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Research Article

SURFACTANT ASSISTED SILICA- GRAPHENE COMPOSITE AS EFFECTIVE ADSORBENT AGAINST METHYLENE BLUE DYE

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ABSTRACT

Surfactant based composites have good capability for elimination of colored pollutants from industrial waste water. In this study, two different Silica-Graphene (SG) and Surfactant assisted Silica-Graphene (SSG) composites was prepared by sol-gel technique and used as adsorbents for the removal of methylene blue (MB) dye from aqueous solution. The adsorption properties of prepared composite materials were characterized by Scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray phase diffraction and Raman spectroscopy. The adsorbent characteristic property of the composites was studied using UV-Vis spectrophotometer and zeta potential measurements. Batch adsorption experiments were carried out to study the effect of percentage removal versus contact time on dye adsorption properties at different pH. The developed colloidal silica-graphene was porous structure with a size > 200 nm is uniformly distributed and significantly enhances adsorption capacity. The isotherm analysis indicated that the adsorption data can be represented by Langmuir isotherm model. Surface charge of developed composite was assessed by Zeta potential measurement result showed negative charge -28.3mV at all pH value. The results show that the electrostatic interaction between cationic dyes and the negative surface of composite has a great effect on adsorption capacity.

Keywords: Graphene, SiO_2, Surfactant, Composite, Methylene blue dye, Adsorption

1. INTRODUCTION

Nanocomposites like silica graphene are currently attracting immense role as new class of adsorbent and play a promising role towards the removal of dyes or pesticides from aquatic environment [1]. Over the past decades, increasing discharge of dyes and pesticides has been detected in the aquatic environment which caused serious health and environmental problems. Dye in aqueous environment creates a temperature driven in equality; reduce the penetration of sunlight and harms aquatic life. The method of dye removal from industrial effluents includes coagulation, flotation, biological treatment, adsorption and oxidation [2]. Among these options, adsorption is most preferred method [3]. Activated carbon is the most widely used sorbent, and it has excellent sorption properties for a considerable number of synthetic dyes removal [4]. However, the development of inexpensive adsorbent materials remains a challenging task and researchers continue to work on it. Carbon based adsorbent is generally energy intensive, making commercially available products relatively expensive. Generally, a large amount of costly carbon sorbent is needed to remove the dye from a large volume of effluent, which hinders its commercialization [5]. Adsorption has emerged as the most efficient, simple and promising fundamental technique in the waste water treatment process which certainly aims for the removal of organic pollutants. It is based on physico-chemical technique that separates dye from aqueous effluent waste. The various adsorbents used for the removal of dye from aqueous solution are as mentioned in table1.

Table 1: Various adsorbents used for the removal of dye from aqueous solution

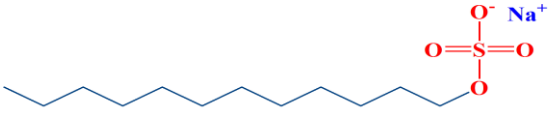
Methylene Blue	Kaolinite, Cellulose-based adsorbent from saw [6]
Malachite Green	Pithophorasp, saw dust [7]
Anionic dyes Cross-linked	chitosan beads [8]
Dye and related compounds	Silica [9]
Orange II and Crystal Violet	Chitosan [10]
Satranine	Rice husk carbon [11]
Basic dyes	Akashkinari coal [12]

Among these options, silica based material has been found to be ecofriendly and economical. Therefore, the aim of this present research was to develop a composite of silica-graphene (SG) and surfactant assisted silica–graphene (SSG), and evaluate it for the decolorisation of methylene blue (MB) dye from aqueous solution. Since its discovery in 2004 [13], graphene and its derivate have attracted tremendous research interests not only in electronics and energy fields [14], but also in environmental applications [15]. Special properties of silica and graphene based composite, such as large surface area [16], anti-bacterial nature, reduced cytotoxicity [17], and tunable chemical properties [18] make these materials very attractive choices for decolonization of dyes from textile industry of aqueous waste water. Silica-Graphene composite has received great attention as with a high surface area it shows good adsorption capacity with some dye and heavy metals. This study focuses on the development of ecofriendly and cost effective two composites, silica-graphene and surfactant assisted silica-graphene composite and compare their adsorbent efficiency to remove methylene blue dye from aqueous solution. Because of good adsorption capability of composite, non-toxicity and versatility it can be utilized as low cost adsorbent for industrial waste dye treatment and help in purification of waste water.

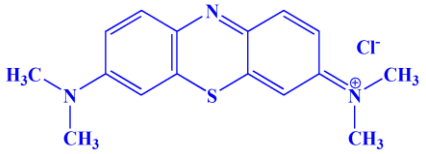
2. EXPERIMENTAL METHODOLOGY

2.1. Materials

Tetraethyloxysilane (TEOS) (99.9% Sigma Aldrich), absolute ethanol (99.9% Merck, India), Sodium Dodecyl Sulfate (SDS), (anionic surfactant), (LobaChemie, India); Graphene powder from Sigma Aldrich and methylene blue (MB) was purchased from Rankem (India) and used as received. Deionized (DI) water was used as the solvent throughout. A stock solution of 1000 mg $L^{-1}$of MB dye was prepared by dissolving the required amount of dye powder in double distilled water. All working solutions of the desired concentrations were prepared by diluting the stock solution with distilled water.



Sodium dodecyl sulphate (SDS, $NaC_{12}H_{25}SO_4$)



Methylene blue (MB, $C_{16}H_{18}ClN_3S$)

Fig. 1: Structural formula of surfactant and dye

2.2. Preparation of Silica-Graphene/Surfactant assisted Silica-Graphene composite

The synthesis of silica-graphene composite was carried out using precursor TEOS as source of silica, ethanol, water and anionic surfactants SDS by green method sol-gel technique. In our previous study nanoparticle of silica was synthesized by using SDS as surfactant [23].Two different types of SiO_2 based composite material were developed. SG composite was fabricate using, 0.19 mol ethanol, 0.16 mol deionized water, 4.45 mmol TEOS and 0.25mg of graphene powder and SSG composite was fabricate using 0.19 mol ethanol, 0.16 mol deionized water, 4.45 mmol TEOS, 0.25 mg of graphene powder and 8.10 mmol of SDS is taken mentioned in table 2.

Table 2. Composition of sols for the preparation of pure SiO2 nanoparticle, SG and SSG composites used for removal of MBfrom aqueous solution

Composition of composite material	Pure SiO_2 nano particle (A)	SiO_2 with Graphene Composite (SG) (B)	SiO_2 with Graphene and SDS Composite (SSG)(C)
TEOS	4.45 mmol	4.45 mmol	4.45 mmol
Ethanol	0.19 mol	0.19 mol	0.19 mol
Water	0.16 mol	0.16 mol	0.16 mol
Surfactant (SDS)	--------	--------	8.10 m mol
Graphene	--------	0.25 mg	0.25 mg

To prepare the homogenous solution, TEOS was mixed with ethanol and sonicated for 30 minutes using a ultra-sonicator bath. After that, distilled water was added to TEOS-ethanol suspension drop by drop.

Graphene powder was added to the TEOS solution slowly and sonicated for 15 min with and without surfactant to form a homogenous solution.

The formation of silicon dioxide requires the removal of two oxygen atoms. The hydrolysis of TEOS was done under acidic as well as basic conditions. Sol-gel reaction involves hydrolysis as well condensation reaction, represented in fig.2. In the first step, precursor tetraethylorthosilicate, chemical formula Si $(OC_2H_5)_4$ (TEOS) is first hydrolyzed by reacting with water in the presence of solvent such as ethanol and the acid catalyst which is used to enhance the hydrolysis rate. In the next step condensation reaction takes place, water and alcohol product formed in the hydrolysis reaction get polymerized and form siloxane bonds.

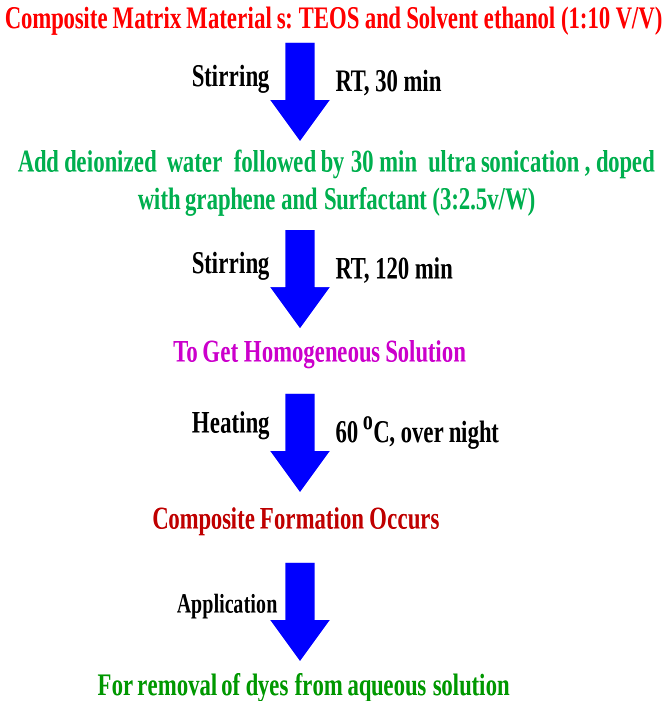


Fig. 2: Schematic diagram of the steps involved in the sol-gel processing to obtain the composite material

2.3. Characterization of SG/SSG Composite

Silica-Graphene surfactant composites were characterized by using different techniques. The presence of graphene and silica was determined by X-ray diffraction (XRD) measurements carried out using a PANalyticalX'Pert PRO XRD with Cu Kα radiation ($\lambda = 0.1548$ nm). The patterns were recorded in 2θ ranging between 10^0 and 70^0 with a step size of 10^0 and a scan speed of 0.5 s until a good signal-to noise ratio was achieved.

Fourier transform infrared (FTIR) spectra were obtained on a PerkinElmer Spectrum Version 10.4.00 scan range of 4000-400 cm^{-1} and at a resolution of 4 cm^{-1}. Raman spectra were measured on LabRam-1B French DilorComand. The microstructure of the composite powder wasstudied by scanning electron microscopy (SEM) Nova Nano FE-SEM 450 (FEI).

3. RESULT AND DISCUSSION

XRD and Raman spectroscopy is an important tool to study the interaction between graphene like material and silica nanoparticle with surfactant. Figure (3a and 3b) shows the XRD pattern of SG/SSG composite. In the XRD pattern of the SG sample the characteristic peak of graphene appears at 26.71, corresponding to a layer-to-layer distance (d-spacing) of 0.338 nm, infers well-packed layered structure of graphene as shown in Figures 3a and 3b. Peak shifts can be observed to a lower angle at $2\theta = 6.63^o$ (d-spacing = 1.32 nm). It may due to the exposed graphene wrapped with SDS surfactant.

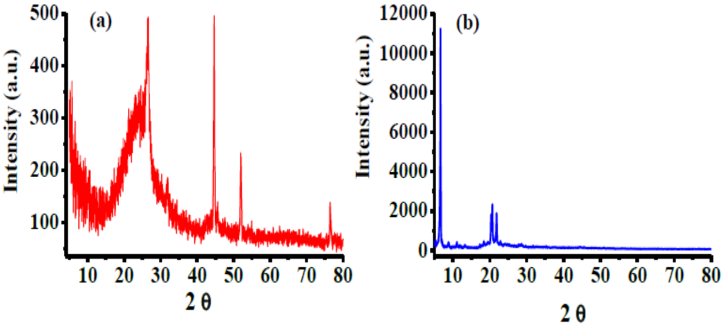


Fig. 3: Powder XRD pattern of (3a) SG and (3b) SSG composite

Fourier transform infrared (FTIR) spectra of the composite SG shows the signal centered at 1068 cm^{-1}which is attributed to the anti-symmetric stretching of the Si–O–Si silica bond and the peak at 964 cm^{-1} is assigned to the stretching mode of Si-OH Figure 4a. The spectra (Figure 4b) due to interaction of SDS with graphene displayed an extra C-H peak resonance at 1468 cm^{-1}, and 2849 cm^{-1}, 2916 cm^{-1} are the characteristic peaks of surfactant SDS that were absent in the spectra in Figure 4a.

Figure 5a shows the Raman spectra of the prepared SG composites along with the operating temperature. There were Si peaks in the SG composites at 519 cm^{-1} and also a strong peak of graphene at 1600 cm^{-1} in the G band and 1350 cm^{-1} in the D band. But when SG composite is modified by adding anionic surfactant then extra peaks at 1298 cm^{-1} and 3000 cm^{-1} appear as shown in Figure 5b.The extra peak may be due to the interaction of graphene with surfactant.

Scanning Electron Microscopic (SEM) images also illustrate presence of graphene on silica nanoparticle.The SiO_2 particles were white circular nano-balls, on the black graphene and the aggregation created a microspore structure (Figure. 6a). The morphology of the SiO_2 nanoparticles experienced change during modification with SDS surfactant. Graphene was highly wrapped with surfactant SDS and forms blocky flakes structure (Figure. 6b). Many wrinkles, considered to be high-energy adsorption sites, appeared on the surface of SSG composite. Compared with the SG composite, certain small extended layers appeared in the SSG; which enhance the surface area.

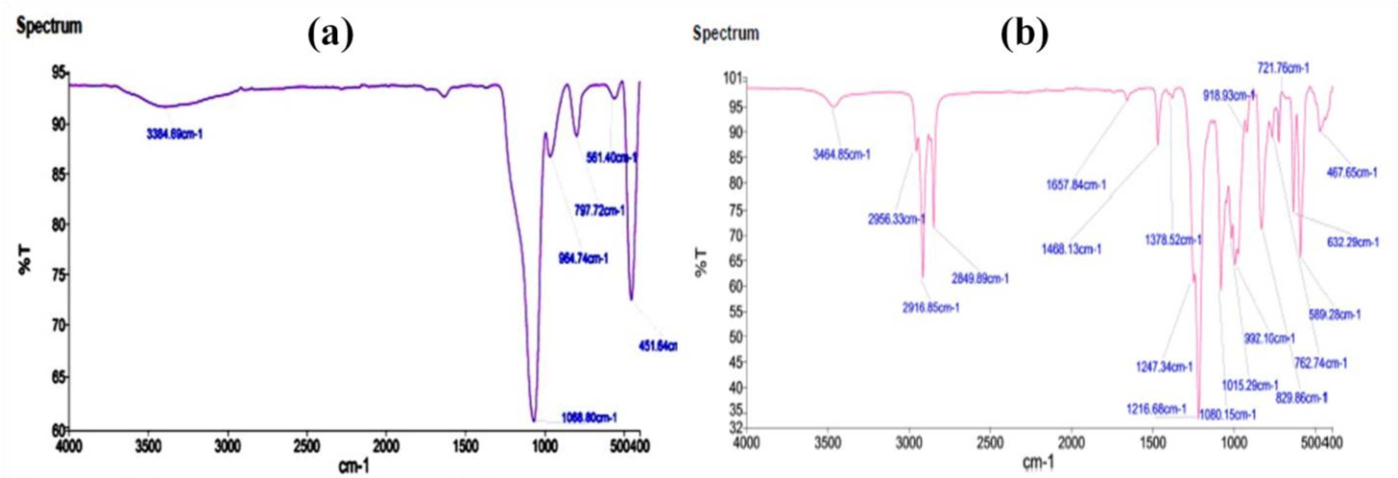


Fig. 4: FT-IR spectra of composite powder (4a) SG and (4b) SSG.

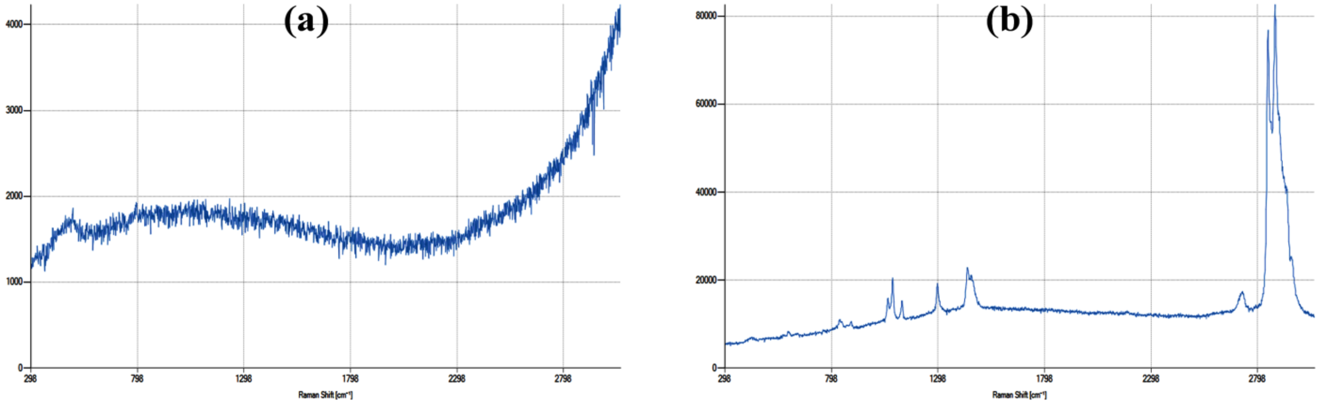


Fig. 5: Raman spectra of the prepared (5a) SG and (5b) SSG composites

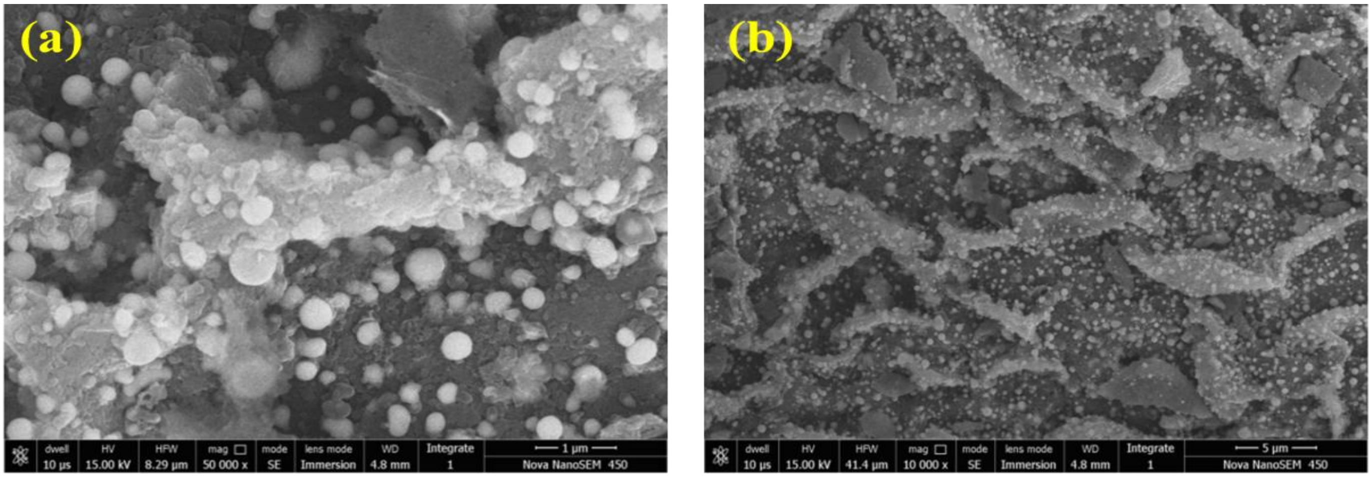


Fig. 6: Microstructure and morphology of the composite powder of (6a) SG and (6b) SSG

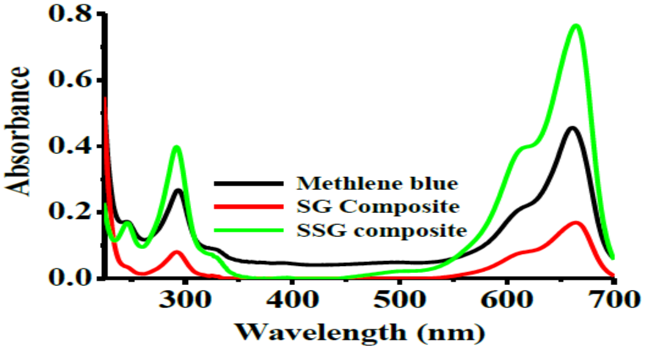


Fig. 7: Absorption spectra of methylene blue dye, SG and SSG composite in aqueous medium.

The exposed graphene interacts with the SDS which results in an increase in the surface area, surface energy and make SSG a superior adsorbent compared to the SG composite. To compare the absorbance of SG/SSG composite a aqueous suspension was centrifuged at 2000 rev/min for 10 min and the absorbance of the supernatant was measured by UV-Vis NIR spectrophotometer. Figure 7 shows standard curve with a maximum at 670 nm of MB dye.

3.1. Adsorption Study

In this study, the adsorption of methylene blue dye on the porous solid SSG composite is illustrated by a pictorial representation in figure 8.The electrostatic attraction between cationic dye and negative surface of composite thought to make important factor for interaction of dye and composite and it also greatly increases the adsorption capacity.

Methylene Blue is a cationic dye and SDS ananionic surfactant gets wrapped on the surface of SSG that enhance the surface area as well as electrostatic attraction between composite and cationic dye. Therefore, anionic nature of composite could selectively remove MB cationic dye.

Fig. 8: Pictorial representation adsorption of MB dye bynanocomposite material

3.2. Adsorption Isotherm

To study the removal efficiency of prepared composite, standards stock solution of MB (1gm methylene blue analytical grade dissolved in 1000 mL of distilled water) was prepared. The different concentration (10, 30 and 50ppm) was taken in a 250 mL stoppered conical flask containing 50.0 mL of MB solution. The pH of initial MB solution was adjusted by sodium hydroxide (0.10 M) and hydrochloric acid (0.10 M). 0.025g amount of the adsorbent SG and SSG was separately added in stoppered conical flask containing 50.0 mL of MB solution. The adsorption of dye at 10 min was found faster and then decreases with increase in time. Residual MB concentration in the supernatant was measured using a UV-vis spectrophotometer.

The adsorption amount (q) and percentage removal (E %) are calculated based on the difference in the MB concentration in the aqueous solution before and after adsorption, according to the following equations.

$$q = \frac{(Co-Cf)V}{W} \qquad (1)$$

$$E\% = \frac{(Co-Cf)100}{Co} \qquad (2)$$

where, *q* (mg/g) represents the amount of MB adsorbed onto adsorbent; *Co* and *Cf* (mg/L) represent MB concentration before and after adsorption, respectively; *V* (mL) is MB solution volume used and *W* (g) is the weight of adsorbent.

The Langmuir isotherm was used for determination of adsorbent dose requirement. The isotherm studied was carried out for optimum condition and adsorption take places as homogeneous sites. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation (shown in equation 3). In order to establish the maximum adsorption capacity, the Langmuir isotherm equation of the following linearized form was applied to the sorption equilibrium at different adsorbents doses.

$$\frac{1}{q_e} = \frac{1}{q_m k_a}\frac{1}{C_e} + \frac{1}{q_m} \qquad (3)$$

Where C_e represents the equilibrium dye concentration in solution (mg/L), q_e is the adsorption capacities (amount of dye adsorbed per weight of adsorbent, mg/g) q_m and *Ka* are Langmuir constant that can be determined from above Langmuir linear equitation. A graph of $1/q_e$ verses $1/C_e$ was plotted. The constants q_m and Ka can be evaluated from the intercept and slope of this linear plot. The slope of this plot is equivalent to $(1/q_mK_a)$ when it intercepts $1/q_m$. Also, by comparing the correlation coefficient (R^2 value) shown in figure 9, the Langmuir isotherm model obtained a better fit ofthe experiment data.

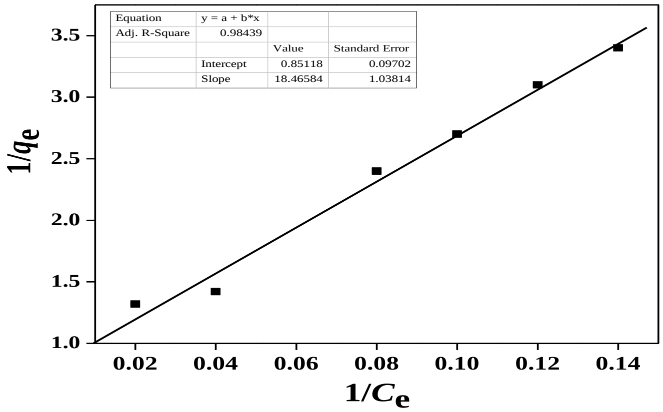


Fig. 9: Langmuir isotherm for MB onto SSG Composite (initial concentration: 60-100 mg/L; time: 200 minutes, pH: 6.5-7; room temperature)

3.3. Study of effective factors (pH and contact time) to optimize adsorption of methylene blue and removal efficiency using SG/SSG composite.

The effect of contact time and pH on adsorption of methylene blue was studied and results are shown in figure 10. In different bottles, 50 ml of the aqueous dye solution at pH of 4, 5, 6, 7, 8, 9, 10, 11 and 12 were prepared and left for different time intervals (12 hours, 24hours and 72 hours). It was observed that dye and SG/SSG composite comes in contact with easily available active sites of composite. As adsorption of the dye occurs, after 10 min, dyes find out more active sites for adsorption on the composites. So, removal percentage is increased within 90 min. As compared to SG, SSG composite decolourised dye more efficiently as shown in figure 11, when left in contact for overnight in order to get maximum removal percentage.

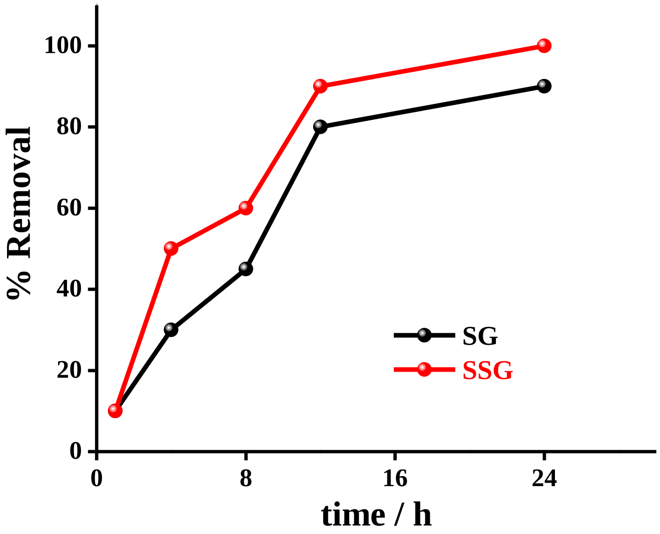


Fig. 10: Effect of contact time of MB dye on % removal of adsorbent dose 0.025g\ml at pH 8

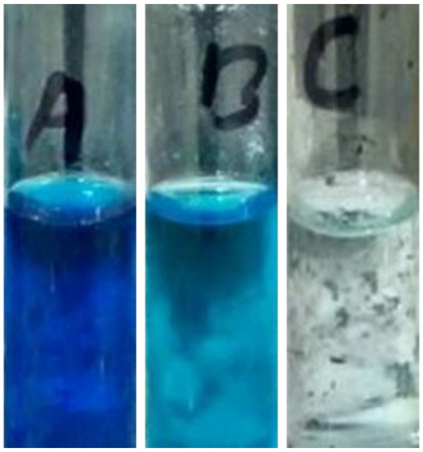


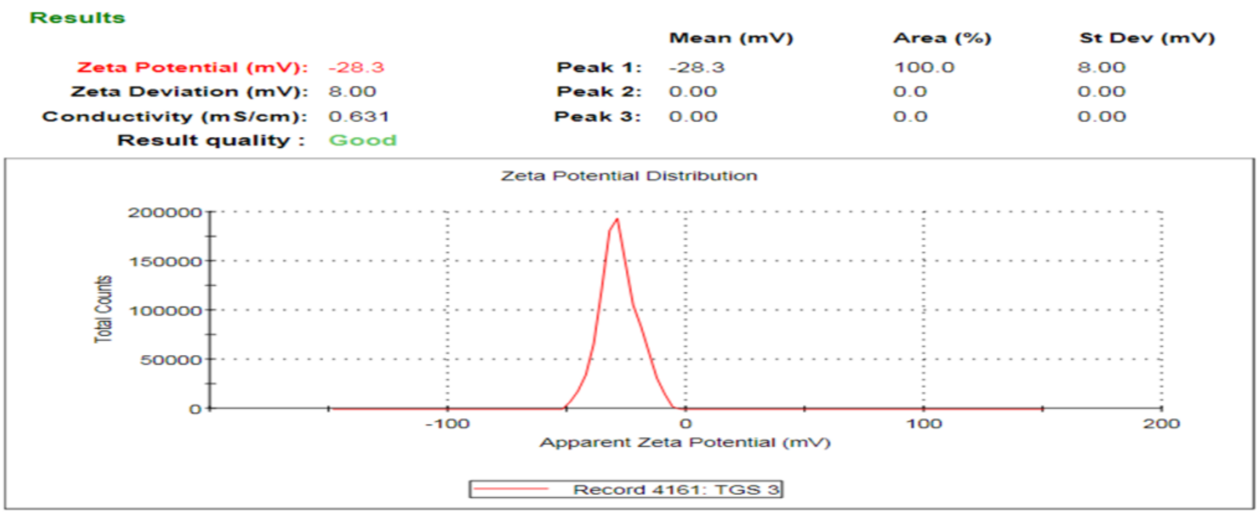
Fig. 11: Pictorial representation of decolourization of methylene blue (A) by SG composite (B) and SSG composite (C) after overnight contact period.

3.4. Zeta potential analysis

Zeta potential is related to interactions between silica-graphene and surfactant SDS and is thought to be an important factor for formation of aggregates. Zeta in specific surface area of SSG composite with additions of 0.5% SDS (as shown in figure 12)

Literature reveals that Zeta-potential value of composite particles which are lower than -30 mV will possess anionic in nature whereas neutral composite particles lies in between -10 and +10 mV and cationic composite particles possess the values greater than +30 mV [24].

potential measurement showed the most improvements From figure 12, nature and value of the synthesized silica -graphene surfactant composite can be inferred. Zeta-potential value of-28.3mV indicates the nature of composite as anionic and having potential adsorption capacity composite with cationic dye MB from aqueous solution.



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Results
                                          Mean (mV)    Area (%)    St Dev (mV)
    Zeta Potential (mV):  -28.3   Peak 1:  -28.3        100.0       8.00
    Zeta Deviation (mV):  8.00    Peak 2:  0.00         0.0         0.00
  Conductivity (mS/cm):  0.631   Peak 3:  0.00         0.0         0.00
       Result quality :  Good
```

Fig. 12: Zeta Potential of SSG composite (mV)

4. CONCLUSIONS

The present investigation showed that surfactant modified silica graphene composites can be effectively and efficiently use to remove the cationic methylene blue dye from aqueous solution. The adsorption process was dependent on pH and contact time, maximum adsorption occurs at pH 8. The isotherm analysis indicated that the adsorption data can be represented by Langmuir isotherm model. The Zeta potential -28.3 mV infers remarkably strong adsorption capacity.

The highly hydrophobic effect due to surfactant SDS and the strong π-π stacking interactions of the exposed graphene with SDS contributed to their superior adsorption of SSG as compared to SG. The removal efficiency also increases upto 99.9% as the solution can be decolorized to nearly colorless. Results reveal that surfactant assisted silica graphene (SSG) composites can be applied in treating industrial effluent and contaminated natural water.

5. ACKNOWLEDGEMENTS

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