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Effective Removal of Toxic Methylene Blue Dye from Textile Industry Wastewater using Graphene Oxide- Silica [GO-Si] Nano Composite Adsorbent

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Abstract : Textile companies release wastewater containing lots of colors including Methylene Blue (MB) dye. Those colors are harrmful for human well being. Various procedures have been utilized to expel the color from industrial wastewater. Out of different methods used in practice, adsorption was observed to be exceptionally successful and effective. The reason behind the especiality is when nanocomposites are utilized as an adsorbent, as it has a better adsorption limit, selectivity, and solidness than nanoparticles. In this research, a peculiar synthesis of adsorbent Graphene Oxide Silica [GO-Si] is carried out and it is used to remove methylene blue dye from texile industry wastewater. Analysing the performance of MB dye removal from the waste water using this adsorbent seems to be more effective. Various studies have been carried out for successful analysis of the performance such as adsorption isotherm study, Freundlich and Langmuir analysis. In addition the adsorption process was well explained by a pseudo-second-order kinetics models.
Keywords : Methylene Blue, Graphene Oxide- Silica, Industrial Wastewater, Adsorption, Nano Composites

I. Introduction

One of the serious issues concerning textile industry is the amount of consistent waste effluent from its production process. Most of the dyes in the effluent are poisonous to life forms and direct release of the effluent without legitimate treatment could affect the biological system in the long term [1]. Cosidering the environmental ecosystem, the deposition of colouring agent will in general block the entry of light through water and reduces the efficiency of photosynthesis in aquatic plants and consequently make an antagonistic

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effect on their development. Colouring agent also can cause extreme harm to individuals, for example, causing kidney dysfunction,affecting reproductive systems and nervous system. An incredible number of studies have been directed to investigate the effect and poisonous quality of colouring agent on the biological system [2].

Among various colouring agents, Methylene Blue (MB) is the most common cationic colouring agent which is used as a mode for colouring the cotton, wood, and silk [3]. Despite the fact that it is not strongly perilous, regardless it have different harmful effects. For example, difficulty in breathing during inward breath or queasiness, vomiting and diarrhoea if being ingested through the mouth [4]. Various treatment procedures have been utilized to expel MB dye and associated colouring agent from wastewater like physical (adsorption, irradiation and layer process), chemical (oxidative procedure, ozonation, ionic exchange, electrocoagulation and coagulation-flocculation) and organic (aerobic and anaerobic) treatment. Among them, regular natural treatment strategies although reported to be efficient in the evacuation of suspended solids and reduction of chemical oxygen demand, yet they are typically observed to be ineffective to accomplish total reduction.

In addditon there are drawbacks of the above methods in generating lot of toxic and cancer-causing byproducts [5]. As of late, adsorption has shown promising and effective results for the removal of colouring agent from aqueous solution and is considered as an attractive technique because of its direct approach of application on removing the pollutant and simplicity of operation [6]. Various adsorbents, for example, activated carbon, zeolite, silica and adsorbents from organic waste product have been evaluated in combination to them. It is essential to have an efficient adsorbent that has rapid evacuation and quick adsorption of lethal debasements inside a couple of minutes of use. Many research gatherings have examined the utilization of nanoparticles as an adsorbent.

Nanoparticles are particles in the scope of 1–100 nm with peculiar size, shape and properties [7]. Considering nanostructure adsorbents they show higher efficiency and quicker expulsion rate of poisonous dye from the wastewater on comparing to the conventional methods [8,9]. Nanomaterial posses higher surface zone, which can prompt higher adsorption performance of pollutant [10]. Graphene is a two-dimensional carbon-based material possessing atomic thickness developing as one of the most promising nanomaterials. Attributable to its remarkable mix of excellent properties that enable it to be used in a wide range of applications extending from gadgets to optics, sensors, and environmental application. GO is hydrophilic and ready to swell in the presence of water. It has high negative charge thickness due to the oxygen containing useful gatherings [11]. GO can go about as weak acid cation exchange resin on account of the ionizable carboxyl groups,which permit particle exchange with metal cations or charged organic atoms [12].Until today, relatively few works that have been accounted for the use of attractive GO especially as adsorbent for removing dye. Therefore, the main focus of this work was to prepare a novel adsorbent graphene oxide silica, GO-Si that exhibits high adsorption rate and phenomenal regenerative ability. Based on evaluation the adsorbent had been prepared to remove toxic dyes from the textile industry waste water [13].

II. Materials and Method

Go-Si Adsorbent

The utilization of mesoporous silica for surface modification of GO provides an ordered pore network. Graphene oxide silica (GO-Si) hybrid composite particles were synthesized by the hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of hydrophilic GO derived from a modified Hummers method [14]. All the analysis suggests that, GO and Si can be considered as a new remarkable material in the adsorption method related to the removal of pollutants. We know that now a days a great deal of colouring agent were discharged in the water bodies. This exploitation of environment is intended to ponder Graphene oxide silica (GO-Si) as a potential adsorbent to evacuate the toxic dyes and hazardous metal ions.

Methylene Blue Dye

Methylene Blue (MB) is a model cationic dye used by industries such as textile industry for various purposes [15]. It is a heterocyclic aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$ which is shown in figure 1. It will cause eye burn, which may lead to permanent injury to the eyes of human as well as animals that lives in the water bodies [16]. Removal of dye named, MB from water bodies by adsorption using GO-Si has been experimentally determined.

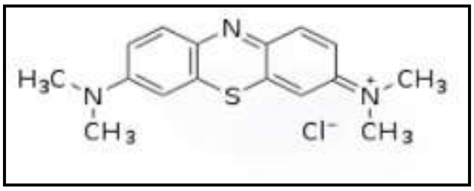

Figure 1: Chemical structure diagram of MB dye

A large amount of adsorption capacity of 174 mg/g is observed. At initial, MB concentrations is lower than 250 mg/L, the removal efficiency is greater than 99% and the polluted water can be decolorized to nearly colorless [17]. The removal process is very quick and more efficient at low temperatures and high pH values. The increased rate of ionic strength and the existence of dissolved organic matter would further increase the removal process when MB concentration is high [18].

III. **Properties and Characteristics**

Analysing the properties and characteristics of GO-Si adsorbent using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) was attempted as shown below. Figure 2 and 3 provides visible evidence of the silica nanoparticles grafted on the surface of GO, that results in Si-GO hybrid composite particles. Energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) spectra indicated the coexistence of silica and GO in the composite particles. The GO-Si hybrid composite particles showed better thermal stability than that of GO.

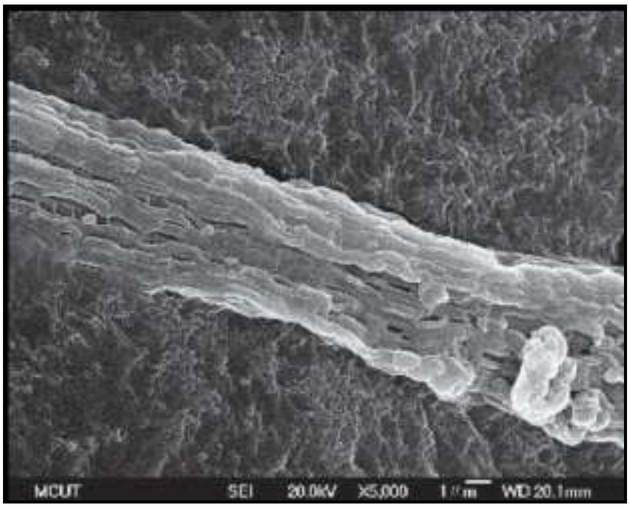

Figure 2: SEM image of GO-Si Composite

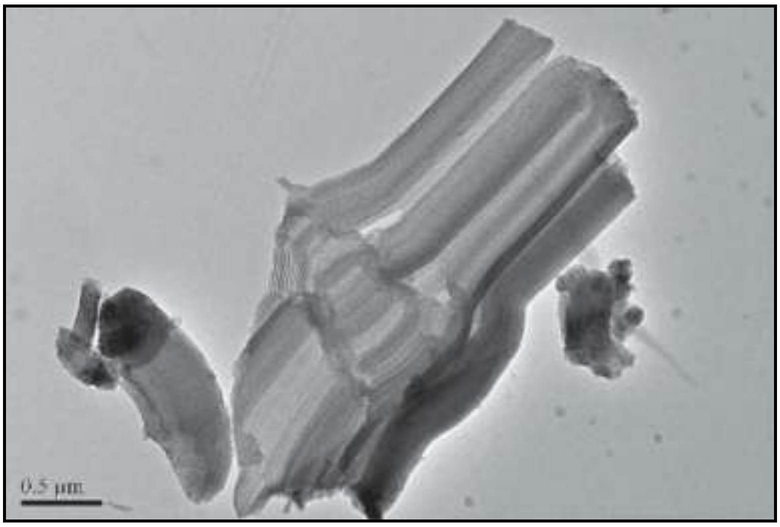

Figure 3: TEM image of GO-Si Composite

GO-Si adsorbs methylene blue effectively under various conditions. MB dye interacts with GO-Si via electrostatic interactions. Figure 4 explains the MB structure electrostatically interacting with GO-Si. The parameters of the experiments include initial concentration of dye, adsorbent amount temperature and adsorption time. The effects of pH, contact time, temperature and dosage on the adsorption properties of methylene blue in graphene oxide Silica nanocomposites were examined [19]. The equilibrium adsorption data were described by the Langmuir and Freundlich isotherms.

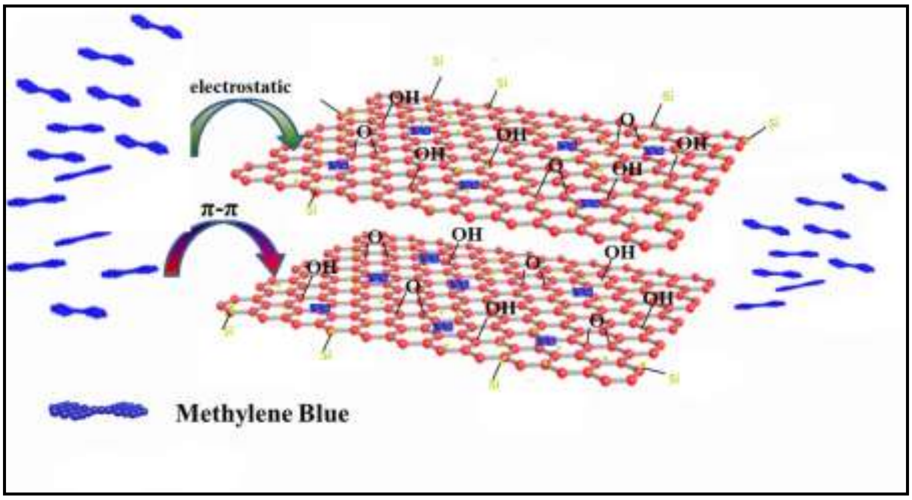

Figure 4: MB dye removal through electrostatic attraction

IV. Adsorption Capacity

Results and discussion

The various parameters were analysed one by one. The adsorption capacities of different doses were determined at definite time intervals by keeping all other factors constant. In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 20 to 100 mg/L. The effect in period of contact for the removal of dye by the adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant which is shown in figure 5 and 6.

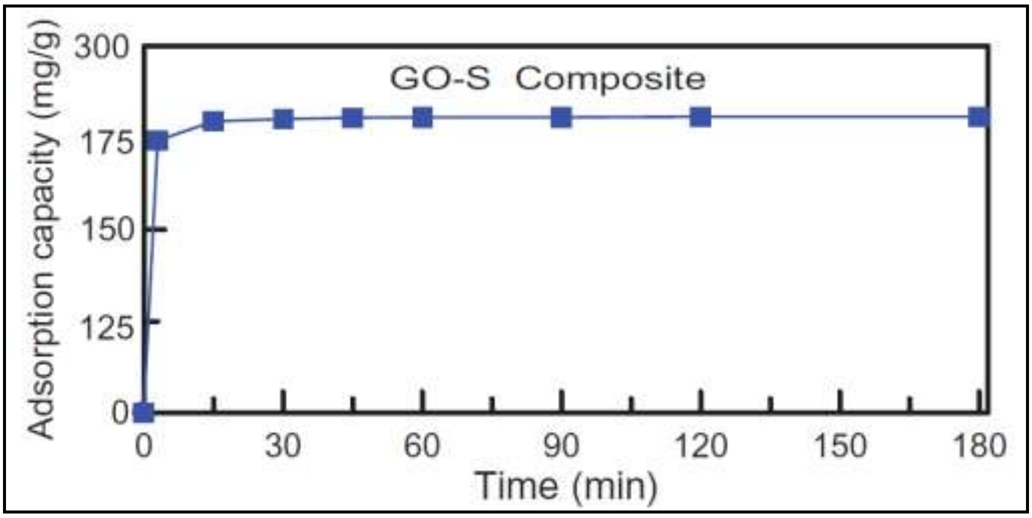

Figure 5: Adsorption Capacity of Methylene Blue by GO-Si Composite

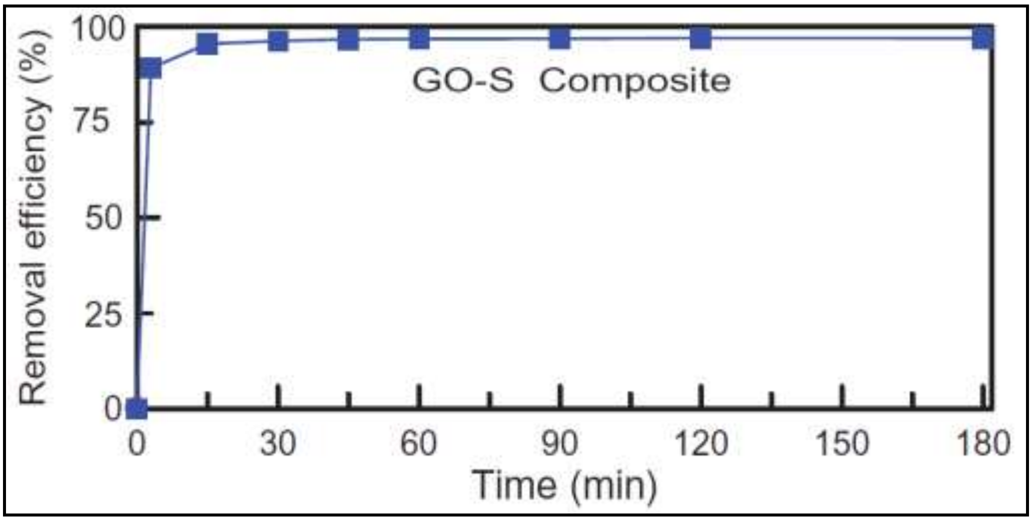

Figure 6: Removal Efficiency of Methylene Blue by GO-Si Composite

V. **Effect of Temperature**

The impact of temperature of MB on GO-Si nanocomposite regarding the adsorption capacity, mirrors the thermodynamics of MB expulsion on GO-Si. It is very well seen from the Figure 7. It describes the adsorption capacity as temperature expanded from 25 to 45^{0}C, while a progressively noteworthy decline was observed over the temperature range from 45 to 65°C. These exploratory outcomes propose that the adsorption and desorption rate were all around rapidly bigger when the temperature is low. Be that as it may, with the temperature builds, the upgrade of the desorption rate was greater than that of adsorption rate. So, the adsorption limit diminished with diminishing temperature.

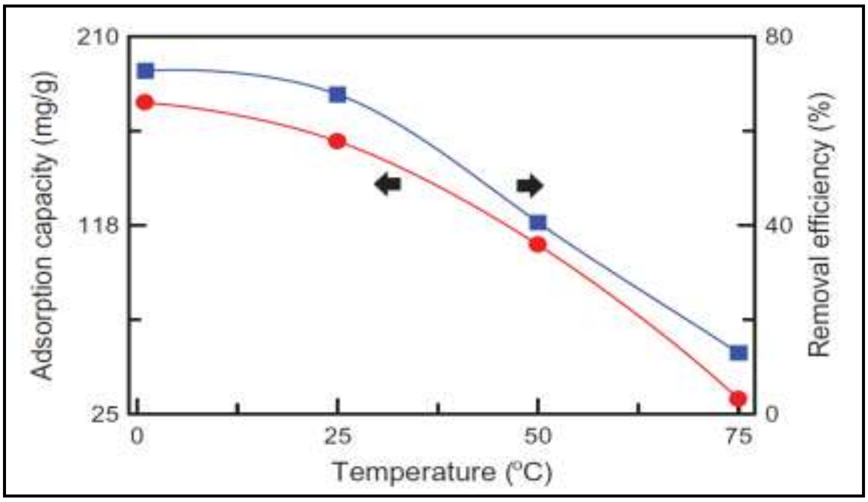

Figure 7: Effect of Temperature of Methylene Blue on GO-Si Composite

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were calculated. The low as well as high pH value pay the way to the optimum amount of adsorption of the dye. The amount of MB adsorbed increases with increase in ionic strength and temperature.

VI. Adsorption Isotherm

Adsorption isotherm of MB in GO-Si was determined and correlated with common isotherm equations. The equilibrium data for MB adsorption well fitted to the Langmuir equation, with a maximum monolayer adsorption capacity of 500.00 mg/g. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. The kinetic parameters of the model were calculated and discussed. Freundlich and Langmuir isotherm models were applied to the equilibrium data which is shown in figure 8 and 9. The Freundlich equation was employed for the adsorption of Methylene blue by the adsorbent.

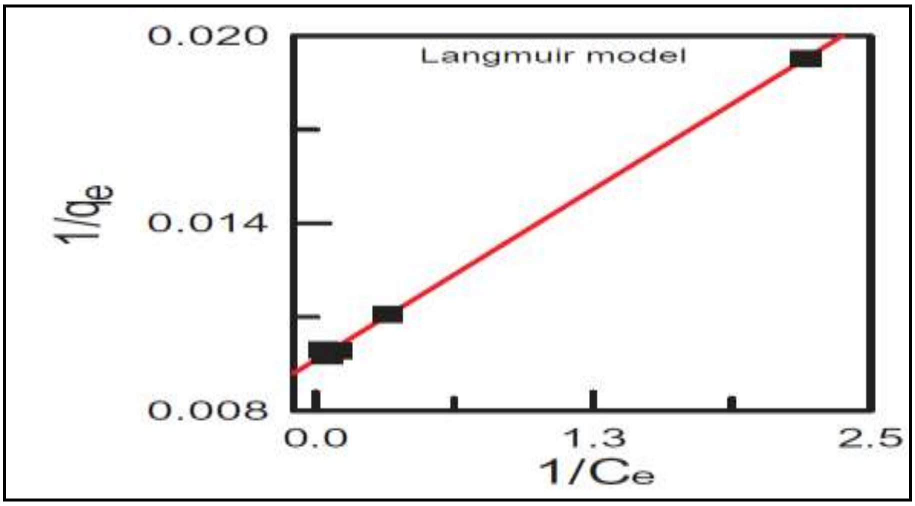

Figure 8: Langmuir Model of Adsorption Isotherm and Kinetics of Methylene Blue on GO-Si Composite

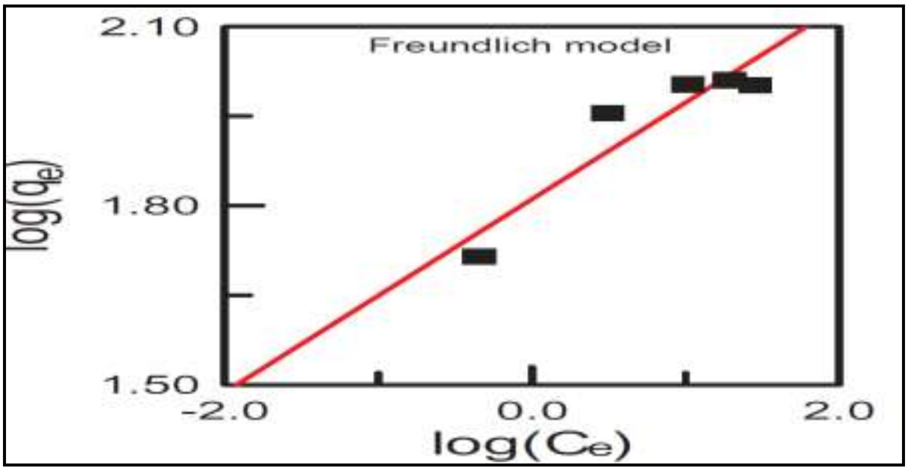

Figure 9: Freundlich Model of Adsorption Isotherm and Kinetics of Methylene Blue on GO-Si Composite

The linear plots of Qe versus Ce suggest the applicability of the Langmuir isotherms. From the results, it is clear that the value of adsorption efficiency Qm and adsorption energy increases with increase in temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed values show that the adsorbent prefers to bind acidic ions and that speciation predominates on adsorbent characteristics, when ion exchange is the predominant mechanism which takes place in the adsorption of Methylene blue, it confirms the endothermic nature of the process involved in the system.

Pseudo- first order Model of Adsorption Isotherm

A plot of qt versus Time (min) gives the relationship in below figure 10 about pseudo-first order model.

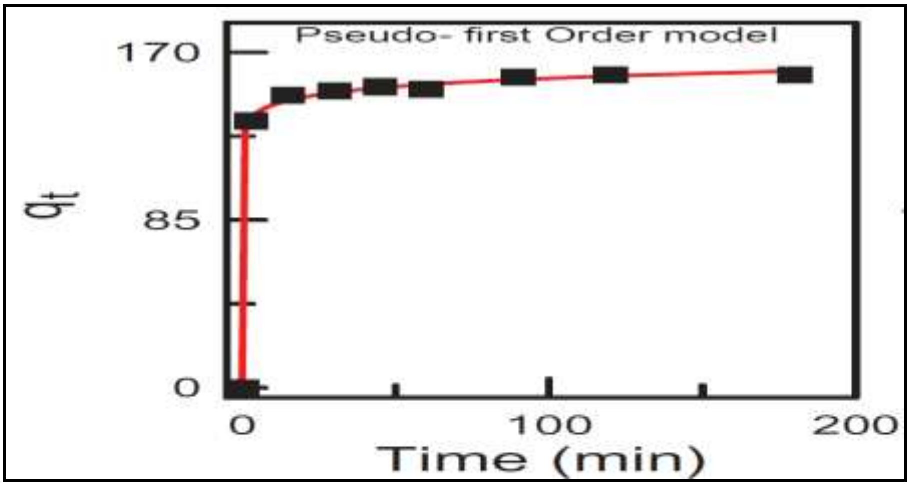

Figure 10: Pseudo- first order Model of Adsorption Isotherm and Kinetics of Methylene Blue on GO-Si Composite

Pseudo- second order Model of Adsorption Isotherm

A plot of t/qt versus Time (min) gives a linear relationship in below figure 11 in pseudo - second order model.

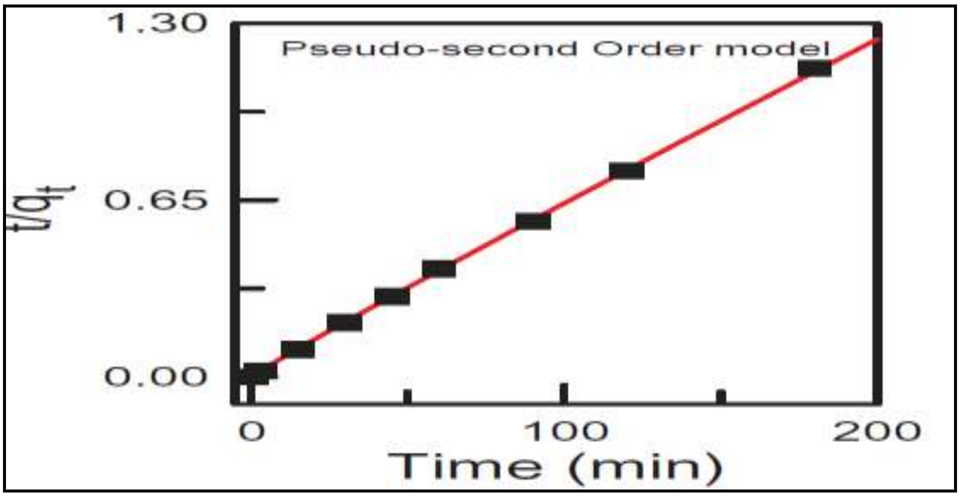

Figure 11: Pseudo-second order Model of Adsorption Isotherm and Kinetics of Methylene Blue on GO-Si Composite

VII. Conclusion

The existance of chemical dyes, pharmaceuticals and many other unavoidable pollutants in wastewater is more critical due to severe effect on the human beings as well as on the environment. Here, adsorption effect of GO-Si was tested for the removal of MB, a cationic dye, from aqueous waste water media. SEM images of GO-Si revealed that it was a nanoparticle. GO-Si composite was the most effective nanoparticle for MB removal and it is more recommended to be utilized in water treatment for its high adsorptive capacity followed by GO nanoparticles. It is more observed that both GO-Si and its reduced forms are excellent adsorbents towards MB. As far as removal of MB is concerned, adsorption investigation of MB on GO-Si and GO have been constantly performed utilizing hydrazine as a reducing special agent. The mesoporous silica nanoparticles were effectively prepared from naturally forming diatomite. The resultant examples were tried in the adsorption of MB from aqueous solutions. The impact of different adsorption parameters including initial pH, adsorbent dose, efficiency, temperature and contact time were analyzed. The test information acquired with mesoporous silica were all around fitted with both the pseudo-second-order kinetic and Langmuir models, Thermodynamic computations demonstrated that the expulsion of MB in GO-Si was an unconstrained and exothermic procedure. The greatest adsorption measure of MB in GO-Si achieved 347.2 mg/g. Additionally, silica could be adequately regenerated by straightforward warming treatment and reused five cycles keep running without critical loss of adsorption limit. Silica arranged from economical crude material were found to be a potential adsorbent towards the expulsion of MB inferable from its easy recovery and eco-benevolence. The low-cost, minimal effort silica arranged from naturally occurring diatomite showed a high adsorption limit and quick adsorption energy for MB. GO-Si from which the intergranular material has been found to adsorb more MB per unit of superficial surface as determined by the air permeability method. The GO-Si showed more porosity. Correlation coefficients of the adsorption models have shown a better matching of MB adsorption by the GO-Si with the Langmuir isotherm model. The results of this study show that the GO-Si can be applied to remove environmental pollutants such as MB due to the low cost and availability.

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