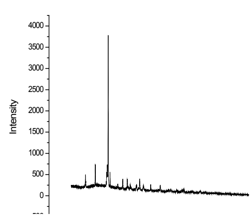

Fig.1: XRD Spectra of Fly ash

SEM Analysis:

Scanning electron microscopy (SEM) is used for studying the surface morphology of substances due to its high magnification imaging capability. Figure 2 shows sub-angular and spherical particles with relatively smooth grains consisting of quartz,

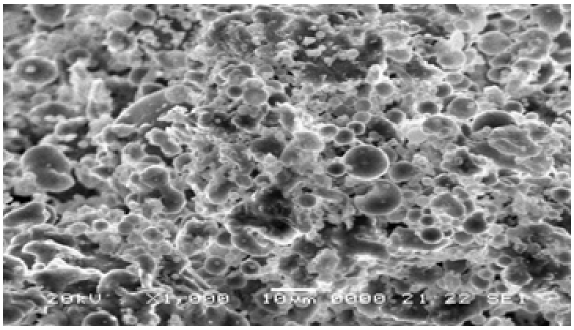

Fig.2: SEM micrograph of Coal Fly Ash

FTIR Analysis

IR spectroscopy of the powder sample was applied using Perkin Elmer FTIR system. The sample was scanned in the region 4000 – 400 $cm^{-1}$and shown in Fig.3. The peaks in IR spectra indicate the presence of Al–O, Si–O and Fe-O bonding.

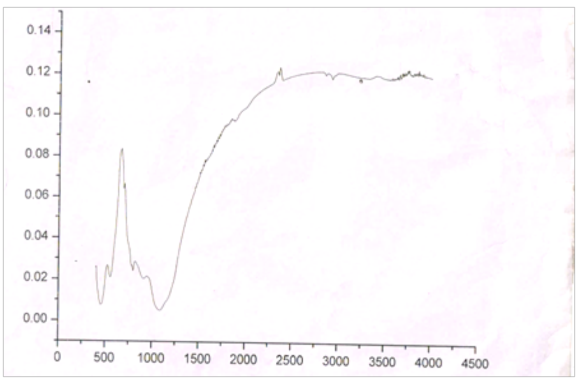

Fig 3: FTIR Spectra of fly ash

Sorption studies

Batch studies

Influence of initial adsorbate concentration and contact time

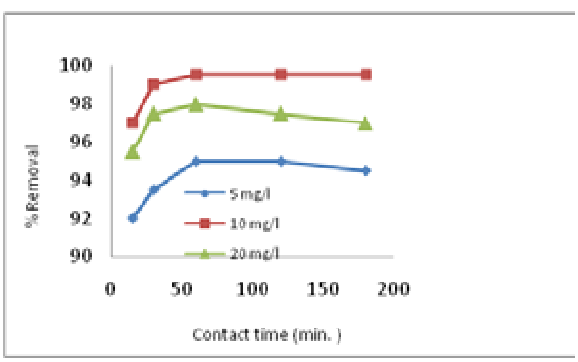

Fig.4. Effect of contact time on adsorption of malachite green

The adsorption data for the uptake of malachite green versus contact time for a fixed adsorbent dose of 10 g/L is shown in fig.4. The initial concentration of 5,10 and 20 mg/L for malachite green were taken for the experiment. These plots indicate that the remaining concentration of malachite green becomes asymptotic to the time axis such that there is no appreciable change in the remaining malachite green concentration after 60 minute. These represent the equilibrium time at which an equilibrium malachite green concentration is presumed to have been attained.

Influence of temperature

The effect of temperature on the adsorption of malachite greens is presented in Fig. 5. The experiments were carried out with fixed adsorbent dose of 10 g/l of fly ash and pH 5. The adsorption followed the order 300C>400C>500C.The decrease in adsorption with increasing temperature indicated exothermic nature of the adsorption process. 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.

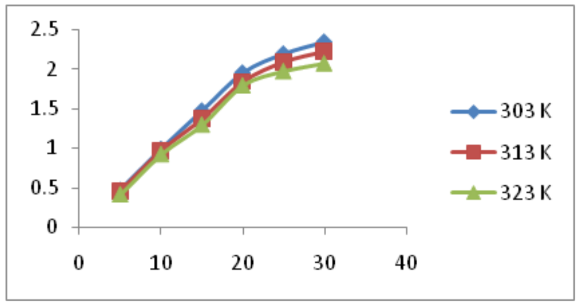

Fig .5.Effect of temperature on adsorption of malachite green

Influence of pH

The plot showing the effect of pH on the adsorption of malachite green is shown in Fig. 6. The initial concentration of 10 mg/L for malachite green was taken for the experiment. It was evident from the plot that the maximum uptake of malachite green occurred at pH 5.0, The pH of the solution was measured before and after the adsorption and no change was noticed in the pH.

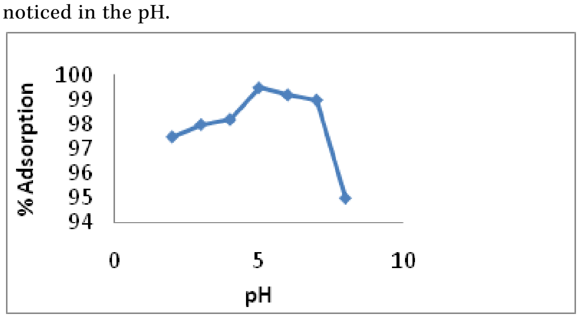

Fig. 6.Effect of pH on adsorption of malachite green

Influence of adsorbent dosage

The effect of the adsorbent dose on the removal of malachite green is shown in Fig. 7.

The percentage removal of malachite green increased with the increase in adsorbent dose initially from 0.1 to 0.2 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 increased initially. But on increasing it further the adsorption efficiency is reduced. It may be due to the overcrowding of phenol molecules which prevent the diffusion through the actual adsorption sites.

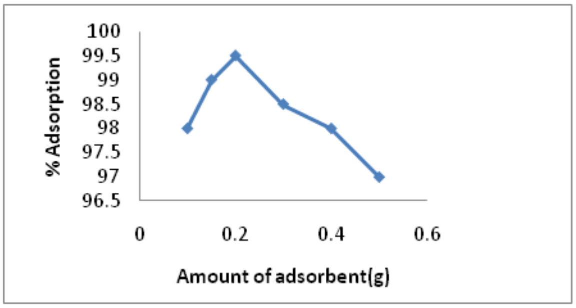

Fig. 7.Effect of adsorbent dosage on adsorption of malachite green

Adsorption isotherms

The results obtained on the adsorption of malachite green and nickel were analysed by the well-known models given by Langmuir and Freundlich.

Langmuir isotherm

The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The rearranged Langmuir isotherm equation can be described as:

$1/q_e = 1/q_m + (1/bq_m)(1/c_e)$ ---------------------------(1)

qm and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption,respectively.The plot of 1/qe vs. 1/Ce yielding straight line (Fig. 8,&9). The Langmuir constants,b and Qm were calculated and the values of these were given in Table 2.

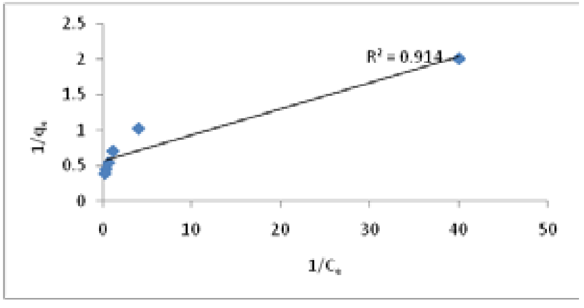

Fig.8. Langmuir isotherm plot of Malachite green -CFA adsorption system at 303 K

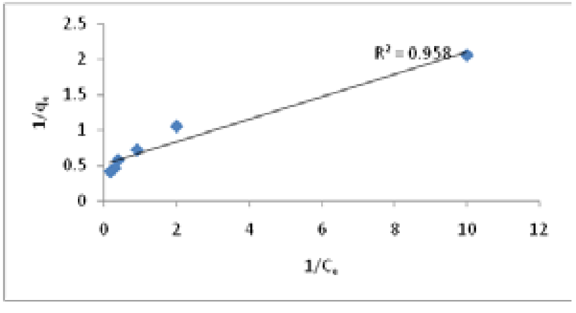

Fig.9. Langmuir isotherm plot of Malachite green -CFA adsorption system at 313 K

Freundlich isotherm

The adsorption data of malachite green is also analyzed by Freundlich model. The linearized form of Freundlich isotherm is given below:

$\text{loqqe} = \log K_f + 1/n \log C_e$ ------------------------------ (2)

The value of Kf and n can be calculated by plotting log qe versus log Ce.Where, Kf is a freundlich constant related to the adsorption capacity (mg/g) and n is adsorption intensity respectively .

The plots of log qe against logCe; for the adsorption data of malachite green are given in Fig. 10&11, which clearly show that the data is fitting very well to the Freundlich model. The Freundlich constants,Kf and n; were calculated from the best-fit lines and the values given in Table 3. The values of constants indicate favourable conditions for adsorption.

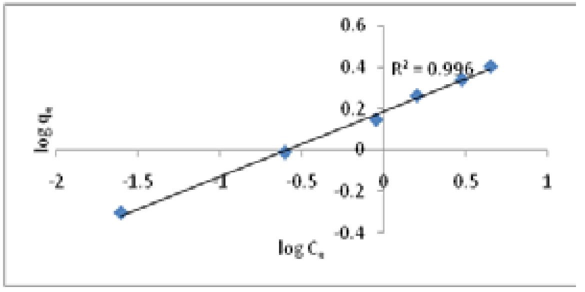

Fig.10.Freundlich isotherm plot of Malachite green -CFA adsorption system at 303 K

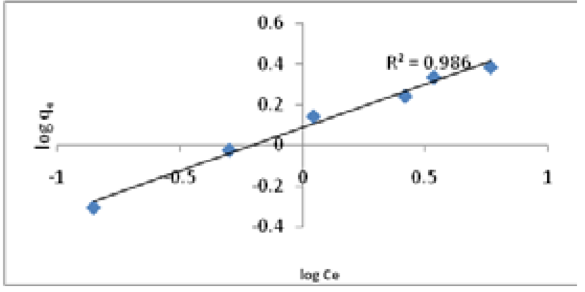

Fig.11. Freundlich isotherm plot of Malachite green -CFA adsorption system at 313 K

Table 2
Langmuir isotherm parameters of Malachite green-CFA adsorption system

Temperature	Q_m (mg/g)	b	R^2
303 K	1.7464	15.6021	0.9144
313 K	2.1505	2.0350	0.9582

Table3
Freundlich isotherm parameters of Malachite green-CFA adsorption system

Temperature	K_f	n	R^2
303 K	1.547	3.1756	0.9996
313 K	1.225	2.3485	0.9867

Kinetic studies

The thermodynamic parameters for the adsorption ofmalachite green were calculated by using thefollowing equations:

$\Delta G = -RT\ln K$ --------------------------------------- - --(3)

$\Delta H = \Delta G + T\Delta S$ ---(4)

Therefore, lnK= -ΔH/RT +ΔS/R ------------------------(5)

Where, K/ the equilibrium constant is defined as,

$K = C_{Ac} / C_e$ ---(6)

Ce is equilibrium adsorbate concentration in solution(mg L^{-1}),

C_{Ac} is the equilibrium concentration on the adsorbent (mg g^{-1}).

R is the universal gas constant and

T is the absolute temperature.

The values of thermodynamic parameters are given in Table 4.A perusal of data indicated that the free energy decreased with an increase in temperature thereby indicating decrease in adsorption at higher temperature and exothermic nature of the adsorption.

Table 4
ThermodynamicParameters

ΔG ($KJmole^{-1}$)	ΔH($KJmole^{-1}$)	ΔS($KJmole^{-1}K^{-1}$)
-6.921	-160.67	-0.5074

CONCLUSION

Coal fly ash obtained from thermal power station is an inexpensive and effective adsorbent for the removal of malachite green from wastewater. The adsorption data fit very well to the Freundlich model in comparison to the Langmuir model. The adsorption was found to be exothermic in nature.

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