MINOR PROJECT REPORT
(MSCH6040)

on

Removal of dyes from aqueous solution using functionalized SiO₂ and magnetite Nanoparticles

Submitted in Partial Fulfilment of the Requirement for the Degree of
M.Sc. Chemistry

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CERTIFICATE

This is to Certify that Mr. **Sandip Kumar Panda** has carried out his minor project

work entitled "**Removal of dyes from aqueous solution using functionalized SiO$_2$**

and Magnetite Nanoparticles" under my supervision. This work is fit for submission

for the award of Master Degree in Chemistry.

(Signature)   **(Signature)**

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ATMA RAM SANATAN DHARMA COLLEGE

University *of* Delhi

Accredited Grade 'A' by NAAC
NIRF All India 14th Rank

STAR COLLEGE SCHEME (DBT)

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(Principal)

Dr. Anil Kumar

Assistant Professor

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CANDIDATE DECLARATION

I hereby declare that the dissertation entitled "**Removal of dyes from aqueous solution using functionalized SiO$_2$ and Magnetite Nanoparticles**" submitted by me in partial fulfillment for the degree of M.Sc. in Chemistry to the Division of Chemistry, School of Basic and Applied Science, Galgotias University, Greater Noida, Uttar Pradesh, India is my original work. It has not been submitted in part or full to this University of any other Universities for the award of diploma or degree.

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ACKNOWLEDGEMENT

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TABLE OF ABBREVIATION AND SYMBOLS

S.NO.	ABBREVIATION	FULL FORM
1.	UV	Ultra Voilet
2.	APTES	3-aminopropyl –tri ethoxysilane
3.	PGA	Poly Glutamic Acid
4.	MNPs	Magnetite Nanoparticles
5.	MB	Methylene Blue
6.	MG	Malachite Green
7.	MO	Methyle Orange
8.	RhB	Rhodamine- B

S.NO.	SYMBOL	NAME	DESCRIPTION
1.	γ	gamma	Used for position of atom in a long chain of chemical compound
2.	α	alpha	Used for position of atom in a long chain of chemical compound
3.	λ_{max}	Lambda maximum	Used to define maximum wavelength of absorbance in UV

ABSTRACT

In this study, the application of functionalised SiO_2 and Magnetite Nanoparticles (MNPs) with 3-aminopropyl –tri ethoxysilane (3-APTES) and biopolymer poly (γ-glutamic acid) (PGA) respectively for the removal of organic dyes from aqueous solution. SiO_2 and MNPs was reported as a novel adsorbent for the removal of organic dyes from aqueous solution.

SiO_2 is functionalised with 3-APTES group covalently linked on this SiO_2 support, adsorption of dyes is due to the electrostatic interaction between NH_2 group present in Si-APTES and cationic dyes (Methylene blue, Malachite Green, Rhodamine-B) and bond formation between NH_2 group and anionic dyes methyle orange (MO). The maximum adsorption capacity was 15.0 mg/g.

Magnetite nanoparticles coated with an anionic biopolymer poly glutamic acid (PGA-MNPs) synthesized and study the capability for adsorption of different organic dyes. Magnetite nanoparticles coated with an anionic biopolymer poly γ-glutamic acid (PGA-MNPs) were synthesized and characterized for their dye adsorption capability. The MNPs was stable in de-ionized water. The maximum adsorption capacity was 69.6 mg/g. Dye removal mechanism by PGA-MNPs was probably due to electrostatic interaction through exchange of protons from side chain α-carboxyl groups on PGA MNPs surface.

1.0

INTRODUCTION

1.0 INTRODUCTION

A dye is a colored substance that chemically bonds to the substrate to which it is being applied, this distinguishes dyes from pigments which do not chemically bind to the material they color. Dyeing dates back to the Neolithic period. Throughout the history, people have dyed their textiles using common and available materials. Nowadays dyes are widely used in various industries including textiles, papers, plastic, rubber and coating etc. Dyes usually have a synthetic origin and a complex structure that makes them persistence to light, oxidation and biodegradable processes. Indeed many dyes were developed to be chemically stable and not degrade easily. The industrial wastewater containing highly stable dyes is very hazardous for the aquatic ecosystem since it consumes oxygen and elevates bio- chemical oxygen demand. Even after degradation of several dyes, the byproducts are found carcinogenic and thus advancement of the efficient and sustainable method for removal of colour from effluents is the necessary for the safe aquatic ecosystem. The following conventional methods used in dye removal from waste water: coagulation and flocculation, oxidation or ozonation, membrane separation and adsorption.

Adsorption is a classical technique which involves a variety of highly porous adsorbents to ensure adequents surface area for adsorption. Adsorption processes have been reported to be low cost promising alternatives for treatment of dyes present in wastewater. The use of activated carbons, modified clays, polymeric resins and zeolites have also been used. Recent advances in nanotechnology offers a class of adsorbents that are ultra- fine with large surface area and posses magnetic properties for efficient separation in shorts time by applying an external magnetic force. Nano- sized iron oxides particles have received considerable attention due to its low cost and easy production compared to activated carbon.

Nano sized particles adsorbs dyes presents in wastewater and dye loaded nanoparticles can easily be removed by applying simple magnetic field. The loaded nanoparticle can also be reused for multiple cycles of adsorption. However the surface coating of iron nanoparticles to avoid agglomeration

through hydrophobic, magnetic van der Waals interactions because of their large surface area to volume ratio and form clusters of increased particles size [3].

PGA (Poly γ-glutamic acid) is an anionic polypeptide synthesized by Bacillus species through a fermentation process and is composed of numerous repetitive glutamic acid units connected by a unusual γ-amide bond leaving the side chain α-carboxyl groups free for conjugation with a wide variety of compounds (-[-NH-CH(COOH-$(CH_2)_2$-CO-]$_n$-) [9] [6]. The PGA being multifunctional, non-toxic and biodegradable finds application in diverse fields including food, medicine, cosmetics, agriculture and wastewater treatment [16] [4] [2]. In several previous studies PGA has been shown to be an effective absorbent for removal of various dyes and metals [7] [8] [9] [6] [17] [18]. Furthermore PGA coated nanoparticles were recently synthesized and evaluated for its cytotoxic and antibacterial activity [5]. However their applications as dye removal still remains to be explored. Therefore the objectives of this study is to synthesize PGA coated iron oxide particles and evaluate their dye removal capacity in a batch mode adsorption process with methylene blue, rhodamine B, malachite green and methyl orange as test dyes.

1.1 METHYLENE BLUE DYE

Methylene Blue ($C_{16}H_{18}ClN_3S$) is a synthetic basic dye also known as Methylthionium blue, methylthionium chloride, basic blue 9, Swiss blue having molecular weight 319.851 gm/mol. [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium chloride is its IUPAC name. Methylene blue stains to negatively charged cell components like nucleic acids. Methylene blue is an organic chloride salt having 3, 7-bis (dimethylamino) phenothiazin-5-ium as the counter ion. Methylene blue is a monoamine oxidase inhibitor (MAOI) [14] and if infused intravenously at doses exceeding 5 mg/kg, may precipitate serious serotonin toxicity, serotonin syndrome, if combined with any selective serotonin reuptake inhibitors (SSRIs) or other serotoninre uptake. Inhibitor (e.g. duloxetine, sibutramine, venlafaxine, clomipramine, imipramine). It causes hemolytic anemia in carriers of the G6PD (favism) enzymatic deficiency.
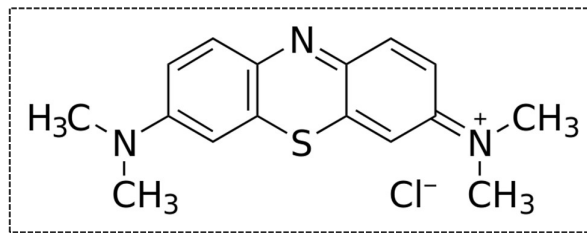
fig. 1.0 METHYLENE BLUE CHEMICAL STRUCTURE

color – Blue (pH >5.4) and Yellow (pH <3.8).
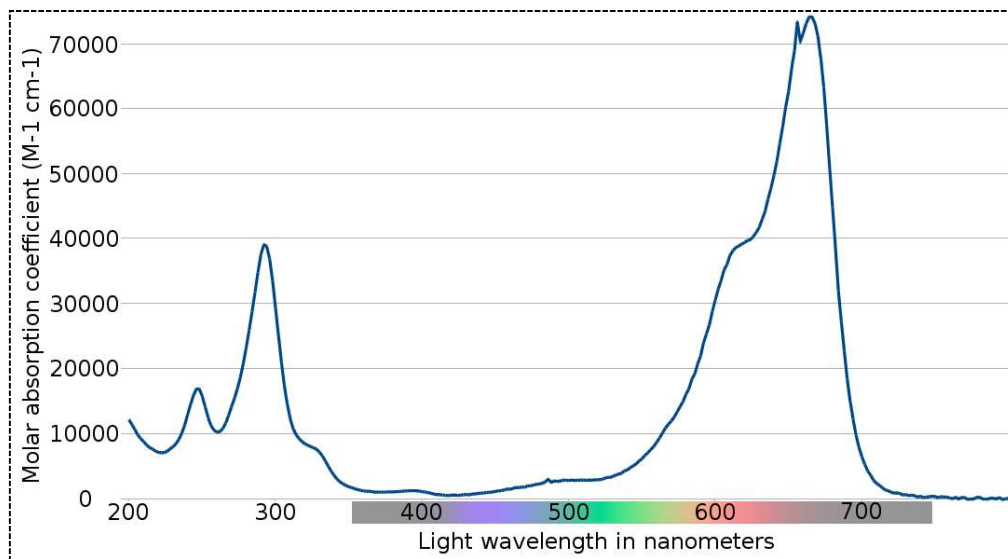
Fig1.1 U V Spectrum of Methylene dye maximum absorbance and molar absorption coefficient at wavelength 664 nm

1.2   RHODAMINE – B DYE

Rhodamine B ($C_{28}H_{31}ClN_2O_3$) is a chemical compound and a dye. It is often used as a tracer dye in water to determine the rate and direction of flow and transport. Rhodamine dyes fluoresce and can thus be detected easily and inexpensively with fluorometers.
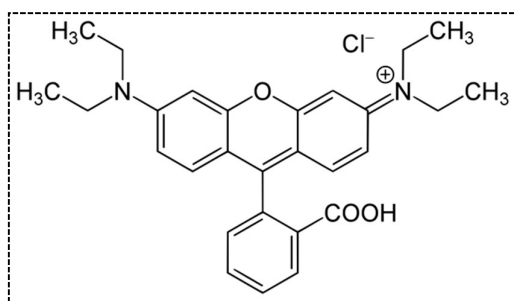
Fig 1.2 chemical structure of Rhodamine- B

In California, USA, Rhodamine B is suspected to be carcinogenic and thus products containing it must contain a warning on its label [13]. Cases of economically motivated adulteration, where it has been illegally used to impart a red color to chili powder, have come to the attention of food safety regulators [11].
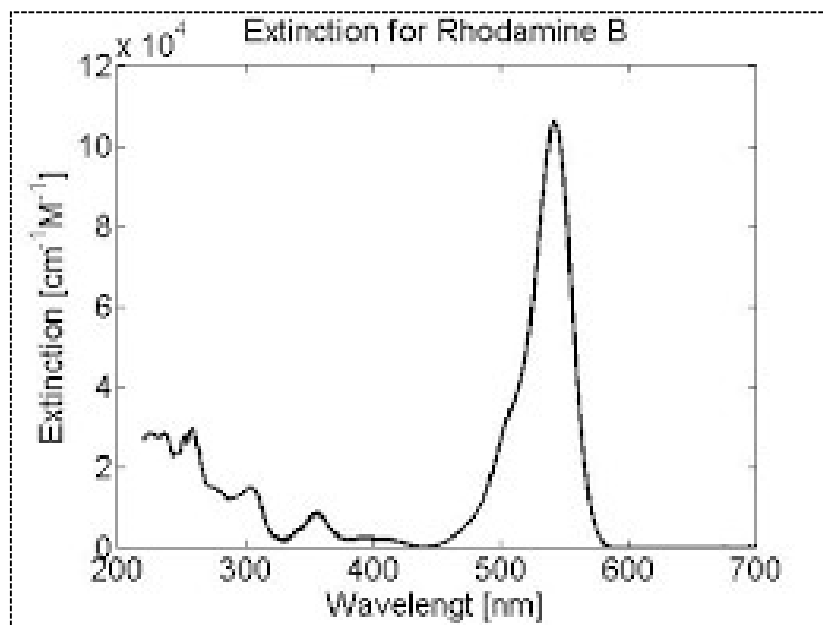
Fig 1.3 UV Spectrum of Rhodamine-B maximum absorbance at wavelength 554 nm

1.3   MALACHITE GREEN DYE

Malachite green is also known as Aniline green; Basic green 4; Diamond green B; Victoria green B and4-{[4-(Dimethylamino)phenyl](phenyl)methylidene}-N,N-dimethylcyclohexa-2,5-dien-1iminium chloride is its IUPAC name. Its molecular weight is 364.911 g/mol. Malachite Green is an organic compound that is used as a dyestuff and controversially as an antimicrobial in aquaculture. Despite its name the dye is not prepared from the mineral malachite, and the name just comes from the similarity of colour.

Malachite green (MG) ($C_{23}H_{25}ClN_2$) is water soluble cationic dye that appears as green crystalline powder and belongs to triphenylmethane category. it is also famous as aniline green or basic green. Apart from being used for the dyeing of cotton, paper, jute, silk, wool, leather and acrylic industries it is also used as food coloring agent. They are environmentally persistent and even carcinogenic so they need to be removed.
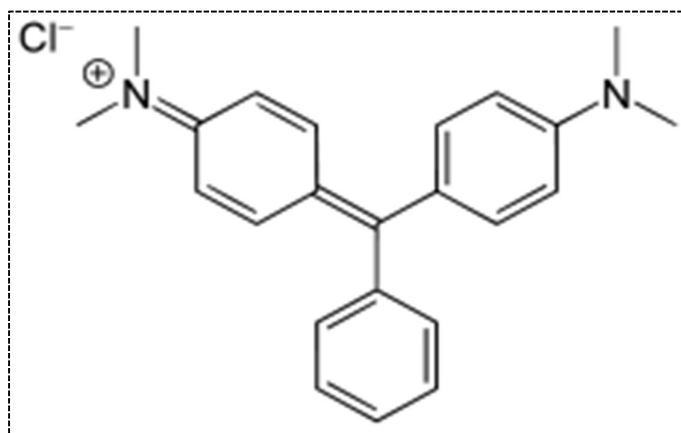
Fig 1.4 chemical structure of Malachite Green

Color – Yellow below pH 0.2 & Green above pH 1.8
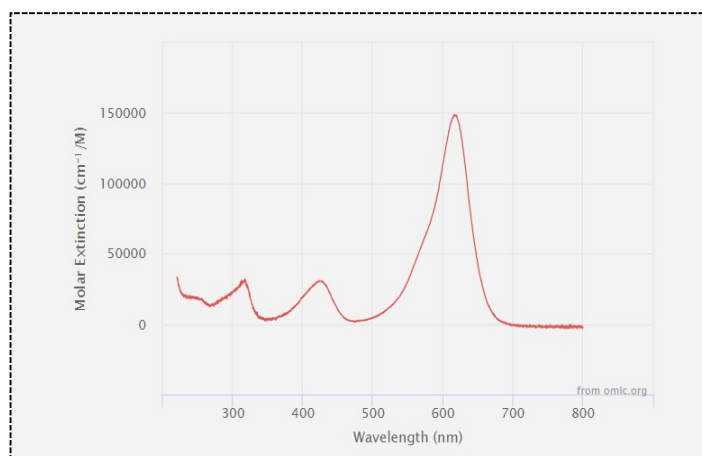
Fig 1.5 UV Spectrum of Malachite Green Maximum absorbance at Wavelength 617 nm

1.4 <u>METHYLE ORANGE DYE</u>

Methyl orange is a pH indicator frequently used in titration because of its clear and distinct color variance at different pH values. Methyl orange shows red color in acidic medium and yellow color in basic medium. Because it changes color at the pH of a mid strength acid, it is usually used in titration for acids. Unlike a universal indicator, methyl orange does not have a full spectrum of color change, but it has a sharp end point [15].
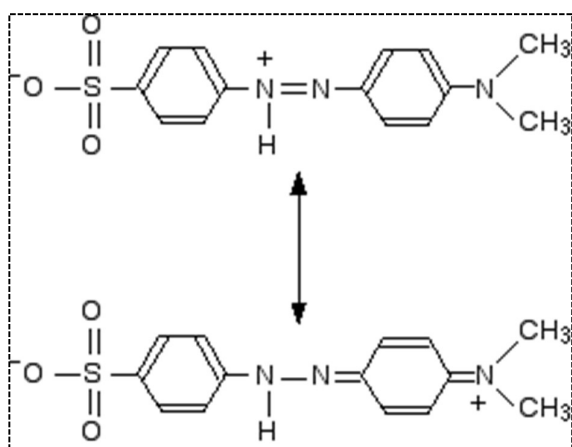
Fig 1.6 Chemical Structure of Methyle Orange
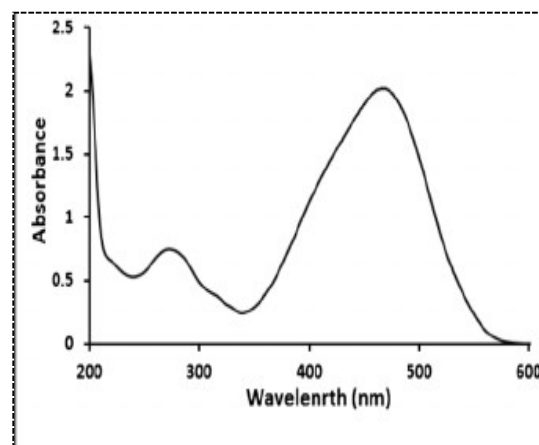
fig 1.7 UV Spectrum of Methyle Orange maximum Absorbance at wavelength 465 nm

2.0

METHODS AND METHODOLOGIES

2.0 <u>METHODS AND METHODOLOGIES</u>

2.1 CHEMICALS

Rhodamine-B , Malachite Green, SiO_2 (silica gel) , Methylene Blue, 3-aminopropyl trimetoxy silane (APTES), Poly Glutamic acid (PGA) chemicals were purchased from Sisco Research Laboratories Pvt. Ltd.(SRL) – India . Ferrous Sulphate ($FeSO_4. 7H_2O$), Ferric Chloride ($FeCl_3 . 6H_2O$) were purchased from Thomas Baker and Ammonium Hydroxide (NH_4OH) was purchased from Rankem – total scientific laboratory solution provider.

2.2 APPARATUS

UV-Visible spectra were recorded on a ELICO SL 177 Scanning Mini UV-Visible spectrophotometer.

Specifications

SPECTRAL		
Range	340 to 1000 nm	
Bandwidth	5 nm	
Readability	1 nm	
Accuracy	± 1 nm	
Repeatability	± 1 nm	
PHOTOMETRIC		
Range	± 2 Abs	
Accuracy	± 0.005 Abs at 1.0 Abs	
Repeatability	± 0.010 Abs at 1.0 Abs	
Stability (Baseline)	± 0.010 Abs/hr. after 2 hour warm up	
Stray Light	<0.05% T at 340 nm	
Readability	%T	0.01
	Abs	0.0001

LIGHT SOURCE	
Tungsten (W) Halogen Lamp	
DETECTOR	
Silicon Photo Diode	
MONOCHROMATOR	
Czerny - Turner type with 600 lines/mm Ruled Grating	
PC CONNECTIVITY	
USB Interface	
SAMPLE ATTACHMENT	
Standard	Motorised 4 position Cuvette holder for 10 mm Path Length Cuvettes.

Other laboratory grade instruments such as pH meter, Magnetic Stirrer, Shaker, and Oven used.

2.3 SYNTHESIS OF FUNCTIONALIZED SiO_2 (Silica gel) ADSORBENT

Modification of silica gel with APTES is eco-friendly. 1.0 mL of APTES was added in 100mL of distilled water acidified with acetic acid (pH 4). Two grams of activated silica gel (dried in oven at 423K for 18 hours) was added in silane solution and stirred for 2 hours at room temperature. The Si-APTES obtained was thus washed with distilled water. Ethanol and acetone for removal of un-reacted material and then dried in the oven at 393 K for 24 hours.

2.4 SYNTHESIS OF BARE MAGNETITE NANOPARTICLES (MNPs) AND PGA COATED MAGNETITE NANOPARTICLES (PGA-MNPs)

6.1g of ferric chloride and 4.2g of ferrous sulphate ($FeCl_3$:$FeSO_4$.$7H_2O$) (3:2) were mixed in deoxygenated de-ionized water and a few drops of concentrated HCl were added for complete dissolution of iron salts. The mixture was then vigorously stirred at 270 rpm on the shaker and after

heating to 85°C, 14.0 mL of ammonium hydroxide (NH₄OH) were rapidly added to co-precipitate ferrous and ferric ions [5]. The black-colored iron oxide nanoparticles obtained were further coated with PGA by adding 50mL of 0.5g PGA in deionized water and stirring for 1hr at 85°C. After completion of the reaction, the precipitated MNPs were washed several times with deionized water and dried. Adopting the same procedure, bare MNPs were also prepared without addition of PGA and the chemical reaction involved was [10] [1]

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 \text{ (black ppt)} + 4H_2O$$
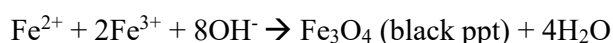
2.5 ADSORPTION OF DYES

1000 ppm or 1000 mg/L concentration stock solution of dyes – Methylene blue (MB), Rhodamine-B (RhB), Malachite Green (MG), Methyl orange (MO) were prepared by adding 250 mg of each dye in 250 mL of de-ionized water into a volumetric flask. The stock solution was diluted to give a series of standard solution of different concentrations as 100 ppm, 50 ppm, 40 ppm, 20 ppm, and 10 ppm. pH of the solution of different concentration is adjusted between 4 to 6.

2.5.1 ADSORPTION OF DYES USING Si-APTES AS AN ADSORBENT

Before adsorption, the adsorbent was dried overnight at 100°C and was kept in desiccators. Then 0.03 g of Si-APTES sorbent was shaken up with a 20 mL of the dyes solutions, at a concentration between 10 PPM and 100 PPM for 4 hours at room temperature. Solution was taken out for UV analysis [12].

2.5.2 ADSORPTION OF DYES USING BARE MNPs AND PGA-MNPs

0.02 g of bare MNPs and PGA-MNPs were added into 20.0 mL of dyes solution at a concentration between 10 PPM and 100 PPM and shaken up for 4 hours at room temperature. Then MNPs were separated by using a magnet and solution was taken up for UV analysis. After extraction supernatant was diluted to get best result is UV-Visible spectrophotometer [1].

100 ppm (95% diluted), 50 ppm (92% diluted), 40 ppm (92% diluted), 20 ppm (90% diluted), 10 ppm (90% diluted)

2.6 UV analysis

The decanted supernatant of dye after adsorption experiment were examine in UV-Visible spectrophotometer for determination of actual concentration of dye left or adsorbed by the adsorbent.

A quantitative determination of dye concentration was achieved by using the linear regression equation obtained from the calibration curve prepared with a range of dye concentration 1 to 10 ppm.

> For Methylene Blue dye---at λ_{max} = 664 nm

Linear regression equation is y = 0.095x - 0.088

calibration curve for MB dye

y = 0.0953x - 0.0884
R² = 0.9839
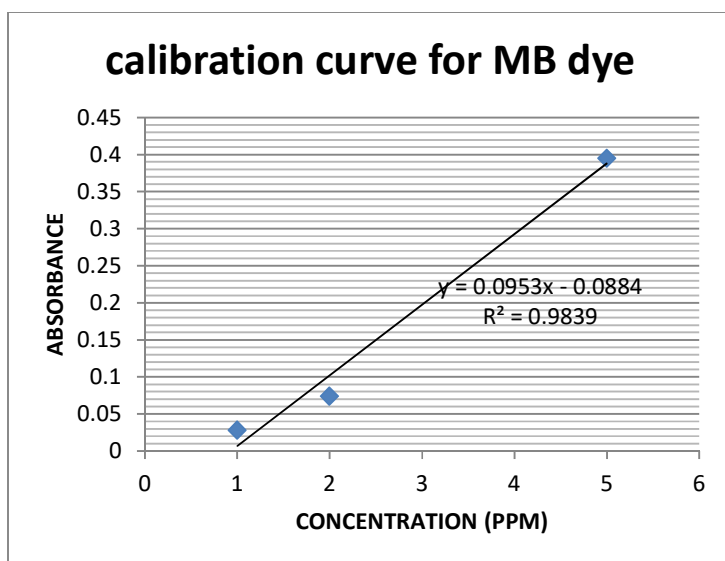
CONCENTRATION (PPM)	ABSORBANCE
1	0.028
2	0.074
5	0.395

➢ For Rhodamine-B dye at λ$_{max}$ = 554 nm

Linear regression equation is y = 0.156x + 0.030

Calibration curve for Rhodamine B dye

y = 0.1564x + 0.0305
R^2 = 0.9962
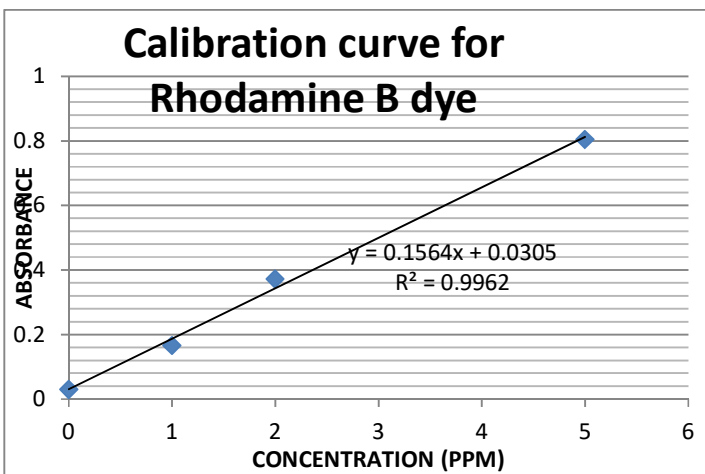
CONCENTRATION (PPM)	ABSORBANCE
1	0.166
2	0.372
5	0.805

➢ For Malachite Green Dye λ$_{max}$ = 617 nm

Linear regression equation is y = 0.038x + 0.045

MALACHITE GREEN CALLBRATION CURVE

y = 0.0388x + 0.0456
R^2 = 0.9951
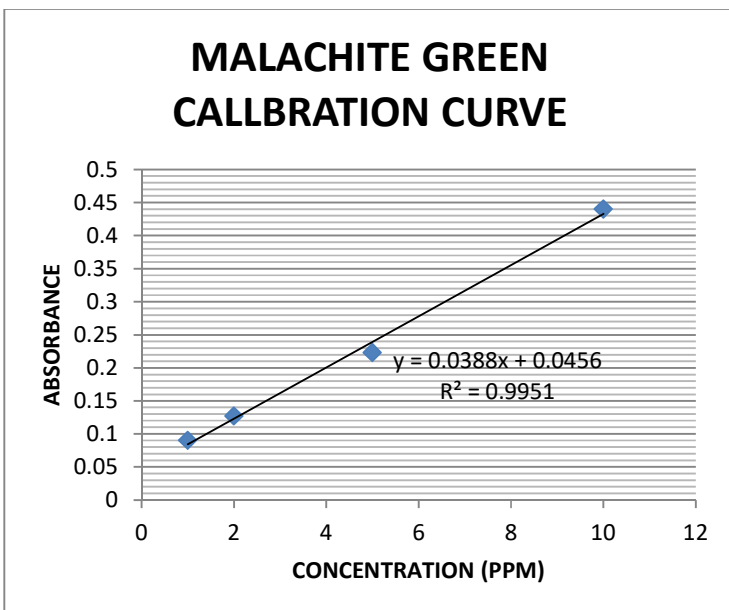
CONCENTRATION (PPM)	ABSORBANCE
1	0.09
2	0.127
5	0.223
10	0.44

➤ For Methyl Orange Dye λmax = 465 nm

Linear regression equation is y = 0.077x + 0.023

METHYL ORANGE CALIBRATION CURVE

y = 0.0774x + 0.023
R² = 0.9985

ABSORBANCE (y-axis)

CONCENTRATION (PPM) (x-axis)
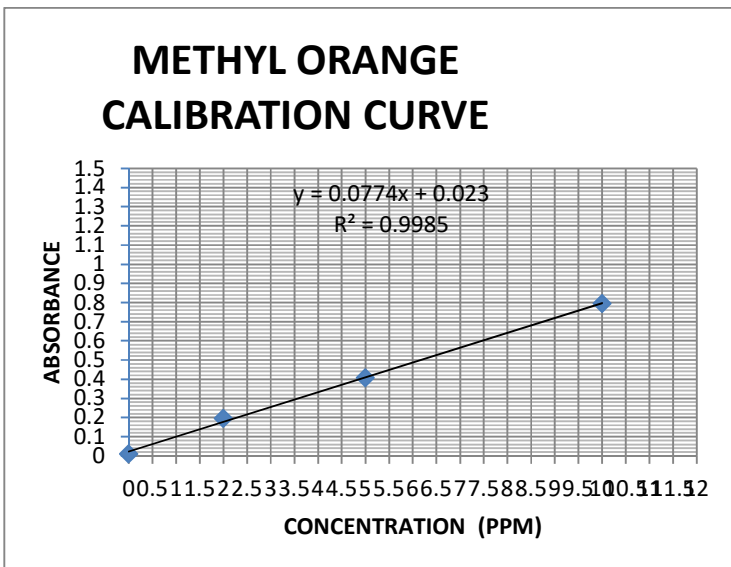
CONCENTRATION (PPM)	ABSORBANCE
1	0.061
2	0.196
5	0.407
10	0.795

3.0

RESULTS AND DISCUSSION

3.0 RESULTS AND DISCUSSION

3.1 RESULTS OF ANANLYSIS FOR METHYLENE BLUE DYE BY UV METHOD

3.1.1 ADSORPTION USING Si-APTES

CONCENTRATION	DILUTION	CONCENTRATION2	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	664nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.168	0.769	7.69	2.31	1.54
20	90%	2	0.081	1.744	17.44	2.553	1.702
40	92%	3.2	0.17	2.76	34.492	5.5058	3.672
50	92%	4	0.231	3.308	41.356	8.644	5.763
100	95%	5	0.301	4.09	81.8	18.19	12.131

After extraction the solutions were diluted to different concentration so it can be analyzed by UV spectrometer so result comes in range of spectrometer. In the above table concentration2 is calculated concentration after dilution if extraction not done (before extraction) and Actual concentration2 is concentration of solution after extraction done.

Adsorption using Si-APTES adsorb minimum 1.54 mg/g (at low concentration) and maximum 12.131 mg/g (at high concentration) of MB dye. The adsorption is due to the electrostatic interaction and formation of coordinate bond between NH_2 and cationic center in the MB dye. (MB is a cationic Dye).
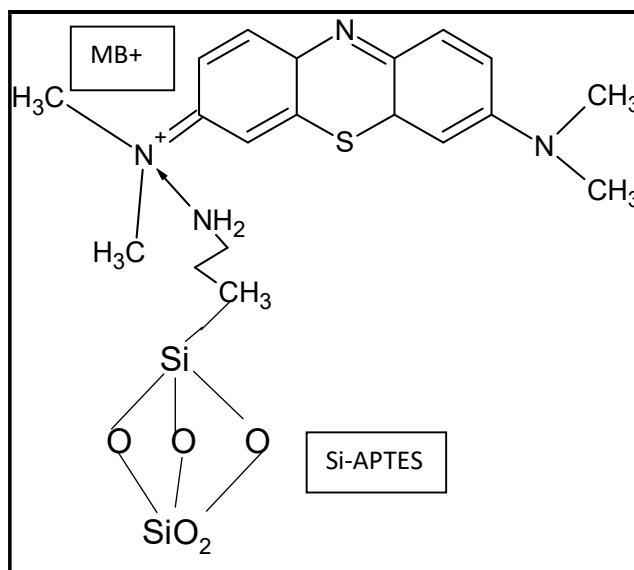
Fig 1.8 Interaction between Si-APTES and MB dye

3.1.2 *ADSORPTION USING BARE MNPs AND PGA-MNPs*

WITH BARE MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	After Dilution (PPM)	664nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.02	0.748	7.48	2.52	2.52
20	90%	2	0.07	1.628	16.288	3.712	3.712
40	92%	3.2	0.15	2.495	31.19	8.101	8.101
50	92%	4	0.2	2.99	37.39	12.603	12.603
100	95%	5	0.24	3.483	69.67	30.33	30.33

WITH PGA-MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	664nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.06	0.337	3.37	6.63	6.63
20	90%	2	0.03	1.268	12.68	7.32	7.32
40	92%	3.2	0.101	2.02	25.24	14.76	14.76
50	92%	4	0.35	4.61	57.64	42.36	42.36
100	95%	5	0.056	1.52	30.4	69.6	69.6

Adsorption of MB dye using bare MNPs is due to the physical adsorption on the large surface area or pores provided by the magnetite nanoparticle,[10][1] minimum adsorption was 2.52 mg/g and maximum adsorption was 30.33 mg/g. While in case of PGA-MNPs adsorption is chemisorptions due to the interaction between alpha carboxyl group of PGA and cationic centre present in MB dye shows minimum adsorption 6.63 mg/g and maximum adsorption was 69.6 mg/g which is nearly double of result shows by bare MNPs.
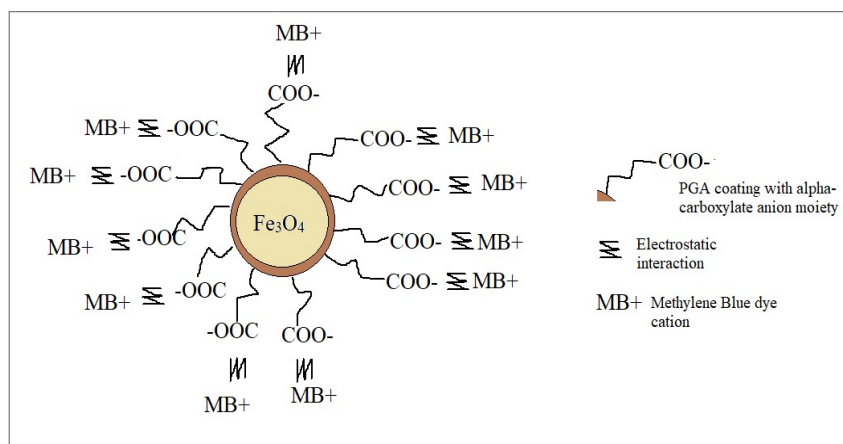
Fig 1.9 schematic diagram showing the proposed mechanism of MB dye adsorption on PGA-MNPs

3.2 RESULT OF ANALYSIS FOR RHODAMINE-B DYE BY UV METHOD

3.2.1 *ADSORPTION USING Si-APTES*

CONCENTRATION	DILUTION	CONCENTRATION2	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILLUTION (PPM)	554nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.164	0.85	8.5	1.5	1
20	90%	2	0.312	1.79	17.9	2.1	1.4
40	92%	3.2	0.45	2.71	33.97	6.03	4.02
50	92%	4	0.51	3.097	38.72	11.28	7.52
100	95%	5	0.65	3.99	79.96	20.04	13.36

Adsorption using Si-APTES adsorb minimum 1.0 mg/g (at low concentration) and maximum 13.36 mg/g (at high concentration) of RhB dye. The adsorption is due to the electrostatic interaction and

formation of coordinate bond between NH_2 and cationic center in the RhB dye. (RhB is a cationic Dye).
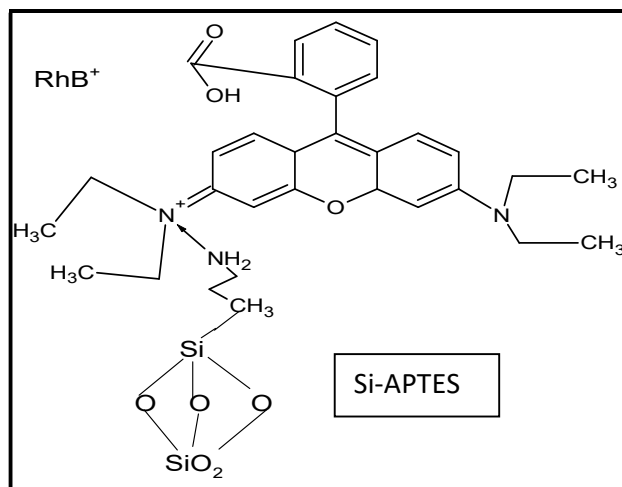
Fig 2.0 interaction between Rhodamine B dye and Si-APTES

3.2.2 *ADSORPTION USING BARE MNPs AND PGA-MNPs*

Adsorption of RhB dye using bare MNPs is due to the physical adsorption on the large surface area or pores provided by the magnetite nanoparticle.

 WITH BARE MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	554nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.153	0.78	7.8	2.2	2.2
20	90%	2	0.295	1.69	16.9	3.1	3.1
40	92%	3.2	0.44	2.605	32.57	7.43	7.43
50	92%	4	0.514	3.09	38.625	11.375	11.375
100	95%	5	0.592	3.59	71.8	28.2	28.2

WITH PGA-MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILJUTION (PPM)	554nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					$X\{100/(100-Y)\}$		
10	90%	1	0.64	0.36	3.6	6.4	6.4
20	90%	2	0.21	1.15	11.5	8.5	8.5
40	92%	3.2	0.331	1.92	24	16	16
50	92%	4	0.163	0.84	10.5	39.5	39.5
100	95%	5	0.281	1.6	32	68	68

Minimum adsorption was 2.2 mg/g (at low concentration) and maximum adsorption was 28.2 mg/g. (at higher concentration). While in case of PGA-MNPs adsorption is chemisorptions due to the interaction between alpha carboxyl group of PGA and cationic centre present in RhB dye shows minimum adsorption 6.4 mg/g (at lower concentration) and maximum adsorption was 68.0 mg/g (at higher concentration) which is nearly double of result shows by bare MNPs.

Fig 2.1 schematic diagram showing the proposed mechanism of RhB dye adsorption on PGA-MNPs

3.3 RESULT OF ANALYSIS FOR MALACHITE GREEN DYE BY UV METHOD

3.3.1 *ADSORPTION USING Si-APTES*

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	617nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.05	0.11	1.1	8.9	5.93
20	90%	2	0.078	0.84	8.4	11.6	7.73
40	92%	3.2	0.129	2.15	26.875	13.125	8.75
50	92%	4	0.154	2.8	35	15	10
100	95%	5	0.195	3.85	77	23	15.33

Adsorption using Si-APTES adsorb minimum 5.93 mg/g (at low concentration) and maximum 15.33 mg/g (at high concentration) of MG dye. The adsorption is due to the electrostatic interaction and formation of coordinate bond between NH_2 and cationic center in the MG dye. (MG is a cationic Dye).
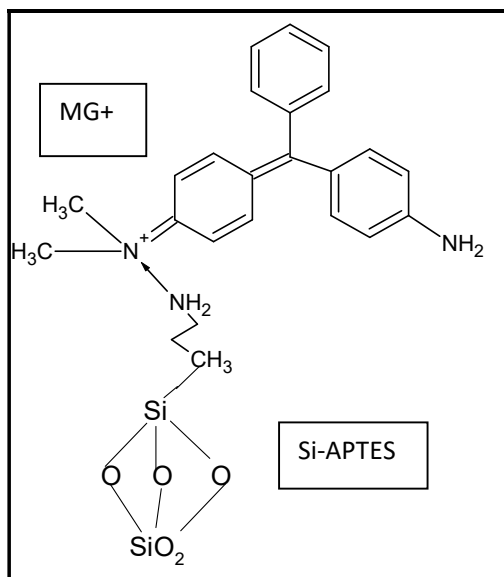
Fig 2.2 interaction between Malachite Green dye and Si-APTES

3.3.2 *ADSORPTION USING BARE MNPs AND PGA-MNPs*

WITH BARE MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	617nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.076	0.78	7.8	2.2	2.2
20	90%	2	0.109	1.64	16.4	3.5	3.5
40	92%	3.2	0.147	2.62	32.75	7.25	7.25
50	92%	4	0.168	3.16	39.5	10.5	10.5
100	95%	5	0.19	3.73	74.6	25.4	25.4

WITH PGA-MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	617nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.059	0.34	3.37	6.63	6.63
20	90%	2	0.095	1.27	12.7	7.3	7.3
40	92%	3.2	0.129	2.15	26.87	13.125	13.125
50	92%	4	0.077	0.81	10.12	39.88	39.88
100	95%	5	0.128	2.13	42.6	57.4	57.4

Adsorption of MG dye using bare MNPs is due to the physical adsorption on the large surface area or pores provided by the magnetite nanoparticle. Minimum adsorption was 2.2 mg/g (at low concentration) and maximum adsorption was 25.4 mg/g. (at higher concentration).

Fig 2.3 schematic diagram showing the proposed mechanism of MG dye adsorption on PGA-MNPs

While in case of PGA-MNPs adsorption is chemisorptions due to the interaction between alpha carboxyl group of PGA and cationic centre present in MG dye shows minimum adsorption 6.63 mg/g (at lower concentration) and maximum adsorption was 57.4 mg/g (at higher concentration) which is nearly double of result shows by bare MNPs
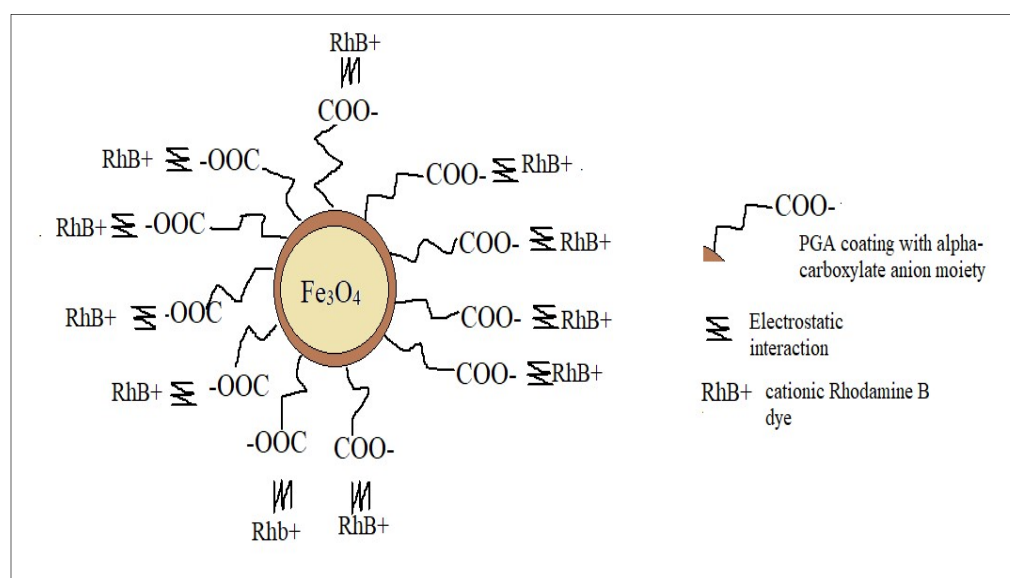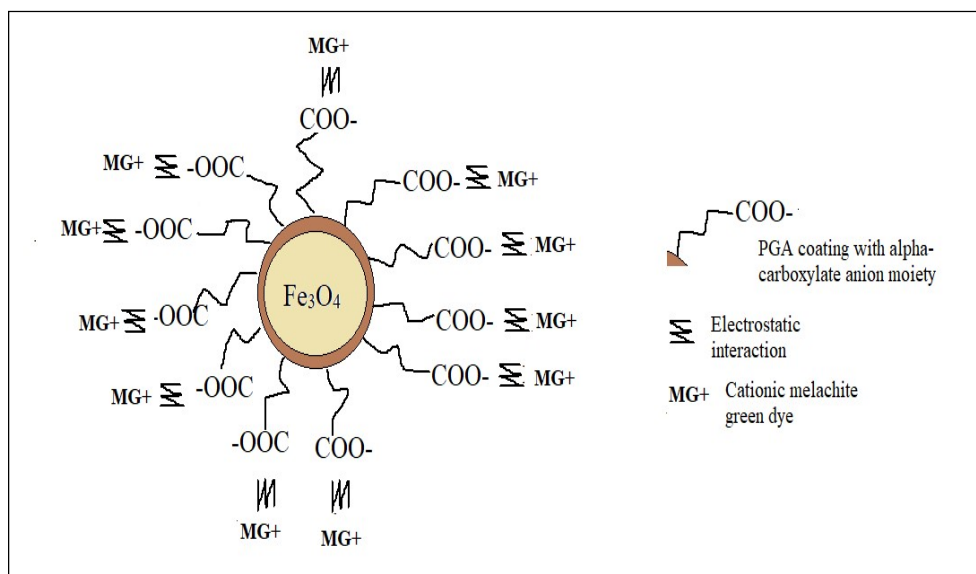
3.4 RESULT OF ANALYSIS FOR METHYL ORANGE DYE BY UV METHOD

3.4.1 *ADSORPTION USING Si-APTES AS AN ADSORBANT*

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	465nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
20	90%	2	0.159	1.9	19	1	0.66
40	92%	3.2	0.209	2.53	31.625	8.375	5.583
50	92%	4	0.248	3.02	37.75	12.25	8.16
100	95%	5	0.32	3.93	78.6	21.4	15

At acidic pH (the dissociation constant pK_a for MO is 3.46, so MO molecules predominantly present as monovalent anions) MO was protonated and hence the electrostatic attraction between protonated MO and NH_2 group in Si-APTES occure which causes adsorption of MO dye on surface of Si-APTES. Adsorption using Si-APTES adsorb minimum 0.66 mg/g (at low concentration) and maximum 15.0 mg/g (at high concentration) of MO dye. The adsorption is due to the electrostatic interaction and formation of coordinate bond between NH_2 and cationic center in the MO dye [12].

3.4.2 ADSORPTION USING BARE MNPs AND PGA-MNPs

WITH BARE MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	465nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					X{100/(100-Y)}		
10	90%	1	0.068	0.75	7.5	2.5	2.5
20	90%	2	0.14	1.66	16.6	3.4	3.4
40	92%	3.2	0.216	2.62	32.75	7.25	7.25
50	92%	4	0.242	2.95	36.875	13.125	13.125
100	95%	5	0.289	3.54	70.8	29.2	29.2

Adsorption of MO dye using bare MNPs is due to the physical adsorption on the large surface area or pores provided by the magnetite nanoparticles. Minimum adsorption was 2.5 mg/g (at low concentration) and maximum adsorption was 29.2mg/g (at higher concentration).

WITH PGA-MNPs

CONCENTRATION	DILUTION	CONCENTRATION	ABSORBANCE	CONC. (PPM)	ACTUAL CONC.2	CONC. ADSORBED	EFFICIENCY
PPM	Y	AFTER DILUTION (PPM)	465nm	X	(PPM)	PPM	mass of dye(mg)/mass of sorbent(g)
BEFORE EXTRACTION		BEFORE EXTRACTION		AFTER EXT.	AFTER EXTRCT.		mg/g
					$X\{100/(100-Y)\}$		
10	90%	1	0.056	0.59	5.9	4.1	4.1
20	90%	2	0.121	1.42	14.2	5.8	5.8
40	92%	3.2	0.2	2.42	30.25	9.75	10.112
50	92%	4	0.227	2.76	34.5	15.5	15.5
100	95%	5	0.26	3.17	63.14	36.86	35.5

While in case of PGA-MNPs adsorption is chemisorptions due to the interaction between alpha carboxyl group of PGA and cationic centre present in MO dye shows minimum adsorption 4.1 mg/g (at lower concentration) and maximum adsorption was 35.5 mg/g (at higher concentration) which is nearly double of result shows by bare MNPs .

4.0

CONCLUSION

4.0 <u>CONCLUSION</u>

- ✓ Si-APTES can be used as an adsorbent for removal of dyes from aqueous solution , but it is efficient for lower concentrated solution of dyes , at higher concentration bare MNPs and PGA coated MNPs gives better result.

- ✓ Polyglutamic acid based sorbent is very efficient to remove dyes from aqueous solution as it doubles the efficiency of adsorption compare to bare MNPs. MNPs are also easily decanted by using a magnet which suggest that in place of Si-APTES we can use bare magnetite nanoparticles.

- ✓ In case of cationic dyes such as methylene blue (MB), Malachite Green (MG), and Rhodamine B (RhB) PGA coated MNPs are highly efficient because of permanent cationic centre present in the the dye but in Case of Methyl Orange dye it is less efficient because cationic centre is not permanently exist or may be less stable. So in case of MO dye the efficiency of adsorption is nearly same for bare MNPs and PGA-MNPs.

- ✓ Magnetite Nanoparticles (Fe_3O_4) were easily prepared in laboratory and stable in de-ionized water. The challenge is to store it, because it is readily oxidize in air at 60^oC so it should be placed or store in vacuum or deoxygenated water.

5.0

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5.0 REFERENCES

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