REMOVAL OF CATIONIC TEXTILE DYE METHYLENE BLUE (MB) USING STEEL SLAG COMPOSITE

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ABSTRACT

Steel slag is generated during the steel production of around 10–15% per tonne. Steel slag composite has various metal oxides mainly composed of iron, aluminum, manganese and calcium along with silica. Dyes of textile industry effluent are one of the major threats to the environment. Methylene Blue (MB) a cationic dye originated from various dyeing processes of textile industries. In this research work, Induction Furnace (IF) steel slag is utilized in the removal of cationic textile dye Methylene Blue (MB). Steel slag materials were thermally activated at 600°C for 4 hrs. UV-Vis spectroscopy is used to determine the removal properties of IF steel slag on MB dye. Adsorbent dosage, initial dye concentration and pH with various contact time were studied. Surface morphology and structural bonding of steel slag materials over dye molecule were studied using Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) analysis respectively. The removal mechanism of textile dye (MB) using industrial by-product slag composite has been explored.

Keywords: Steel Slag, Methylene Blue, Core-shell Formation, Dye Removal, Wastewater Treatment.

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INTRODUCTION

Steel slag an industrial by-product during the steel manufacturing process and is generated nearly 10-15% in the manufacture of one ton steel¹. Due to globalization, the production of steel is increasing and so the slag. Steel slag applications include concrete,^{2,6} radiation shielding,^{7,8} heavy metal removal,^{1,9} fire resistance,¹⁰ agriculture,¹¹ coral rehabilitation¹² and CO₂ sequestration¹³. Prevention of water bodies from pollution and toxicity is a major responsibility during the promotion of industrialization. Textile dye pollution is a huge threat to water bodies¹⁴ and its living species in the ecosystem by disturbing their growth and causes serious health issues. Generally, the discharge from industries is directed to the nearest water source¹⁵. Industries such as textiles, leather, plastics and other relevant industries use various dyes to impart color in products and also consume the substantial volume of water¹⁶ which ends up with colored wastewater being discharged into the environment and causing water pollution¹⁷. Various industries using different dyes hurt living organisms within short exposure periods¹⁸. Throughout the world, approximately 7 x 10⁵ tones of 10,000 types of dyestuff are produced every year¹⁹. In the textile industry dyeing process, 10–15% of the unutilized/uncoated dye is discharged as dye effluents²⁰ and affecting water bodies. Wastewater treatment studies have been done already by researchers using steel slag²¹⁻²³ to reduce the toxicity level in water bodies.

Methylene Blue a cationic textile dye is widely used for dyeing fabrics and various techniques to remove MB in wastewater were employed. LiFe(WO₄)₂ a heterogeneous Fenton-like catalyst used decolorizes wastewater containing MB²⁴. Dried sewage sludge has been treated at 200°C - 700°C for the adsorption of MB dye and the maximum adsorption was recorded at 700°C²⁵. H₂SO₄ and Fe₃O₄ combined chitosan

adsorbent is prepared for the removal of MB and the adsorption was effective where the compositions of 0.35 g chitosan, 0.5 g Fe_3O_4 and 0.02 M H_2SO_4 ²⁶. The behavior of MB over bentonite clay is studied and the adsorbent removed 95% of MB with spontaneous nature of adsorption ($-\Delta G^\circ$)²⁷. Porous carbon derived from tea waste precursors under thermochemical condition using phosphoric acid acts as an activating agent and the maximum adsorption capacity of tea waste was found over MB was 402.25 mg g^{-1} ²⁸. Decomposition of MB was studied using sodium persulfate in the presence of microwave irradiation (MWI) and the maximum decomposition were obtained 99.9% for 50 mg L^{-1} dye concentration, where the time and temperature were kept 8 min and 90°C respectively²⁹. Also, MB was removed using diatomite modified with BaCl_2 ³⁰ and terrestrial weeds³¹. Induction Furnace steel slag is not used in cement production due to less calcium and this study is an initiative to effectively utilize IF steel slag due to high iron content. Though various steel slag materials have been used for dye removal, to the best of our knowledge this is the first report in the utilization of IF steel slag for the removal of dyes. In the present study, thermally activated industrial by-product slag (600°C for 4 hrs) has been utilized for the removal of textile industry cationic dye Methylene Blue from synthetic aqueous solution.

EXPERIMENTAL

Preparation of Steel Slag Composite

Induction Furnace steel slag samples were obtained from Jeppiaar furnace and Steels Pvt. Ltd., Kanchipuram, Tamilnadu, India. The size of the slag used in the present study is less than 90 micron (μ) and it is achieved by the continuous ball milling process. The steel slag sample is washed with deionized water for the removal of surface impurities. The washed steel slag samples were dried in a hot air oven at 200°C. The dried IF steel slag samples were thermally activated at 600°C for 4 hrs and further kept in a desiccator until used for experimental studies. IF steel slag ($< 90 \mu$) utilized in the present study is shown in Fig.-1.

Fig.-1: Induction Furnace Steel Slag Composite

Preparation of Synthetic Dye Solution

Methylene Blue (MB) was procured from SRL chemicals, India (AR grade). The dye is used without further purification throughout the study. Stock solutions were prepared by dissolving the required quantity of dye in de-ionized water. Various concentrations of dye solutions were prepared and HCl (0.1M)/NaOH (0.1M) was used to adjust pH of the solution.

Techniques Involved

Surface morphology of IF steel slag before and after removal of dyes was studied using high-resolution scanning electron microscopy (HR-SEM, Hitachi S-4800). The composition of metal oxides present in IF steel slag was determined by using X-ray fluorescence spectroscopy (XRF, Bruker S8 Tiger) analysis. Structural bonding of IF steel slag before and after adsorption were determined using Fourier Transform Infrared Spectroscopy (FTIR, IRAffinity-1S Shimadzu) to identify the changes in the functional group of the sample (4000 to 500 cm^{-1}). The samples were prepared as pellets using hydraulic pelletizer, the ratio of sample and KBr is 1:10 respectively. Removal of MB was studied using absorption values of supernatant before and after the removal process by UV spectrophotometer (Shimadzu UV-800).

Dye Decolorization Studies

The experimental studies were carried out in 250 mL conical flasks with a known initial dye concentration of 100 mg L⁻¹ dye solution. The sorption system is allowed to reach equilibrium using orbital shaker at 120 rpm and 28°C in different contact times. Supernatants were collected for removal studies at regular time intervals. Maximum absorption (λ_{max}) of MB has been fixed at 663 nm in a UV spectrophotometer. The removal efficiency of IF steel slag were determined by the following equation:

$$\text{Removal \%} = [(C_0 - C_e) / C_0] \times 100 \quad (1)$$

Where, (C_0) and (C_e) is the initial and residual dye concentrations (mg L⁻¹), respectively.

Quantity of adsorbed dyes at equilibrium was calculated from the following equation,

$$q_e = [(C_0 - C_e) V] / W \quad (2)$$

Where, C_0 is the initial concentration (mg L⁻¹), C_e is the dye concentration at various time intervals (mg L⁻¹), V is the volume of experimental solution (mg L⁻¹) and W is the weight of IF steel slag (g). The experimental study is performed in triplicate (identical conditions) and the average values were taken for further studies.

RESULTS AND DISCUSSION

Characterization of Steel Slag Composite

Elemental composition of IF steel slag has been determined using Energy Dispersive X-Ray Analysis (EDAX) and is given in Table-1. Silicon, iron, aluminum and calcium are the elements present in IF steel slag. Chemical composition of IF steel slag has been analyzed using XRF and is listed in Table-2. SiO₂, Fe₂O₃, Al₂O₃, MnO and CaO are the major oxides present in IF steel slag with some traces.

Table-1: Elemental Composition of Steel Slag Composite

Element	App Conc.	Intensity Conc.	Weight%	Weight% Sigma	Atomic%
O	7.53	1.2403	42.58	1.89	62.12
Al	0.92	0.8529	7.59	0.71	6.57
Si	3.02	0.8645	24.58	1.21	20.43
Ca	0.28	1.0009	1.99	0.55	1.16
Fe	2.80	0.8442	23.27	1.78	9.72
Totals			100.00		

Table-2: Compounds Present in Steel Slag Composite

Formula	Concentrations (%)
SiO ₂	43.22
Fe ₂ O ₃	28.09
Al ₂ O ₃	14.46
MnO	4.32
CaO	2.97
Cr ₂ O ₃	1.62
TiO	1.14
MgO	0.97
Na ₂ O	0.75

Impact of Parameters on Textile Dye MB Removal

In basic pH, metal oxide in solution forms an aqua complex, yielding a negatively charged surface. In the basification process (NaOH) metal ions in IF steel slag such as Fe, Al and Ca tend to form metal hydroxides associated with Na⁺ ions. The Na⁺ ions will subsequently lead to an exchange of cationic dye. Adsorption studies carried out between 4 to 8 pH and the other parameters were kept constant

(dosage - 5 g, initial conc. 10 mg and shaker rpm - 120). For pH 4, 5, 6, and 7 the removal percentage of MB dye is 60.96, 68.04, 74.20, and 79.45 respectively. The maximum sorption of cationic dye MB (81.28%) occurs at pH 8 (Fig.-2). The number of possible cationic exchanging site increases the efficiency of MB dye removal via the ion exchange process.

Fig.-2: Effect of pH in Dye Removal Efficiency of Steel Slag Composite

The effect of initial dye concentration of MB is shown in Fig.-3. The decrease in removal percentage of MB is observed by increasing initial MB concentration (10-50 mg L⁻¹). The rate of MB dye removal is rapid and the adsorption is 78.02, 74.20, 68.22 and 59.54%. The maximum removal of MB dye (10 mg L⁻¹) is 80.29% at pH-8 and is observed at 60 min resulting in complex formation, beyond that saturation occurs due to the nonavailability of metal ions in the reaction mixture. The graph is plotted for different concentrations (10–50 mg) for 90 minutes and the decolorization percentage is shown in Fig.-4. At higher dye concentration, the greater number of MB molecules quickly exchange cations and this process causes a decrease in the percentage removal of further MB due to the limited exchanging ions on the surface of IF steel slag.

Fig.-3: Effect of the Initial Concentration of Dye Solution in the Removal Efficiency of Steel Slag Composite

Fig.-4: Effect of Contact Time in the Removal Efficiency of Steel Slag Composite

The experimental results indicate that, an increase in the dosage of IF steel slag leads to maximum removal of MB dye and is shown in Fig.-5. Adsorption increased from 62.08% to 80.26% when the dosage of IF steel slag is increased from 1 to 5 g. The observed enhancement of adsorption of dye is due to an increase in the number of possible cationic exchanging sites of the adsorbent.

Fig.-5: Effect of Steel Slag Composite Dosage in the Removal of Dye Solution

Mechanism of Dye Removal on Steel Slag Composite

A mixture of metal oxides present in IF steel slag tends to exchange its metal ions to MB dye molecules. pH of the reaction mixture is a major factor in the removal of dyes via the cationic exchange of metal ions present in IF steel slag. Due to the large surface area/metal ions in IF steel slag, the higher dosage of adsorbent increases the removal. An increase in pH of the reaction mixture leads to the formation of the negatively charged surface and favors the textile cationic dye (MB) removal. The number of possible cationic exchanging site increases the efficiency of dye removal via the ion exchange process. The possible mechanism *vis* ion exchange of MB textile dye with IF steel slag metal ions are as follows:

Adsorption Characterization of Slag Composite

SEM images of IF steel slag before adsorption reveals that the surface morphological features and surface characteristics of IF steel slag (Fig.-6). Various shapes and sizes of the elements/particles present in IF steel slag inferred from the SEM image. EDAX analysis of IF steel slag is shown in Table.2 and the elements present in IF steel slag are in oxide forms of Si-24.58%, Fe-23.27%, Al-7.59% and Ca-1.99%. These metal oxides tend to form metal hydroxides [$M^{x+}(\text{OH})_y$] in aqueous solution. The formation of positive or negative ions on the surface of steel slag is caused by the acidic or basic dissociation *via* solid-solution interface³². Fig.-7 shows the surface morphology of IF steel slag after the dye (MB) removal. SEM images infer that, dye molecules in aqueous solutions are exchanged with its cation and are adsorbed on the surface of IF steel slag leading to the formation of core-shell structure.

Fig.-6: Surface Morphology of Steel Slag Composite

Fig.-7: Steel Slag Surface Morphology after MB Dye Removal

Figure-8 shows the FTIR spectrum of IF steel slag. Major peaks appeared in the spectrum are 3315, 2924, 2374, 1664, 1402, 1116, 651, 601, and 464 cm^{-1} . Figure-9 shows the FTIR spectrum of adsorbent after the adsorption of MB dye. The major peaks that appeared in the spectrum are 3315, 3197, 2360, 1670, 1402, 1097, 794, 601 and 462 cm^{-1} . The peaks 1602, 1116 and 835 cm^{-1} are shifted to 1670, 1097 and 794 cm^{-1} respectively. The peaks from the region 1670 to 1402 cm^{-1} have been disappeared due to strong adsorption of MB dye on the surface of IF steel slag in basic environment.

Fig.-8: FTIR Analysis of IF Steel Slag before MB Removal

Fig.-9: FTIR Analysis of IF Steel Slag after MB Removal

CONCLUSION

This study mainly focuses on the effective utilization of industrial by-product slag, available in large quantities for the removal of textile cationic dye Methylene Blue. Optimization of various parameters such as pH, concentration of adsorbate (MB dye), adsorbent dosage (IF steel slag) and contact time were studied. The maximum removal of 10 mg of MB cationic dye solution is 81.28% for 5 g of IF steel slag dosage at pH-8. This process can be scaled up further for the utilization of IF steel slag as a cost-effective adsorbent and it can minimize the toxicity effects of textile industry effluents resulting to a better environment.

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REFERENCES

1. J. Baalamurugan, V. G. Kumar, K. Govindaraju, B. S. N. Prasad, V. K. B. Raja, R. Padmapriya, *International Journal of Nanoscience*, **16**, 1760013(2017), DOI:10.1142/S0219581X17600134
2. R. Padmapriya, V. K. B. Raja, V. G. Kumar, J. Baalamurugan, *Rasayan Journal of Chemistry*, **12**(4) 1744(2019), DOI:10.31788/RJC.2019.1245211
3. Y. Biskri, D. Achoura, N. Chelghoum, M. Mouret, *Construction and Building Materials*, **150**, 167(2017), DOI:10.1016/j.conbuildmat.2017.05.083
4. R. Padmapriya, V. K. B. Raja, V. G. Kumar, J. Baalamurugan, *International Journal of Earth Science and Engineering*, **8**(5), 2138(2015), DOI:10.1016/j.anucene.2011.08.010
5. A. S. Brand, J. R. Roesler, *Cement & Concrete Composites*, **60**, 1(2015), DOI:10.1016/j.cemconcomp.2015.04.006
6. Z. Ghoulch, R. I. L. Guthrie, Y. Shao, *Journal of CO₂ Utilization*, **18**, 125(2017), DOI:10.1016/j.jcou.2017.01.009
7. M. A. González-Ortega, I. Segura, S. H. P. Cavalero, B. Toralles-Carbonari, A. Aguado, A. C. Andrello, *Construction and Building Materials*, **51**, 432(2014), DOI:10.1016/j.conbuildmat.2013.10.067
8. J. Baalamurugan, V. G. Kumar, S. Chandrasekaran, S. Balasundar, B. Venkatraman, R. Padmapriya, V. K. B. Raja, *Journal of Hazardous Materials*, **369**, 561(2019), DOI:10.1016/j.jhazmat.2019.02.064
9. N. Shao, S. Li, F. Yan, Y. Su, F. Liu, Z. Zhang, *Journal of Hazardous Materials*, **382**, 121120(2020), DOI:10.1016/j.jhazmat.2019.121120
10. N. T. Abdel-Ghani, H. A. Elsayed, S. AbdelMoied, *HBRC Journal*, **14**, 159(2018), DOI:10.1016/j.hbrj.2016.06.001
11. X. Gao, M. Okubo, N. Maruoka, H. Shibata, T. Ito, S. Y. Kitamura, *Mineral Processing and Extractive Metallurgy*, **124**(2), 116(2015), DOI:10.1179/1743285514y.0000000068
12. T. A. Mohammed, H. Aa, H. Nf, E. E-A. Ma, E-M. I. Khm, *International Journal of Environmental Protection*, **2**(5), 1(2012),
13. W. M. Mayes, A. L. Riley, H. I. Gomes, P. Brabham, J. Hamlyn, H. Pullin, P. Renforth, *Environmental Science & Technology*, **52**(14), 7892(2018), DOI:10.1021/acs.est.8b01883
14. M. L. Firdaus, F. E. Madina, S. Y. F, R. Elvia, N. Soraya, D.R. Eddy, A. P. Cid-Andres, *Rasayan Journal of Chemistry*, **13**(1), 249(2020), DOI:10.31788/RJC.2020.1315496
15. N. Barka, M. Abdennouri, M. E. L. Makhfouk, *Journal of Taiwan Institute of Chemical Engineers*, **42**(2), 320(2011), DOI:10.1016/j.jtice.2010.07.004
16. M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, *Journal of Hazardous Materials*, **177**(1-3), 70(2010), DOI:10.1016/j.jhazmat.2009.12.04
17. S. Selvakumar, R. Manivasagan, K. Chinnappan, *3 Biotech*, **3**(1), 71(2013), DOI:10.1007/s13205-012-0073-5
18. S. Dhananasekaran, R. Palanivel, S. Pappu, *Journal of Advanced Research*, **7**(1), 113(2016),

[DOI:10.1016/j.jare.2015.03.003](https://doi.org/10.1016/j.jare.2015.03.003)

19. M. S. Mahmoud, *HBRC Journal*, **12**(1), 88(2016), [DOI:10.1016/j.hbrj.2014.07.005](https://doi.org/10.1016/j.hbrj.2014.07.005)
20. M. Daniel, G. D. Luna, E. D. Flores, D. Angela, D. Genuino, C. M. Futralan, M. Wan, *Journal of the Taiwan Institute of Chemical Engineers*, **44**(4), 646(2013), [DOI:10.1016/j.jtice.2013.01.010](https://doi.org/10.1016/j.jtice.2013.01.010)
21. Y. Gao, J. Jiang, S. Tian, K. Li, F. Yan, N. Liu, M. Yang, X. Chen, *Scientific Reports*, **7**(1) 1(2017), [DOI:10.1038/s41598-017-11682-3](https://doi.org/10.1038/s41598-017-11682-3)
22. M. E. M. Ali, T. A. Gad-Allah, M. I. Badawy, *Applied Water Science*, **3**(1), 263(2013), [DOI:10.1007/s13201-013-0078-1](https://doi.org/10.1007/s13201-013-0078-1)
23. L. Kang, Y. J. Zhang, L. L. Wang, L. Zhang, K. Zhang, L. C. Liu, *Integrated Ferroelectrics An International Journal*, **162**(1), 8(2015), [DOI:10.1080/10584587.2015.1037197](https://doi.org/10.1080/10584587.2015.1037197)
24. F. Ji, C. Li, J. Zhang, L. Deng, *Desalination*, **269**(1-3), 284(2011), [DOI:10.1016/j.desal.2010.11.015](https://doi.org/10.1016/j.desal.2010.11.015)
25. H. D. Utomo, X. C. Ong, S. M. S. Lim, G. C. B. Ong, P. Li, *International Biodeterioration & Biodegradation*, **85**, 460(2013), [DOI:10.1016/j.ibiod.2012.12.004](https://doi.org/10.1016/j.ibiod.2012.12.004)
26. Rahmi, Ismaturrehmi, I. Mustafa, *Microchemical Journal*, **144**, 397(2019), [DOI:10.1016/j.microc.2018.09.032](https://doi.org/10.1016/j.microc.2018.09.032)
27. Y. AM, A-A MM, A. MA, *Journal of Analytical & Bioanalytical Techniques*, **5**(1), 1(2014), [DOI:10.4172/2155-9872.1000179](https://doi.org/10.4172/2155-9872.1000179)
28. L. Borah, M. Goswami, P. Phukan, *Journal of Environmental Chemical Engineering*, **3**(2), 1018(2015), [DOI:10.1016/j.jece.2015.02.013](https://doi.org/10.1016/j.jece.2015.02.013)
29. Y-B. Kim, J-H. Ahn, *International Biodeterioration & Biodegradation*, **95**, 208(2014), [DOI:10.1016/j.ibiod.2014.03.023](https://doi.org/10.1016/j.ibiod.2014.03.023)
30. L. V. Tan, L. T. Hung, *Rasayan Journal of Chemistry*, **9**(3), 478(2016).
31. A. Singh, S. Kumar, V. Panghal, S. S. Arya, S. Kumar, *Rasayan Journal of Chemistry*, **12**(4), 1956(2019), [DOI:10.31788/RJC.2019.1245401](https://doi.org/10.31788/RJC.2019.1245401)
32. S. M. Ahmed, *Canadian Journal of Chemistry*, **44**(14), 1663(1966), [DOI:10.1139/v66-411](https://doi.org/10.1139/v66-411)
[RJC-5715/2020]