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Soil Pollution By Malachite Green Dye And Dye Recovery From Effluent

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ABSTRACT

Silica and water are the major constituents in the earth. Hence silica was used as adsorbent for determine the pollution tendency between soil and ground water. This was analyzed by adopting two step processes of adsorption and desorption. The silica was characterized with FT-IR, BET surface area and active site analysis. The experimental conditions for adsorption step like contact time, concentration of dye solution, temperature, pH and dosage of silica were studied. The maximum uptake was observed at 6 hrs contact time and pH 5 to 7. The concentration effect had been studied between 50 to 300 ppm and observed that adsorption decreases with increase the concentration, but adsorption increases with increase of silica dosage from 50 to 450mg. The temperature effect had been evaluated between 30 to 90^{0}C and observed that the adsorption increases upto 80^{0}C and decreases above the temperature. Then the desorption step of malachite green from silica surface had been studied by using solvents like water, ethanol, methanol and oxalic acid(0.1%) and found that desorption increases in the order of water<oxalic acid<ethanol<methanol. Among this solvents water was a poor desorption solvent than other solvents proved that the malachite green has more pollution onto soil than ground water.

KEYWORDS

Ground water;
Silica;
Adsorption;
Malachite green.

INTRODUCTION

Water pollution by organic dyes is a major problem in areas of cosmetics, rubber, plastics, paper manufacturing industries and textile dyeing industries[1]. It was estimated that 12% of dye was discharged from these dyeing industries and dye manufacturing industries[2]. These dyes not only pollute surface water but also soil and ground water. The dyes are found to be toxic to human and living beings[3-5]. Malachite green is an important basic(cationic) dye used for dyeing wool, silk, leather, cotton, jute, etc. It is also used as fungicide and ectoparasiticide in aquaculture and fisheries[6,7]. It is found that MG is easily reduced to persistable leuco-malachite green in the tissues of fish and mice, which is a tumor promoter[8,9]. The MG detection in human consumable like milk and food stuffs alarms the health hazards in human beings[10,11]. Moreover, these dyes are harmful to symbiotic bacteria present in water, hence biodegradation of dyes are very less[12]. On the other hand, the conventional methods commonly used for dye removal from aqueous solutions are adsorption, oxidation, flotation, coagulation, photochemical destruction, ion exchange and membrane filtration[13]. However all these methods are costly and required additional chemicals. Hence these methods are not much suitable to treat industrial effluents. The adsorption methods have been widely used for removal of colorants from waste water. Adsorbents like activated carbon[14], natural zeolites[15], saw dust[16], fly ash[17] modified clays and molecular sieves[18,19] have been used for dye removal. MG adsorption studies were already reported in rice husk based carbon[20], activated carbon[21], bottom ash[22], and hen feathers[23]. On the basis of literature survey silica was not used as an adsorbent for removal of MG, but adsorption of astrazone blue, basic blue 3, basic red 22, acid blue 25[2,24] were carried out by silica. To our knowledge no work was reported for adsorption and desorption of MG on silica and pollution tendency determination between soil and ground water. Hence we attempted to study the possibility of using silica as an adsorbent for MG and to determine the behavior of MG between soil and ground water in the earth.

EXPERIMENTAL

Physico-chemical characterization

FT-IR spectrum of the silica was recorded in nicolet(Avatar 360) FT-IR spectrophotometer using KBr pellet technique. About 15mg of the sample was pressed into a self-supported wafer of 13mm diameter. This pellet was used to record the infrared spectra in the range 4000-400cm^{-1}. Surface area of the material was measured by nitrogen adsorption at 77K with an ASAP-2010 porosimeter from micromeritics corporation(Norcross, GA, USA). Before nitrogen adsorption-desorption measurements, the sample was out gassed at 523K under 10^{-5} mbar pressure for 3hr in the degas port of the adsorption analyzer. The surface area of the sample was determined from BET plot. Total active sites present on silica surface were calculated from monolayer capacity obtained from the langmuir plot. The experiments for this study were carried out at pH 5 and temperature 37^0C.

Adsorption experiments

The silica(Merck) was activated before the absorption experiment at 150^0C for 10hrs in hot air oven. The required amount of silica was taken from this activated silica for all the experiment. The oxalate form of MG dye(Merck) was used for adsorption. The chemical formula is $C_{48}H_{50}N_4O_4.2C_2H_2O_4$, molecular weigh 927.02, C.I.No. 420000 and λ_{max} 616-620nm.

The stock solution 1000mg/l was prepared by dissolving 1g of dye in 1 liter double distilled water in a standard measuring flask. The working solutions of the desired concentration were prepared by successive dilution of the stock solution. The dye concentration was analyzed with UV-Visible spectrophotometer [Elico-model-SL171].

The activated silica(0.25g) was added with 50ml of MG solution in 100ml conical flask. The mixture was stirred on a magnetic stirrer(Remi-model-1MLH) and at the end of the experiment the solution was centrifuged off. The final concentration of the solution was measured spectrophotometrically at 617nm. The contact time was studied up to 25hrs to find out the equilibrium adsorption time. The adsorption pro-

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cess of MG on silica was studied in the concentration range of 50-500mg/l. The initial and final pH values were measured for all concentration by using pH meter(Elico-model LI 613). The temperature effect of MG adsorption on silica was studied in the range of 30-90^{0}C. The silica dosages were studied in the range of 150-550mg.

Desorption experiment

The known amount of dye 14.89mg adsorbed onto 250mg of silica was dried at 110^{0}C for 5 hrs. It was added with 20ml of various solvents like water, ethanol, methanol and oxalic acid(0.1%) and shaken well. The ethanol and methanol solvents were distilled out and the MG was dissolved in water and amount of dye desorbed was estimated by spectrophotometrically.

RESULTS AND DISCUSSION

Physico-chemical characterization of silica

The silica structure was characterized with FT-IR spectra(Figure 1). The Si-O-Si asymmetric stretching observed at 1106cm^{-1} proved that the silica is in the form of tetrahedral structure. The symmetric stretching and bending mode silica were observed at 674 and 466cm^{-1} respectively. Then the broad peak at 3423cm^{-1}observed in the spectrum is due to the uncondensed OH groups present in the silica. BET surface area of the silica was calculated from the N_2 adsorption and was found to be 230m^2/g. The total active sites are calculated from the Langmuir adsorption isotherm. From the Langmuir isotherm, the monolayer capacity of silica was estimated (4.9189×10^{-5}mol/g). The active sites present on the silica surface are 2.9627×10^{19} per gram calculated from the monolayer capacity of silica.

Effect of contact time

Effect of contact time for maximum adsorption of MG was studied upto 25hrs. The adsorption of MG increases with increase of time upto 6 hrs and further increases the time not much increase the adsorption(Figure 2). This indicates that the adsorption equilibrium was established within 6hrs.

Effect of concentration of dye

The effect of concentration of the MG for maximum uptake was studied between the concentration ranges of 50-300ppm at room temperature. The absorption capacity of the dye was found to be increases upto 100ppm and further increases of concentration decrease the uptake of MG (Figure 3). This may be due to the aggregation of dye molecule in the higher concentration leads to liberate oxalic acid from the dye molecule (Figure 4) which was preferentially adsorbed on silica surface than the aggregated dye molecule. This was verified from the adsorption isotherms Langmuir and Frendlich. The R^2 value is very low for both Langmuir(0.1781) and Frendlich(0.2743). This low values were proved that the oxalic acid was disturbed the MG adsorption. This fact was proved by carried out the MG adsorption with oxalic acid solution (Figure 5) and observed that the dye up-

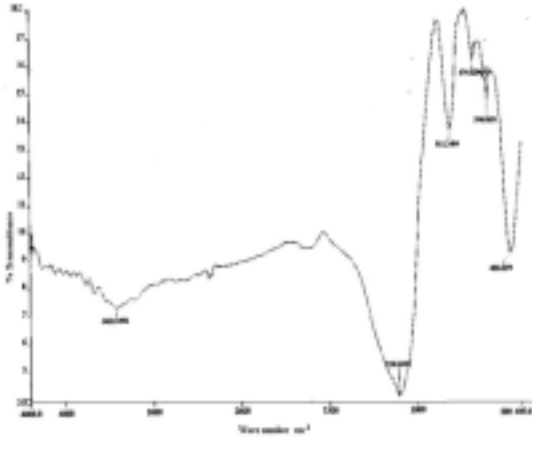
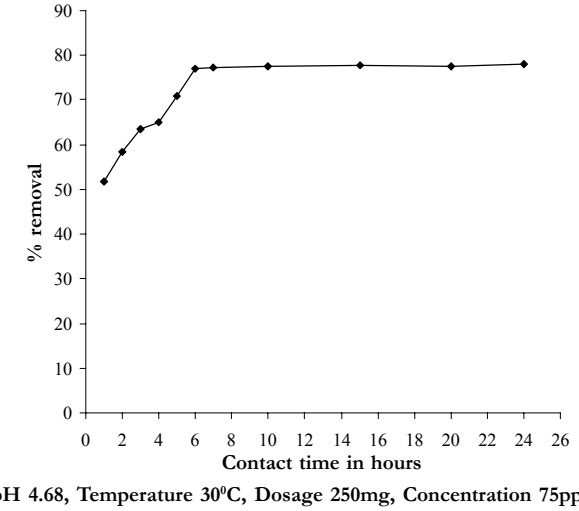
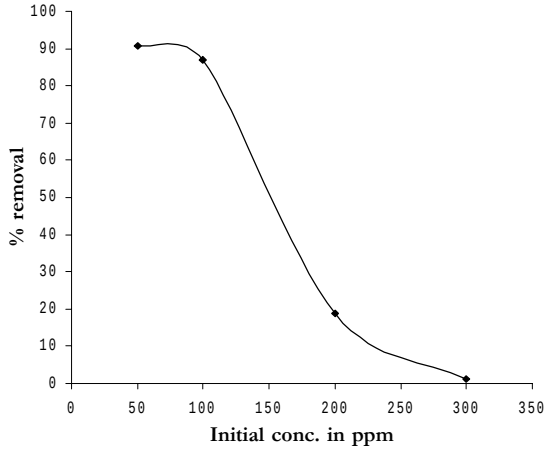


Figure 1: FT-IR spectrum of silica



pH 4.68, Temperature 30^{0}C, Dosage 250mg, Concentration 75ppm

Figure 2: Effect of contact time of MG adsorption on silica



pH 4.68, Temperature 30°C, Contact time 6 hrs, Dosage 250mg

Figure 3: Effect of concentration of MG adsorption on silica

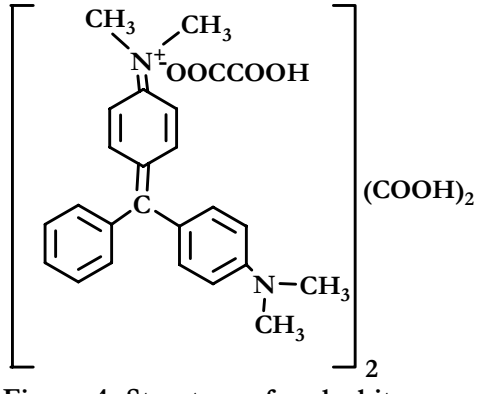
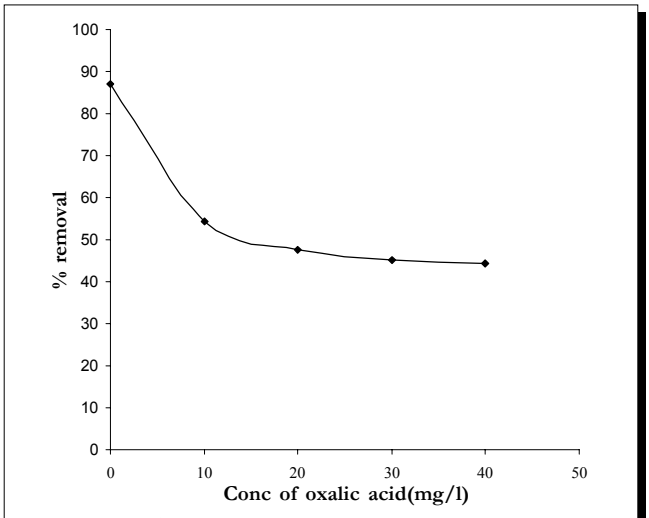


Figure 4: Structure of malachite green

take decreases from 80% to 45% with increases the oxalic acid concentration of 10-40mg/l. This confirm that the oxalic acid prevent the MG adsorption on silica. Hence, the MG adsorption decreases with increases of concentration and also not follows the Langmuir and Frendlich absorption isotherms. But at pH 5, the MG adsorption follow the Langmuir and Frendlich absorption isotherms. Because the liberated oxalic acid not preferentially adsorbed on silica surface at pH 5 and hence, the MG adsorption follows the Langmuir and Frendlich absorption isotherms.

The initial and final pH of the MG solution(50-300ppm) was measured before and after the adsorption experiments. The initial pH of MG solutions decreases from 4.74 to 3.93 with increase of dye concentration from 50-300ppm(TABLE 1). After the adsorption process, the final pH of the solution were measured and observed that the pH increases nearer



Temperature 30°C, Dosage 250mg, Concentration 75ppm, Contact time 6hrs

Figure 5: Effect of oxalic acid on adsorption of MG on silica

TABLE 1: pH changes after and before the adsorption of MG.

Concentration ppm	Initial pH	Final pH	% removal
50	4.74	7.40	90.68
100	4.64	7.18	87
200	4.50	6.05	18.8
300	3.93	4.61	1.2

to water pH with increase adsorption from 1.2% to 90.68%.

Effect of temperature

The effect of temperature on the removal of MG was studied in the range of 30 to 90°C. The adsorption was found to be increase with increase of temperature (Figure 6). The adsorption was increased from 65 to 90% when the temperature was increased from 30-80°C and further increase the temperature decreases the adsorption 4%.

Effect of pH

Adsorption of MG was studied over the pH range 3 to 7. Maximum uptake of dye(99%) was achieved at pH range 5 to 7(Figure 7). At pH 3, the uptake was 30%, at pH 4 the uptake was 20% and further increase the pH 5 to 7 leads to maximum adsorption up to 99%. The pH 5 to 7 silica surface has high negative charge. Hence, uptake of cationic dye MG increases in the pH range 5 to 7. The reduction of adsorption from 30% to 20% at pH 3 to 4 may be

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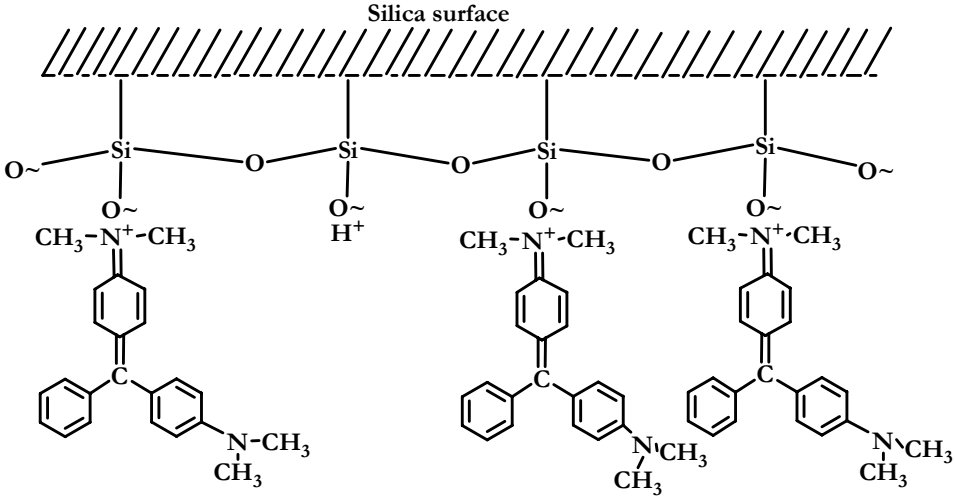
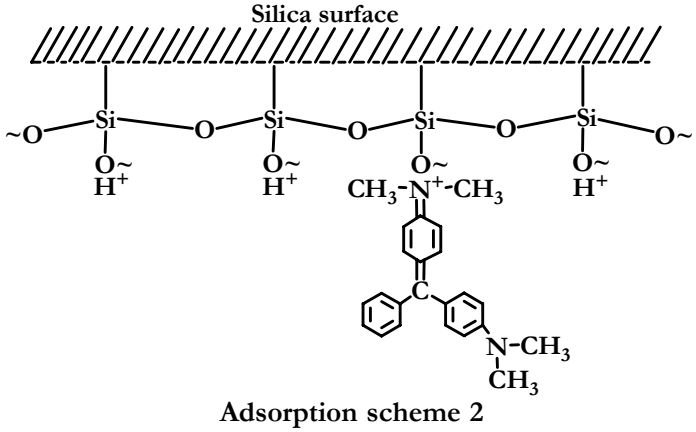
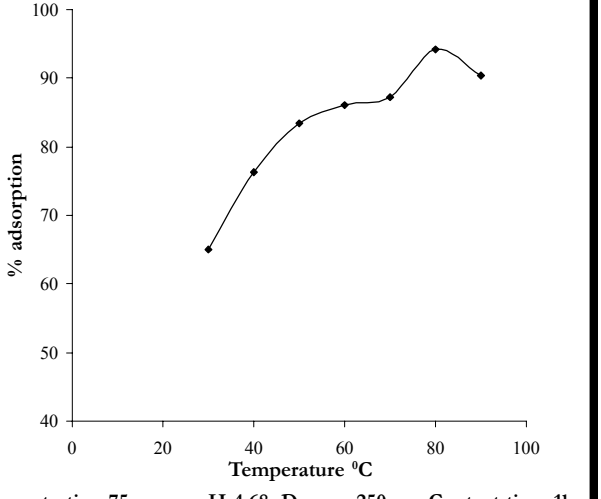


Adsorption scheme 1

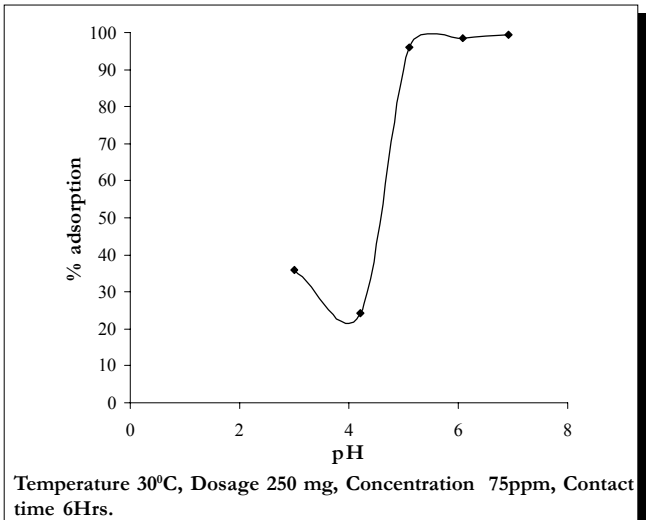


Adsorption scheme 2



Concentration 75 ppm, pH 4.68, Dosage 250mg, Contact time 1hr

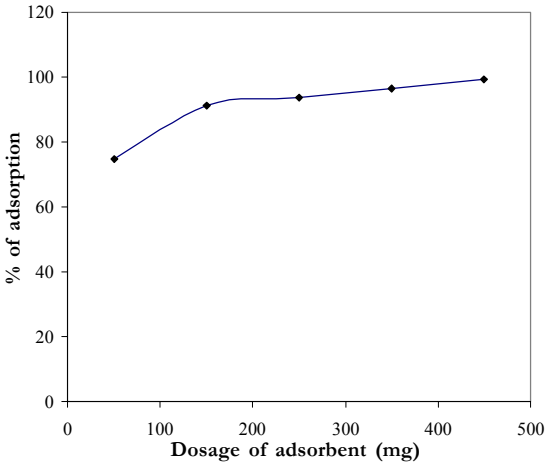
Figure 6: Temperature effect of MG adsorption on silica



Temperature 30⁰C, Dosage 250 mg, Concentration 75ppm, Contact time 6Hrs.

Figure 7: Effect of pH on adsorption of silica

attributed to zero surface charge of silica at pH 4[25] and at pH 3 surface charge become positive hence the cationic MG adsorption only 30%. But the 30% and 20% MG uptake at pH 3 and 4 may be due to the physisorption of MG on silica surface.



Concentration 75ppm, Temperature 30^{0}C, Contact time 5h, pH 4.68.

Figure 8: Effect of silica dosage for MG adsorption

Effect of dosage

The effects of silica dosages 50 to 450mg were carried out for maximum uptake of 75ppm MG solution. The percentage removal of the dye was found to be increases with increase of adsorbent dosage (Figure 8). The increase of dosage increases the surface area and active sites hence adsorption of MG increases.

Desorption of MG

Desorption of MG from silica was carried out with water, oxalic acid (0.1%), ethanol and methanol at room temperature(TABLE 2). The maximum desorption of MG was observed in methanol(50%) and very low desorption observed in water(3.47%), which indicates that the MG has more affinity on silica than water. This fact proved that the MG pollutes the soil to a maximum extent than water.

In the view of recovering the MG from the silica, methanol is a suitable solvent than ethanol, oxalic acid solution and water. Then the methanol can be recovered by distillation of methanol dye solution at the 65^{0}C. The dye recovered from this method was dissolved in water and characterized spectrophotometrically and observed that the λ for the recovered dye was 618 nm, this value is compared with the original dye λ_{max} which is in the range of 616-620nm. This confirms that the MG dye structure has no change during the recovery process.

TABLE 2: Desorption of malachite green in various solvents

Solvent	Volume of solvent (ml)	Dye adsorbed on 250mg silica (mg)	Desorption (%)
Water	20	14.89	3.47
Oxalic acid	20	14.89	11.80
Ethanol	20	14.89	26.85
Methanol	20	14.89	50.00

Temperature 30^{0}C

CONCLUSION

The physico-chemical characterization shown that the silica has tetrahedral structure, surface area is 230m^2/g and the active sites present on the surface area are 2.9627×10^{19}. The adsorption step of MG indicates that the maximum uptake attained at 6 hrs contact time and pH 5 to 7. The adsorption increases with increase of temperature up to 80^{0}C and further increases the temperature decreases the MG uptake. The MG adsorption on silica was found to be decreases with increase of MG concentration and adsorption increases with increase of silica dosage.

The desorption step of MG from silica surface was in the increasing order of water<oxalic acid <ethanol<methanol solvents. The poor desorption of MG in water confirm that the MG pollute the soil to the maximum extent than the ground water.

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