GREENER APPROACH OF TREATING INDUSTRIAL DYE WASTEWATER BY GRAPHENE OXIDE SYNTHESIZED FROM WASTE ACTIVATED SLUDGE

Dynisha.S [1], A.P.Arthi [2], P. Sivaanuma [3]

[1,] Francis Xavier College of Engineering, Tirunelveli.

[2 ,]Anna University regional campus, Tirunelveli.

[3,]National College of Engineering, Marthakulam, Tirunelveli.

ABSTRACT:

Sludge is a semi liquid residue from the treatment of domestic and various industrial processes. Sludge contains major amount of water with lesser of solid materials which is removed from treatment of wastewater. Disposal of sludge without treatment can cause bad odour, contamination of ground water and land pollution which is hazardous to environment. Waste Activated Sludge (WAS) is an important by-product of wastewater treatment processes. This study focuses on the potential of utilizing "waste-treats-waste" by synthesis of Graphene Oxide using waste activated sludge as a source material. The synthesized GO nanoparticles from dry sludge are used to treat the industrial dye wastewater. Synthetic dyes have been widely used in textile, food, cosmetics and in pharmaceutical industries. The dye wastewater contains high concentration of dyes and floating solid materials. This is the major problem which needs to be solved. In this research the adsorption of Acid Blue, Acid Red and Acid Orange by Graphene Oxide is studied and the optimum dye concentration, pH and temperature are found from the experimental analysis. The optimum temperature for removal of color from dyes was achieved in 25°C at 100mg/l concentration. The adsorption of acid Blue was identified in acidic medium and the optimum pH value was found to be 2, while the adsorption of Acid Orange was favoured at alkaline medium with optimum pH 8.

KEYWORDS: Graphene Oxide, WAS, pH, adsorption, Acid Red, Acid Orange, and Acid Blue.

---

1 .INTRODUCTION

Wastewater treatment in textile and dye industry mainly involves treatment of highly colored wastewater containing variety of dyes in different concentrations. The wastewater needs to be treated prior to discharge by effectively removing dye color in order to protect environment and as per the statutory guidelines. Biological treatment processes are frequently used to treat textile effluent. These processes are generally efficient for biochemical oxygen demand (BOD) and suspended solids removal (TSS) but they are largely ineffective for removing color from the dye wastewater.

In recent years, considerable research has been done on the removal of color from textile effluent. Graphite Oxide is a compound of carbon, oxygen and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. The bulk material disperses in basic solutions to yield mono molecular sheets, known as Graphene Oxide (GO). In 1859, Graphite oxide was first prepared by Oxford chemist Benjamin C.Brodie. In 1957 Hummers and Offeman developed a safer, quicker, and more efficient process called Hummer's method. In this method a mixture of sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) is widely used in various proportions. Graphene oxide are also prepared by using a "bottom-up" synthesis method (Tang-Lau method) in which the sole source is glucose. This process is safer, low cost, facile, simpler and more environmentally friendly compared to traditional "top-down" method, in which strong oxidizers are used. Tang-lau method is also capable of scaling up for mass production.

The sewage sludge is a semi solid material that is produced as a by-product during the wastewater treatment process of industrial and municipal sewage. In a sewage treatment plant, the activated sludge process is a biological process that can be used for one or several purposes which includes oxidizing carbonaceous biological matter, removing nutrients (nitrogen and phosphorous), oxidizing nitrogenous matter mainly ammonium and nitrogen in the biological matter.

The activated sludge process is a type wastewater treatment process for treating sewage and industrial wastewaters using aeration and a biological floc composed of bacteria and protozoa. In the biological process, the aerobic microorganisms will digest the organic matter in sewage and it produces the liquid that is relatively free from suspended solids and organic material. The flocculated particles will settle down and can be removed as a primary sludge. The amount of sludge produced from the activated sludge process is directly proportional to the amount of wastewater treated. The total sludge production consists of the sum of primary sludge from the primary sedimentation tanks as well as waste activated sludge (WAS) from the bioreactors. The activated sludge process produces about 70- 100kg/ML of WAS. The sewage sludge is undergoes further sludge treatments includes sludge thickening, dewatering, drying, lime stabilization, anaerobic digestion, composting and land application. After treatment, the sewage sludge is disposed of in landfills, dumped in the ocean or applied to the land. This practice leads to environmental pollution, land pollution and ground water contamination. Hence the sludge should be utilized effectively.

Hence, in this research we focused on the green technological concept "waste-treats-waste" by synthesizing Graphene Oxide from waste activated sludge to treat the industrial dye wastewater.

2. MATERIALS AND METHODS

2.1 COLLECTION OF MATERIALS

The waste activated sludge was collected from the Effluent Treatment Plant and it was stored under 4°C

2.2 PREPROCESSING AND GO NANOPARTICLES PREPARATION

The waste activated sludge was collected and sundried for seven days. The sun dried sludge was then placed in a hot air oven at 80˚C for 48 hours for moisture removal. Oven-dried sludge was then placed in muffle furnace at 450˚C for 45 min in N_2 atmosphere. The moisture removed dry sludge was then crushed and sieved to get a homogenous powder of less than 50µm. It is used as a substitute material for graphite in GONp synthesis by Hummer’s method. 10 g of dry sludge powder was taken in Erlenmeyer flask and 100 ml of concentrated H_2SO_4 was added to the powder. This flask was then placed on an ice tray to reduce the heat reaction of acid. $KmnO_4$ was then slowly added to the acidic mixture. It was stirred for 30 minutes at room temperature. After 30 minutes, 75 ml of distilled water was slowly added to the flask. It was then placed in an incubator shaker at 45 ˚C for 3 hours. Then 100 ml of distilled water was added to the mixture followed by 75mL of 30% H_2O_2 solution. The reaction mixture turned yellow indicating the successful synthesis of Graphene Oxide Nanoparticles (GONps). The slurry was then placed in a digital ultrasonic cleaner for 15 minutes to get GONps of uniform particle size. Finally, the slurry was repeatedly washed with deionized water (till it attained neutral pH) and filtered to separate GONps from solution. The GONps obtained as residue were dried overnight in a hot air oven at 60˚C and stored for characterization.

2.3 PREPARATION OF DIFFERENT DYE SOLUTION

The adsorbate solution was prepared from various dyes (Acid Red, Acid Orange, and Acid Blue) by weighing and dissolving the required amount in deionized water.

Table 2.1 Types and properties of dyes

Dye Name	Type	Color	Molecular Formula	Molecular Weight (g/mol)	Absorption maxima (nm)
Acid Red 73	Azo	Light Red	$C_{22}H_{14}N_4Na_2O_7S_2$	556.48	507
Acid Blue 25	Anthraqui-none	Dark Blue	$C_{20}H_{13}N_2NaO_5S$	416.38	600
Acid Orange 7	Azo	Orange	$C_{16}H_{11}N_2NaO_4S$	350.32	483

2.4 PREPARATION OF DYES FOR VARIOUS pH

10g of NaOH pellets is dissolved in to 250ml of distilled water to make 1N of base solution. 6.9ml of H_2SO_4 is dissolved in to 250ml of distilled water to make 1N of acid solution. Desired pH is attained by adding of 1N of acid or base solution to dye solution.

2.5 DYE REMOVAL EXPERIMENT

The dye removal experiment was performed in Erlenmeyer flask containing 100mL of dye solution with appropriate concentration and 1g of GO nanoparticles. The pH of the solution is adjusted using sodium hydroxide or sulphuric acid. The dye solution contained flask is kept in a shaker at 150rpm. Then 4ml of sample is taken at different time intervals (5, 10, 15, 20, 25, 30, 40, 50, 60, 120, 150, 180 mins). The collected samples were then centrifuged for 15mins at 15000rpm. After centrifuging process, the supernatant solution was kept in the spectrophotometer to find the absorbance values of different dye solution at various concentration and pH.

3. RESULT AND DISCUSSION

3.1INITIAL CHARACTERISTICS

The initial characteristics of dry sludge was determined includes moisture content and ash content.

3.1 .1 MOISTURE CONTENT DETERMINATION:

Moisture content was find out by oven drying the Waste Activated Sludge for 24 hours at 105°C at the presence Nitrogen gas (N_2) in hot oven. Percentage of moisture content of the dry sludge is shown in the following table 3.1

Table 3.1 Moisture Content Determination of Dry Sludge

S.No	Initial Weight (g)	Final Weight (g) (after oven drying)	Percentage of Moisture Content (%)
1	93	14	84.94
2	84	17	79.76
3	126	15	88.09
4	53	9	83.01
5	78	15	80.77
		Average	83.143

3.1.2 ASH CONTENT DETERMINATION

Ash content was determined by placing the oven dried dry sludge in the muffle furnace between 550°C to 600°C. Percentage of ash content of the sludge is shown in the following table 3.2

Table 3.2 Ash Content Determination of Dry Sludge

S.No	Initial Weight(g) (oven dried sample)	Final Weight (g) (ash sample)	Percentage of Ash Content (%)
1	14	4.1	29.28
2	17	4.9	28.82
3	15	3.7	24.67
4	9	2.1	23.33
5	15	4.4	29.33
		Average	27.09

3.2 EFFECT OF ADSORBATE CONCENTRATION

The adsorption study is conducted for the different concentration of different dyes (50, 100, 200, 250mg/l) and other parameters are set as constant (pH=7, room temperature).

3.2.1 Effect of concentration on Acid Blue

From the fig: 3.1, the maximum removal was found in 50mg/l for Acid Blue. When the concentration of adsorbate solution increase more than 50mg/l leads results to reduction of removal % which may be due to excessive concentration of dye when the amount of Graphene Oxide (GO) is less when compared to Acid Blue dye concentration of the solution. The efficiency of color removal is drastically decreased from 50mg/l to 150mg/l. After 150mg/l the color removal efficiency is gradually decreased.

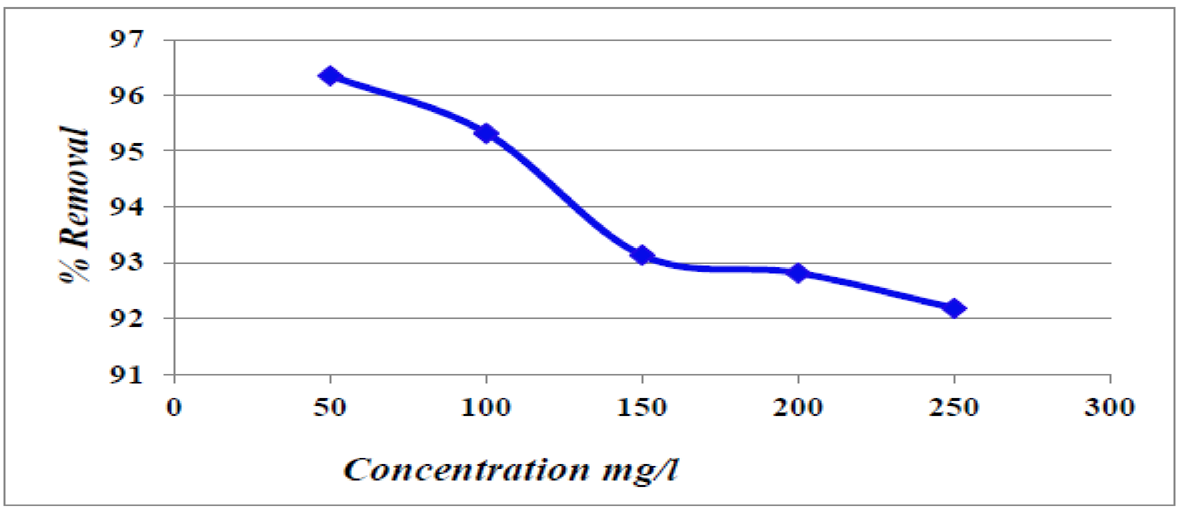

Figure 3.1 Effect of concentration on Acid Blue

3.2.2 Effect of concentration on Acid Red

From the fig: 3.2, The maximum removal was found in 50mg/l for Acid Red. The efficiency of color removal is gradually decreased from 50mg/l to 150mg/l. After 150mg/l the color removal efficiency is drastically decreased.

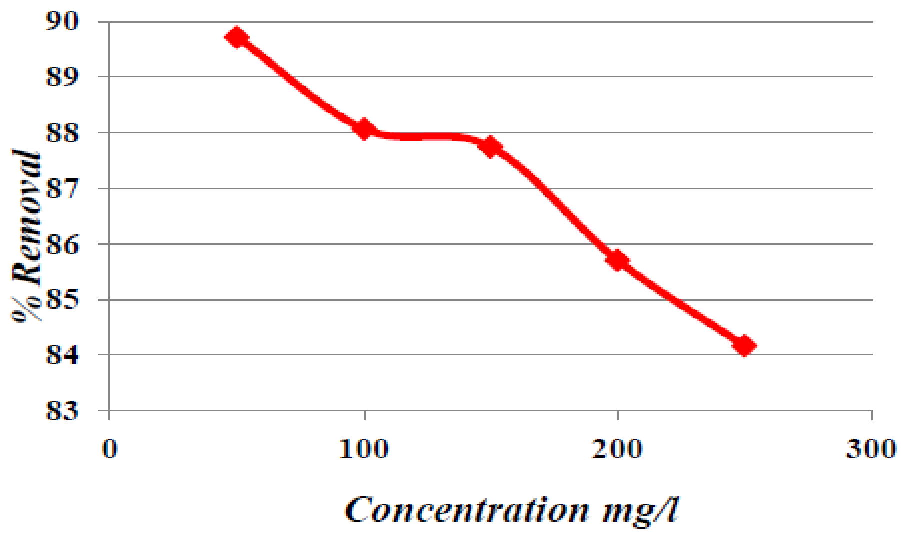

Figure 3.2 Effect of concentration on Acid Red

3.2.3 Effect of concentration on Acid Orange

From the fig: 3.3, the maximum removal was found in 50mg/l for Acid Orange. The efficiency of color removal on 50mg/l is 91.08%. The efficiency of color removal is gradually decreased from 50mg/l to 250mg/l. The graph for the effect of concentration on Acid Orange is shown below.

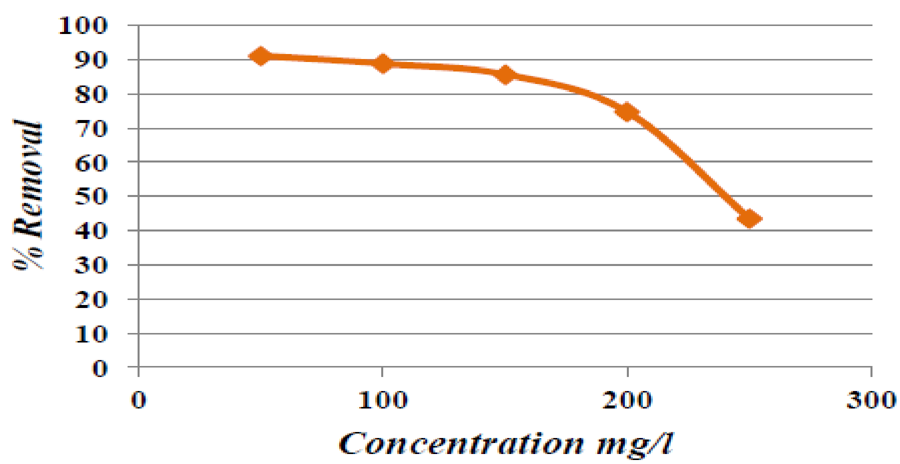

Figure 3.3 Effect of concentration on Acid Orange

ISSN NO: 0776-3808

3.3 EFFECT OF ADSOBATE ON pH

pH plays an important role in adsorption process. The removal of dye color was carried out using Graphene Oxide at various pH ranging from 2, 4, 6 and 8 for various concentrations of 100 mg/l, 150 mg/l, 200 mg/l and 250 mg/l. The following results were show that Acid Blue has the higher removal efficiency at the lower pH and the Acid Orange has the higher removal efficiency at pH 8. The optimum removal efficiency for Acid Red is at pH 6.

3.3.1 Efficiency of color removal on 250mg/l concentration

It was concluded from the fig: 3.4, the adsorption capacity was reduced for Acid Blue when there was an increase in pH.

The absorption capacity was increased upto the pH range of 6 and it decreased at pH 8 for Acid Red Dye. The optimum pH was found at pH 6.The efficiency of color removal is reduced for Acid Orange when there was a decrease in pH. The graph is shown below for different pH range at 250mg/l concentration.

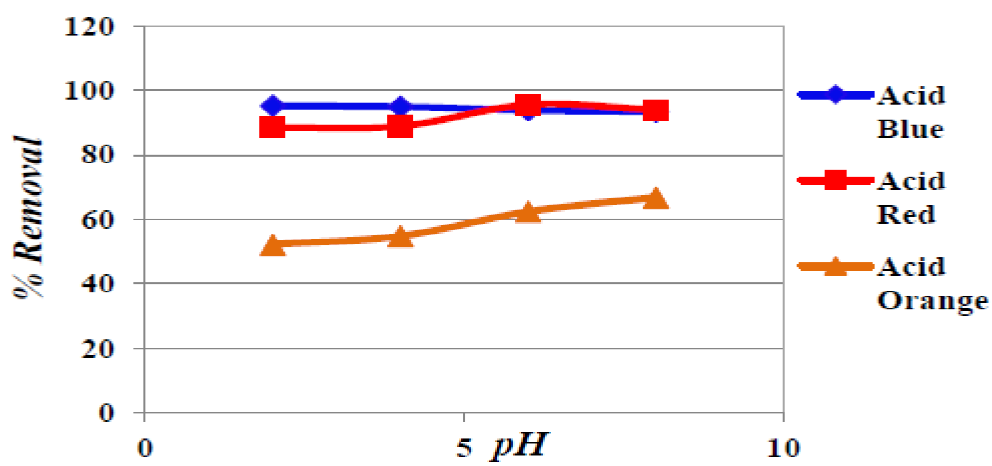

Figure 3.4 Efficiency of color removal on 250mg/l concentration at various pH

3.3.2 Efficiency of color removal on 200mg/l concentration

The fig: 3.5 shows, that the adsorption capacity was reduced for Acid Blue when there was an increase in pH which is similar to the efficiency of color removal on 250mg/l concentration.

The absorption capacity was increased upto the pH range of 6 and it decreased at pH 8 for Acid Red Dye. The optimum pH was found at pH 6.

The efficiency of color removal is reduced for Acid Orange when there was an decrease in pH and the color removal efficiency is increased at higher pH. But the overall removal efficiency is very low for Acid Orange comparatively with the other two dyes. The highest removal efficiency for Acid Orange at the pH range 8 is 75.15%

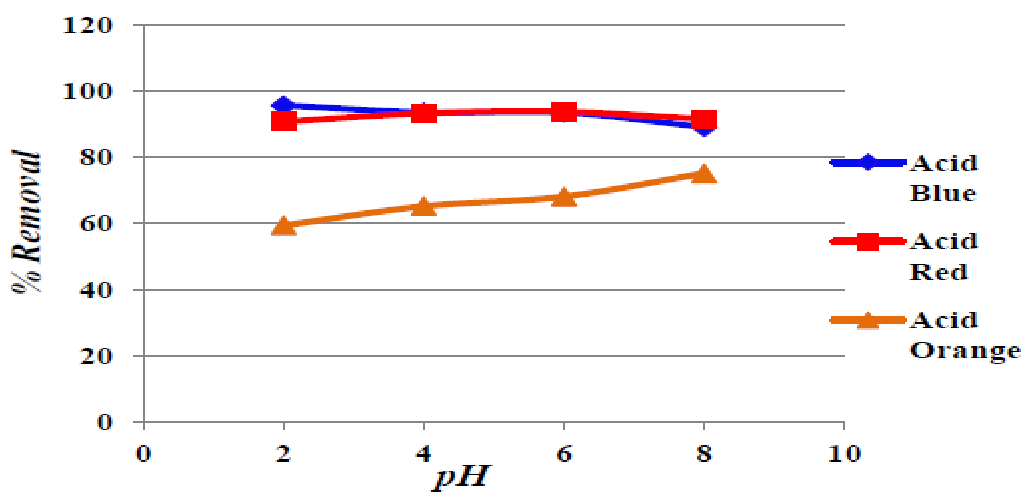

Figure 3.5 Efficiency of color removal on 200mg/l concentration at various pH

3.3.3 Efficiency of color removal on 150mg/l concentration

It was concluded from the experimental results shown in fig: 3.6, that the adsorption capacity was reduced for Acid Blue when there was an increase in pH and the adsorption capacity was increased when the decrease in pH. The optimum pH was found to be around pH 2.The absorption capacity was increased upto the pH range of 6 and it decreased at pH 8 for

Acid Red Dye. The optimum pH was found at pH 6.

The efficiency of color removal is reduced for Acid Orange when there was a decrease in pH and the efficiency of color removal is optimum at higher pH range. The highest removal efficiency for Acid Orange at the pH range 8 is 85.23%.

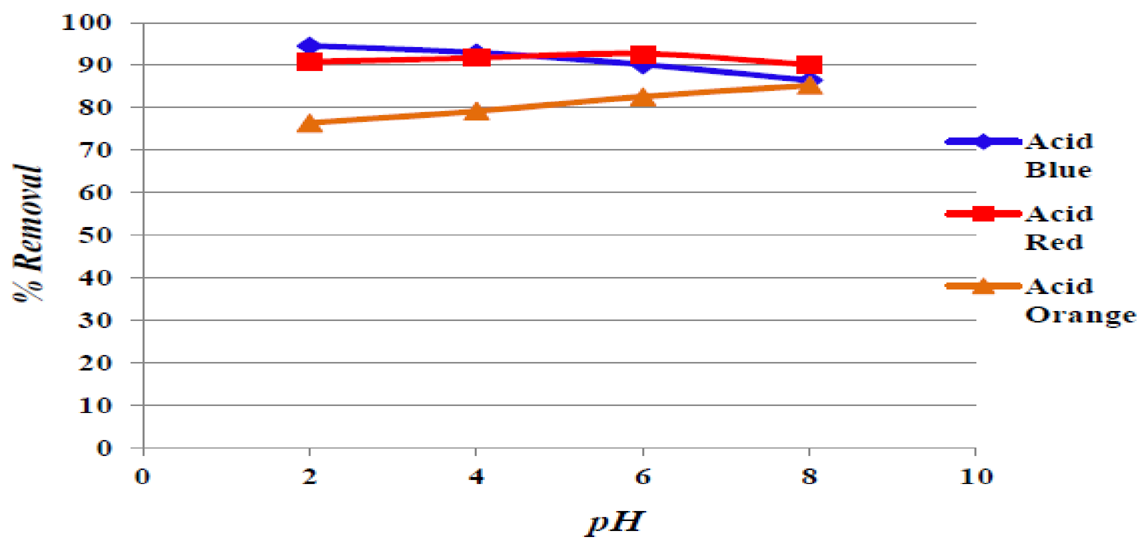

Figure 3.6 Efficiency of color removal on 150mg/l concentration at various pH

3.3.4 Efficiency of color removal on 100mg/l concentration

From the fig: 3.7,the optimum pH was found to be around pH 2.The absorption capacity was increased upto the pH range of 6 and it decreased at pH 8 for Acid Red Dye. The optimum pH was found at pH 6 and the efficiency is 93.08%.

The efficiency of color removal is reduced for Acid Orange when there was a decrease in pH and the efficiency capacity was increased at higher pH range. The maximum color removal efficiencies was obtained at 100mg/l concentration whereas the removal efficiency was very low for the other concentration of dye solution. The highest color removal efficiency for Acid Orange dye at the pH range of 8 is 92.16%.

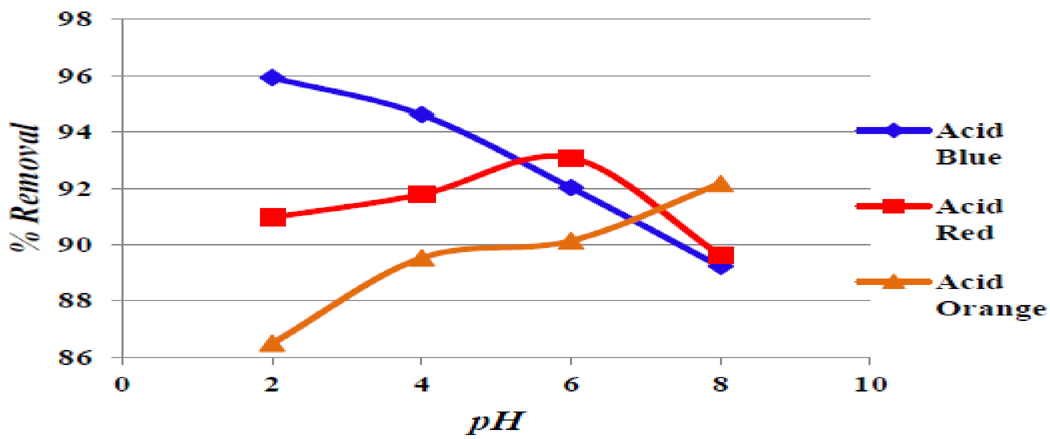

Figure 3.7 Efficiency of color removal on 100mg/l concentration at various pH

3.4 EFFECT OF TEMPERATURE

Temperature is an important parameter in adsorption process. The removal of color is done by the prepared GO in different temperatures and other parameters are set as constant (pH is 7, optimum concentration of 100mg/l). The removal efficiency of GO will decrease when the temperature increase. From the fig: 3.8, the maximum removal was found at 25°C.

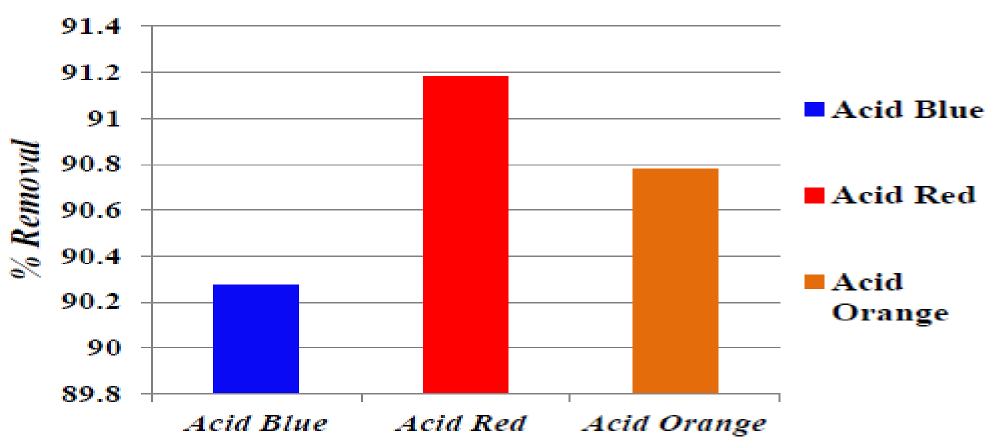

Figure 3.8 Efficiency of color removal at 25°C

CONCLUSION

This work involves the utilization of Waste Activated Sludge (WAS) by synthesizing Graphene Oxide (GO). The synthesized GO shows a relatively high surface area and large micro pore volumes and it was found out to be a most promising adsorbent for dye removal from aqueous solutions. The adsorption efficiency of dyes was increased with the decrease in concentration of the solution, while the adsorption efficiency of dyes was decreased with the increase in temperature and dye concentration. The optimum temperature for removal of color from dyes was achieved at 25°C in the concentration of 100mg/l. The adsorption of acid Blue was achieved in acidic medium with optimum pH 2, while the adsorption of acid Orange was favored at alkaline medium with an optimum pH 8. This research revealed that the Graphene Oxide synthesized from Waste Activated Sludge (WAS) is an effective and low-cost adsorbent for treating Industrial dye wastewater.

REFERENCES

[1] Anirudhan, T.S., Radhakrishnan, P.G., 2008. Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell. J.Chem. Thermodyn. 40, 702–709.

[2] Attia, A.A., Rashwan, W.E., Khedr, S.A., 2006. Capacity of activated carbon in the removal of acid dyes subsequent to its thermal treatment. Dyes Pigm.69, 128- 136.

[3] Banerjee, P., Das, P., Zaman, A., Das, P., 2016. Application of graphene oxide nanoplatelets for adsorption of Ibuprofen from aqueous solutions: Evaluation of process kinetics and thermodynamics. Proc. Saf. Environ. Protec.101, 45–53.

[4] Banerjee, P., Sau, S., Das, P., Mukhopadhayay, A., 2015. Optimization and modelling of synthetic azo dye wastewater treatment using Graphene oxide nanoplatelets: Characterization toxicity evaluation and optimization using Artificial Neural Network. Ecotoxicol. Environ. Saf. 119, 47–57.

[5] Botas, C., Álvarez, P., Blanco, C., Santamaria, R., Granda, M., Ares, P., Reinoso, F.R., Menéndez, R., 2012. The effect of the parent graphite on the structure of graphene oxide. Carbon 50, 275–282.

[6] Bulur, Y., Aydm, H.A., 2006. Kinetics and thermodynamics study of methylene blue adsorption on wheat shells desalination. 194, 259–276.

[7] Cheriaa, J., Khaireddine, M., Rouabhia, M., Bakhrouf, A., 2012. Removal of triphenyl methane dyes by bacterial consortium. Chien, S.H., Clayton, W.R., 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci. Soc. Am.J. 44, 265–268.

[8] Derringer, G., Suich, R., 1980. Simultaneous optimization of several response variables. J. Qual. Technol. 12, 214-219.

[9] Dubinin, M.M., Radushkevich, L.V., 1947. The equation of the characteristic curve of activated charcoal. Dokl. Akad. Nauk (SSSR) 55, 327–329.

[10] Ferrero, F., 2007. Dye Removal by Low Cost Adsorbents: Hazelnut Shell in Comparison with Wood Saw Dust. J. Colloid. Interf. Sci. 142, 144–152.

[12] Foo, K.Y., Hameed, B.H., 2011. Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption. Chem. Eng. J. 166, 792–795.

[13] Freundlich, H.Z., 1906. Uber die adsorption in losungen. Z. Phys. Chem. 57, 385–470.

[14] Hashemian, S., Salari, K., Yazdi, Z.A., 2014. Preparation of activated carbon from agricultural wastes (almond shell and orange peel) for adsorption of 2-pica from aqueous solution. J. Indus. Eng. Chem. 20, 1892–1900.

[15] Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Proc. Biochem. 34, 451–465.

[16] Ho, Y.S., McKay, G., 1998. Sorption of dye from aqueous solution by peat. J. Chem. Eng.70, 115–124.

[17] Hu, B.B., Wang, K., Wu, L., Yu, S.H., Antonietti, M., Titirici, M.M., 2010. Engineering carbon materials from the hydrothermal carbonization process of biomass. Adv. Mater. 22, 813–828.

[18] Hummers, W., Offeman, R., 1958. Preparation of Graphitic Oxide. J. Am. Chem. Soc.80, 1339-1339.

[19] Inagaki, M., Kim, Y.A., Endo, M., 2011. Graphene: preparation and structural perfection. J.Mater.Chem.21, 3280–3294.

[20] Jin, S., Chen, H., 2007. Near-infrared analysis of the chemical composition of rice straw. Ind.Crops Prod. 26, 207–211.

[21] Khan, T.A., Nazir, M., Khan, E.A., 2013. Adsorptive removal of rhodamine B from textile wastewater using water chestnut (*Trapa natans* L.) peel: adsorption dynamics and kinetic studies. Toxicol. Environ. Chem. 95, 919–931.

[22] Labada, J., Sabate, J., Liorens, J., 2011. Experimental and modeling study of the adsorption of single and binary dye solutions with an ion-exchange membrane adsorber. Chem. Eng. J. 166, 536–543.

[23] Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. K. Sven.Vetenskapsakad.Handl. 24, 1–39.

[24] Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J.Am. Chem. Soc. 40, 1361–1403.

[25] Nasuha, B.N., Hameed, B.H., Azam, T., Din, M., 2010. Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. J. Hazar. Mater. 175, 126–132.

[26] Purkait, M.K., Maity, A., DasGupta, S., De, S.J., 2007. Removal of congo red using activated carbon and its regeneration. J. Hazar. Mater. 145, 287–295.

[27] Roosta, M., Ghaedi, M., Daneshfar, A., Sahraei, R., Asghari, A., 2014. Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology. Ultrason. Sonochem. 21, 242–252.

[28] Satapathy, M.K., Banerjee, P., Das, P., 2013. Plant-mediated synthesis of silver-nanocomposite as novel effective azo dye adsorbent. Appl. Nanosci. 5, 1–9.

[29] Senthilkumaar, S., Kalaamani, P., Subburaam, C.V., 2006. Liquid phase adsorption of Crystal violet onto activated carbons derived from male flowers of coconut tree. J. Hazar. Mater. 136,800–808.

[30] Sierra, U., Álvarez, P., Blanco, C., Granda, M., Santamaría, R., Menéndez, R., 2016. Cokes of different origin as precursors of graphene oxide. Fuel 166, 400– 403.

[31] Temkin, M.I., Pyzhev, V., 1939. Kinetics of ammonia synthesis on promoted iron catalyst. J. Phys. Chem. (USSR) 13, 851-867.