INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE & TECHNOLOGY
© VISHWASHANTI MULTIPURPOSE SOCIETY (Global Peace Multipurpose Society) R. No. MH-659/13(N)
www.vmsindia.org

DYE REMOVAL CAPACITY OF GRAPHENE OXIDE-IRON NANO PARTICLE COMPOSITE AS AN ADSORBENT

Jyoti N. Thakre[1], Sanjay R. Thakare[2] , P. T. Kosankar[3] and Kavita Gour[4]

[1] St. Vincent Pallotti College of Engineering and Technology, Nagpur,
[2]Institute of Science, Nagpur
[3]Yashwant Rao Chauhan College of Engineering and Technology, Nagpur
[4]J. L. College of Engineering , Nagpur
E-mail: jyoti2772@rediffmail.com

ABSTRACT:
Thousands of dyes have since been prepared and, due to the vastly improved properties imparted upon the dyed materials; organic dyes have replaced the traditional natural dyes. Nano-scale zero valent iron particles provide cost effective solution to many of the environmental problems. The green synthesis of zero valent iron nano particle by using green tea was carried out. Graphene oxide has numerous adsorption abilities being well explored towards water purification. In this study, a novel environmental adsorbent iron nano particle immobilized on graphene oxide was prepared. The effects of various experimental parameters such as contact time, pH and dosage of the adsorbent graphene oxide- iron nano particle composite on methylene blue (MB) removal were investigated. 100mg/100ml was sufficient to remove 95% of dye in 70 minutes from 10ppm dye solution. The equilibrium adsorption data were described by the Langmuir and Freundlich's adsorption isotherms. The unprecedented adsorption performance may be attributed to both the synthesis methodology and adsorption conditions.

KEYWORDS: Graphene oxide; Ferric Chloride; Green Tea; Iron nano particle; Methylene blue, Adsorption etc.

INTRODUCTION

Nano scale zero valent iron is of very interest for use in environmental remediation, water and waste water treatment. Nano scale zero valent iron has high reactivity due to a greater surface area to volume ratio. Dyes have become an important chemical to be used in our lives. The use of various dyes in coloring clothes, metals, drugs and automobiles has resulted in to their leaching in water bodies and hence pollution. Numerous innovative and efficient methods; such as membrane separation, flocculation, coagulation, ozonation, aerobic or anaerobic treatment and adsorption have been explored to eradicate dyes from dyeing wastewater (1). Though, surrounded by these methods, adsorption is the most comprehensively used technology because it is unfussy, low cost and effectual for removing dyes from waste streams. An assortment of adsorbents, such as rice husk (2), garlic peel (3), pyrolyzed petrified sediment (4), coir pith carbon (5), activated clay (6), carbon nanotubes (7), activated desert plant (8), and activated carbon (9), have been calculated for adsorption of dyes from aqueous solutions.

Graphene and graphene oxide (GO), new types of carbon nanomaterials, have fascinated massive research interests not only in electronics (10) and mechanics (11), but also in wastewater treatment. It has been used for the adsorption of fluoride ions (12), heavy metals (13), Cu (14), Pb and Cd (15), etc.), dyes (methylene blue (16), methyl violet, orange-G, rhodamine-B (17), etc.) and eloquent good adsorption property.

It is imperative to develop an adsorbent capable of performing efficiently without spreading the hazardous effects. In this connection a highly efficient adsorbent Graphene oxide- iron nano particle composite has been developed for its dye removal capacity. The methodology for preparation of adsorbent is so chosen to attribute both towards efficient removal and efficient adsorption.

MATERIALS AND METHODS

Synthesis of Graphene oxide

Graphene oxide (GO) was synthesized from 99.99% pure natural graphite powder, according to a modified Hummers method [18].

Synthesis of Zero valent Iron nano particle

The 0.1M Ferric Chloride was prepared using double distilled water. Green tea was taken washed with distilled water and dried .The dried leaves were made to powdered form. This powdered leaves were heated at 70-80^{0}C with distilled water for 5 minutes. The extract was then filtered using Whatman's No.1 filter paper. The filtrate was collected in a clean conical flask. The 50ml extract and 50ml 0.1M Ferric solution was stirred till the colour changes from green to black. A black precipitate thus obtained was dried in vaccum dessicator at 60 ^{0}C overnight.

Preparation of Graphene Oxide- Iron Nano particle Composite

10 g graphene oxide was taken in 250 ml distilled water and ultrasonication was done for 30 minutes followed by addition of 5 g iron nano powder prepared in above step. This mixture was stirred for 24 hours, filtered with whatman's filter paper and dried at 60 ^{0}C overnight. The synthesis conditions were strictly followed in every batch of production and dried adsorbent was collected in vacuum sealed glass bottles.

RESULTS AND DISCUSSION

Dye removal

We restrict our decontamination studies with methylene blue dye (MB) with the help of synthesized zero valent iron graphene oxide composite(Fe- GO composite)in the following section.

The stock solution of 100mg/l was prepared by dissolving the appropriate amount of MB (Obtained from s.d fine Chemicals, Mumbai, India) in 100ml, and make to 1000ml with distilled water. Different concentrations ranging between 5mg/l to 50mg/l of MB were prepared from the stock solution. All the chemicals used throughout this study were of analytical grade reagents. Double distilled water was used for preparing all of the solution and reagents. It is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}N_3SCl$, Molecular Weight is 319.85. All adsorption experiments were carried out at 25^{o}C. To study the effect of contact time on dye adsorption, adsorbent was put in contact with 100ml of methylene blue dye and stirred at room temperature. The adsorbed amount of MB dye by adsorbent was calculated at λmax 663nm by UV-Visible spectrophotometer.

The adsorption of MB on Fe –GO composite was studied by changing the quantity of adsorbent (10mg to 100mg) in the test solution while keeping the initial MB concentration (10mg/l), temperature(27 ±2^{o}C) and pH9 constant. The adsorption increased from 45% to 95% as the Fe –GO composite dose increased from 10mg to 100mg /100ml at the equilibrium time 70 minutes. Maximum MB removal was achieved within 30 to 70 minutes. After which MB concentration in the reaction solution was almost constant. The increase in the adsorption with adsorbent dose can be attributed to increased surface area and availability of more adsorption sites.

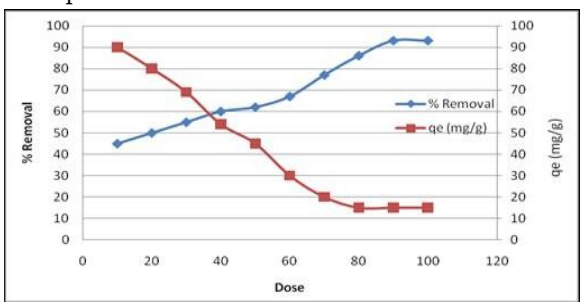

Fig. 1: Adsorbent dose versus percentage removal of MB Dye by Fe-GO Composite

The results shows that, the Fe-GO composite has remarkable methylene blue degradation efficiency & it was increased by increasing amount of it.

The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbents. So, the pH is an important parameter in the dye adsorption process. The hydrogen ion concentration (pH) primarily affects the degree of ionization of the dyes and the surface properties of the adsorbent. As can be seen from Fig. 2. the adsorption of MB dye onto

Fe –GO composite is highly dependent on the initial pH of solution. Higher removal percentages of MB dye from solution was observed for Fe –GO composite at pH 9, being 90%. The adsorption capacity of MB increased with increasing solution pH from 3 to 5. No significant increase was further noted after pH 9 where a rapid adsorption was observed. This result can be attributed to the effect of the solution pH on the charge of reactive group within the adsorbents which in turn makes

them more effective at adsorbing MB dye in alkaline pH.

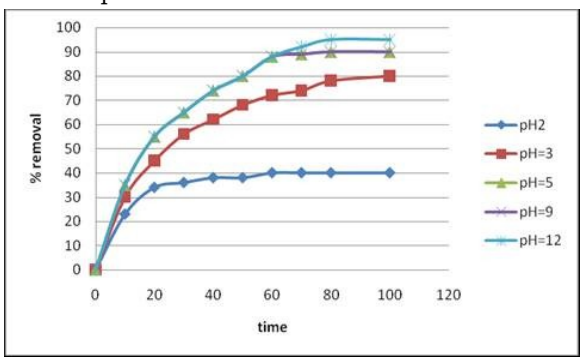

Fig.2: Effect of pH on the removal efficiency of MB Dye by Fe-GO Composite

Fig. 2. suggests the efficient removal performance of Fe-GO composite in basic (pH = 9.0) conditions. The 90% removal is obtained in the first 70 minutes which remained consistent throughout the experiment.

The relation between removal of MB and reaction time was studied. The results of percentage removal of MB with increase contact time using Fe –GO composite are presented in fig 3. It was found that more than 90% removal of MB concentration occurred in the first 70 minutes and thereafter the rate of adsorption of the MB onto Fe –GO composite was slow. The equilibrium was attained at 80 minutes when the maximum MB adsorption onto Fe –GO composite was reached.

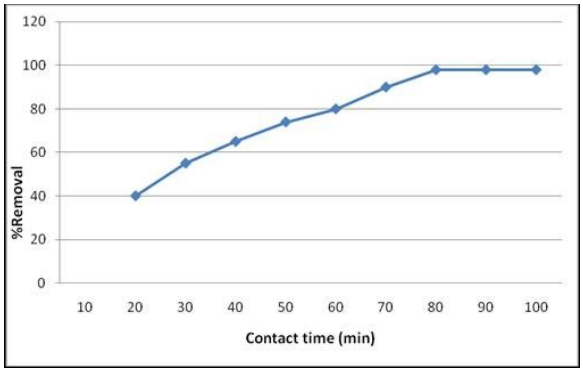

Fig. 3 : Contact time versus adsorption capacity of MB Dye by Fe-GO Composite

The initial concentration provides an important driving force in order to overcome all mass transfer resistance of the dye between the aqueous and the solid phase. The percent removal of MB for composite material decreases with an increase in initial concentration as shown in Fig.4, suggesting that at lower MB concentration, there were many vacant adsorption sites available for the MB molecules to attach to until the surface of the adsorbents was saturated at 80 mg/L where the amount of MB adsorbed did not increase significantly. In addition, the percentage removal of MB dye decreased from 95% to 60% using Fe –GO composite.

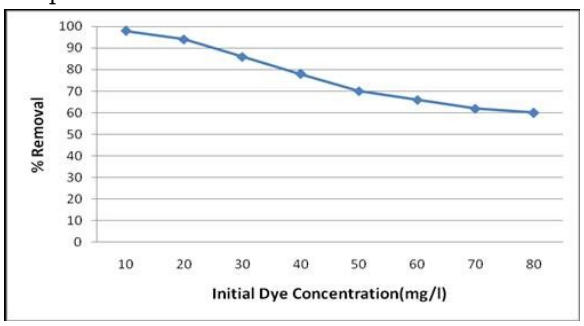

Fig.4 : Effect of initial methylene blue (MB) concentration on removal by Fe-GO Composite

Experimental data were analyzed with adsorption isotherm models including Langmuir and Freundlich isotherms. Langmuir adsorption isotherm states that adsorption takes place at specific homogenous sites within adsorbent and has found successful application to much sorption process of monolayer adsorption. The Langmuir isotherm can be written in the following form

$$C_e/q_e = 1/q_m b + C_e/q_m \quad \text{Eq.(1)}$$

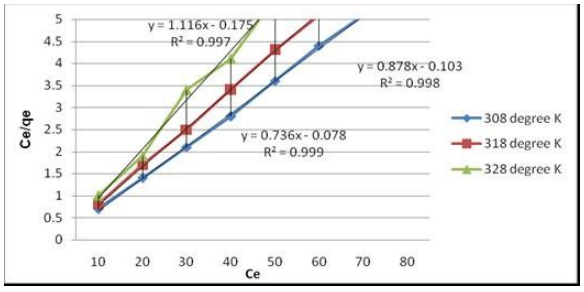

Fig. 5 : Langmuir isotherm for MB Dye adsorption by Fe-GO Composite.

Where q_e the adsorbed amount of the dye is, qm is the monolayer adsorption capacity, C_e is the equilibrium concentration of the dye in the solution. The linear plot of C_e/q_e versus C_e (Fig. 5) with correlation coefficient R^2 was found to be 0.999, 0.998, 0.997 for temperature 308, 318 and 328 K, indicates the accuracy of Langmuir isotherm shown in Fig.5. This indicates a monolayer adsorption of MB onto the adsorbent surface.

The Freundlich isotherm is employed to describe heterogenous system. The linear form of Freundlich equation is given as:

$$\log q_e = \log K_f + 1/n (\log C_e) \quad \text{Eq. (2)}$$

where Ce is the adsorption capacity (mg/g) and n is the empirical parameter. The value of R^2 are 0.974, 0.979, and 0.987 respectively (Fig. 6).

Higher value of correlation coefficient of Langmuir isotherm indicates that adsorption data fits better with Langmuir equation then by Freundlich's isotherm.

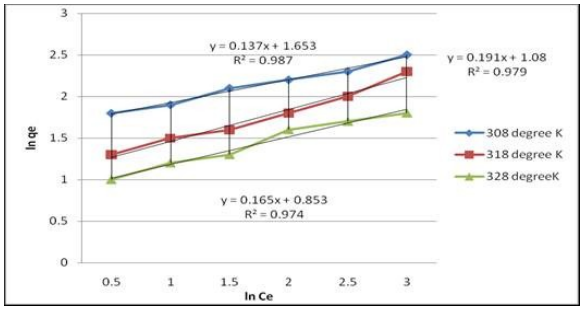

Fig. 6: Freundlich isotherm for MB Dye adsorption by Fe-GO Composite

Table 1: Langmuir isotherm, Freundlich isotherm data at different temperature for dye adsorption

Model	Parameter	Temperature(K)		
		308	313	328
Langmuir isotherm	R^2	0.999	0.998	0.997
Freundlich isotherm	R^2	0.987	0.979	0.974

CONCLUSIONS

A new efficient and eco-friendly adsorbent of Graphene oxide- iron nano particle composite was prepared in this work. Graphene oxide- iron nano particle composite has high adsorption capacity and removal efficiency .The obtained zero-valent iron graphene oxide composite are non-hazardous to the environment and practically usable for removing contamination from water. This study confirmed that the zero-valent iron graphene oxide composite prepared by the green reduction method were effective for the removal of MB dye from aqueous solution. The results showed that the adsorption is highly influenced by the initial concentration, solution's pH, adsorbent dosage and contact time. The adsorption data were adequately interpreted by Freundlich and Langmuir adsorption isotherm for Fe-GO composites. The adsorbent is stable at basic pH. This suggests the efficient Dye removal efficiency of zero valent Iron graphene oxide composite material. The dye adsorption within 80 minutes of addition of adsorbent material also suggests the fast kinetics under simulated conditions of dye removal efficiency (90% removal). The equilibrium adsorption was practically achieved in 80 minutes. The experimental results were analysed by Langmuir and freundlich isotherm and the correlation coefficients for by Langmuir and freundlich equation were well fitted. Adsorption was well described by a monolayer Langmuir type isotherm. The results of this experimental study are highly useful for the remediation of real industrial effluent or MB dye-laden wastewater.

ACKNOWLEDGEMENT

The authors would like to thank ,the Principal, Shri, Shivaji Science College, Congress Nagar, Nagpur for providing the laboratory facilities to carry out the experimental work.

REFERENCES

1. Slokar, Y.M., & Le Marechal, A.M. (1998). Methods of decoloration of textile wastewaters. Dyes and Pigments, 37, 335–356.
2. Li, Y.H., Du, Q., Liu, T., Qi, Y., Zhang, P., Wang, Z., et al. (2011a). Preparation of activated carbon from Enteromorpha prolifera and its use on cationic red X-GRL removal. Applied Surface Science, 257, 10621– 10627.
3. Hameed, B.H., & Ahmad, A.A. (2009). Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. Journal of Hazardous Materials, 164, 870–875.
4. Aroguz, A.Z., Gulen, J., & Evers, R.H. (2008). Adsorption of methylene blue from aqueous solution on pyrolyzed petrified sediment. Bioresource Technology, 99, 1503-1508.
5. Kavitha, D., & Namasivayam, C. (2007). Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Technology, 98, 14–21.
6. Weng, C.H., & Pan, Y.F. (2007). Adsorption of a cationic dye (methylene blue) onto spent activated clay. Journal of Hazardous Materials, 144, 355–362.

7. Yao, Y., Xu, F., Chen, M., Xu, Z., & Zhu, Z. (2010). Adsorption behavior of methylene blue on carbon nanotubes. Bioresourse Technology, 101, 3040–3046.
8. Bestani, B., Benderdouche, N., Benstaali, B., Belhakem, M., & Addou, A. (2008). Methylene blue and iodine adsorption onto an activated desert plant. Bioresource Technology, 99, 8441–8444.
9. Karagöz, S., Tay, T., Ucar, S., & Erdem, M. (2008). Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Bioresource Technology, 99, 6214–6222.
10. Eom, D., Prezzi, D., Rim, K.T., Zhou, H., Lefenfeld, M., Xiao, S., et al. (2009). Structure and electronic properties of graphene Nanoislands on Co(0001). Nano Letters, 9, 2844-2848.
11. Lee, C., Wei, X., Kysar, J.W., & Hone, J. (2008). Measurement of the elastic properties Lee, C., Wei, X., Kysar, J.W., & Hone, J. (2008). Measurement of the elastic properties
12. Li, Y.H., Zhang, P., Du, Q., Peng, X., Liu, T., Wang, Z., et al. (2011b). Adsorption of fluoride from aqueous solution by graphene. Journal of Colloid and Interface Science, 363, 348–354.
13. Mishra, A.K., & Ramaprabhu, S. (2011). Functionalized graphene sheets for arsenic removal and desalination of sea water. Desalination, 282, 39–45.
14. Yang, S.T., Chang, Y.L., Wang, H.F., Liu, G.B., Chen, S., Wang, Y.W., et al. (2010). Folding/aggregation of graphene oxide and its application in Cu2+ removal. Journal of Colloid Interface Science, 351, 122–127.
15. Deng, X.J., Lü, L.L., Li, H.W., & Luo, F. (2010). The adsorption properties of Pb(II) and Cd(II) on functionalized graphene prepared by electrolysis method. Journal of Hazardous Materials, 183, 923–930.
16. Liu, T., Li, Y.H., Du, Q., Sun, J., Jiao, Y., Yang, G., et al. (2012). Adsorption of methylene blue from aqueous solution by graphene. Colloids and Surfaces B, 90, 197-203.
17. Ramesha, G.K., Vijayakumar, A., Muralidhara, H.B., & Sampath, S. (2011). Graphene and graphene oxide as effective adsorbents towards anionic and cationic dyes. Journal of Colloid and Interface Science, 361, 270–277.
18. W.S. Hummers Jr., R.E. Offeman, Journal of the American Chemical Society, 80, (1958), 1339-1339.

❖❖❖❖