Synthesis and Characterization of Graphene Oxide and Chitosan Decorated Nano Zerovalent Iron for Efficient Adsorptive Removal of Hazardous Azo Dye from Aqueous Medium

Monika Thakur and Rupesh Kumar[*]

Department of Chemical Sciences, I.K. Gujral Punjab Technical University, Kapurthala-144603, India

*Corresponding author: E-mail: rupesh.manak@gmail.com

The main aim of the study was to synthesize nano zerovalent iron (NZVI) modified with graphene oxide (GO) and chitosan (CS) in the form of a magnetic ternary nanocomposite. Three ternary nanocomposites *i.e.* GO-CS-NZVI, GO-NZVI-CS and CS-NZVI-GO were synthesized to further understand the possible binding tendencies among these components in the final ternary composite. These ternary composites were characterized by FTIR, SEM and EDS techniques to understand the effect of mutual interaction of the three components during synthesis on the overall structure and morphology of the ternary composite. Furthermore, these ternary nanocomposites were employed in the removal of Congo red (an anionic, carcinogenic, azo dye) and also a mixture of dyes Congo red and Rhodamine B (a cationic, carcinogenic dye). A maximum of 98% removal of Congo red and 98.7% removal from the mixture of dyes was observed with ternary nanocomposite GO-CS-NZVI within 30 min. Equilibrium adsorption efficiency (q_e) was calculated to be 48.15 and 79 mg/g for Congo red and mixture of dyes (Congo red & Rhodamine B), respectively. A comparative analysis of bare NZVI with these ternary nanocomposites was also conducted to further understand the effect of modification of NZVI with graphene oxide and chitosan on the structure, morphology and its dye removal efficiency.

Keywords: Magnetic ternary nanocomposite, Adsorption, Congo red, Rhodamine B.

INTRODUCTION

Quality availability of water is essential for the survival of living beings on earth. However, the quality of this precious natural resource is degrading due to expanding population and fast industrialization, which causes a lot of pollution to get into the water [1,2]. The major water contaminants can be classified as organic industrial waste including dyes, pesticides, tanneries, chlorinated compounds, pharmaceuticals and inorganic pollutants include metals/metalloids, nitrates, phosphates, *etc.* [3,4]. These water pollutants are serious threats to the biosphere as they are responsible for causing skin allergies, poisoning, reduced light penetration in water bodies leading to reduced photosynthesis and many of them reported to be carcinogenic and mutagenic [5]. Mostly textile industries discharge approximately 280,000 tons of untreated dyes per year into waste streams. Therefore, to overcome this problem, an effective and efficient treatment methods to remove these dyestuff from water streams should be applied [6,7]. Most studied techniques include flocculation, chemical coagulation, oxidation/reduction, ion exchange, solvent extraction, photocatalytic degradation, biosorption, adsorption, *etc*. [3,8].

Adsorption is globally accepted method for the treatment of wastewater from these industries due to ease of handling, better performance and availability of many adsorbents [9,10]. A wide range of materials as adsorbents have been reported for removal of dyes from water like activated carbon, natural materials *e.g.* clay and clay based adsorbents, agricultural solid wastes (*e.g.* rice husk, orange peel, *etc.*), industrial byproducts (*e.g.* waste sludge, red mud, *etc.*), biosorbents like chitosan, metal nanoparticles like nanozero valent iron, titanium oxide, iron oxide, zinc oxide, silver, gold and many bimetallic composites polymer nanocomposites like graphene, chitosan, PVA and other polymer based composites [11,12]. Among these adsorbents, nano zerovalent iron (NZVI) lone and modified NZVI with supports like polymers, resins, biochar or other metal nanoparticles being environmentally benign and low cost material, due to its easy magnetic separation has been extensively

studied and used in wastewater remediation due to its enhanced reactivity and stability and lowered self agglomeration after modification [13].

Due to its high electrical conductivity, superior mechanical flexibility, large surface area and unique chemical and thermal stability, graphene has become choice of material for researchers from different areas. Moreover, graphene oxide (GO) is an oxidized form of graphene exhibiting a wide variety of chemical functionality and high surface area and also offers incredible uses in wastewater treatments [14,15]. Incorporation of natural polymers *e.g.* chitosan into graphene oxide leads to drastic increase in the adsorption capacity of the composite due to high surface area and improved porosity. Chitosan (CS) being non-toxic, biodegradable, low cost material and high functionality has been a choice to fabricate composites for water remediation [16].

The synthesis and applications of bare and modified nano-zerovalent iron (NZVI) have been immensely studied for ground water remediation and wastewater treatment. Gul *et al.* [16] reported the removal of anionic and cationic dyes using funct-ionalized magnetic chitosan with GO. They have decorated chitosan with Fe_3O_4 nanoparticles and followed by crosslinking with GO to synthesize Fe_3O_4 supported chitosan-graphene oxide composite (Fe_3O_4@GO) and applied in the adsorption of methyl violet and alizarin yellow dyes. Arora *et al.* [17] reported the degradation of Congo red dye with novel Cu loaded Fe_3O_4@TiO_2 core shell nanoparticles prepared in single pot by coating TiO_2 on Fe_3O_4 nanoparticles followed by Cu loading. Similarly, He *et al.* [18] synthesized core shell zero valent nanoiron nickel (nZVIN) for the removal of Congo red dye.

In present study, we aim to synthesize a ternary magnetic composite of nano-zerovalent iron (NZVI), graphene oxide (GO) and chitosan (CS) but following different synthetic routes to achieve three nanocomposites *i.e.* GO-CS-NZVI, GO-NZVI-CS and CS-NZVI-GO and explored its applicability in the removal of toxic anionic dye Congo red (CR) as well as in the mixture of dyes.

EXPERIMENTAL

Graphite powder, $NaNO_3$, ferrous sulpahte heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium borohydride, potassium permanganate, sodium hydroxide, hydrogen peroxide, conc. sulphuric acid, conc. hydrochloric acid, acetic acid, ethanol were purchased from Fisher Scientific/Avarice. Congo red and rhodamine B dyes were procured from Loba Chemie. Chitosan was procured from Himedia. All the chemicals were of analytical grade and used without further purification.

Characterization: The SEM-EDS analysis was done on digital scanning electron microscope JSM-6510 revealing the surface morphology of the composite. Energy dispersive spect-roscopic (EDS) study was performed to know the elemental distribution in the composite. FTIR was performed on Perkin-Elmer spectrum II with a resolution of 1 cm^{-1} and a scan range from 4000 cm^{-1} to 250 cm^{-1} to detect various functional groups. Digital Lux Meter KM-LUX-200K was used to record light

intensity. UV-VIS spectrophotometer was used to analyze dye removal by observing change in absorbance of dye before and after treatment with as synthesized nanocomposites.

Synthesis: A simple, one pot synthesis approach was followed towards the synthesis of modified NZVI particles. Graphene oxide (GO) was synthesized by modified Hummer's method [19]. Procedure details are same as reported in earlier study [20]. Chitosan (CS) suspension was prepared by dissolving chitosan in a buffer of pH 5. Synthesis of modified NZVI was planned as follows:

(i) GO-NZVI-CS nanocomposite: Graphene oxide (GO) (0.1 g) was sonicated in deionozed water (100 mL) to get GO suspension. To this, 0.1 M solution of $FeSO_4$ was added and magnetically stirred for 30 min. After that, 0.2 M $NaBH_4$ solution was added followed by addition of 100 mL of chitosan suspen-sion with stirring to get ternary nanocomposite GO-CS-NZVI. The black coloured product was filtered and vacuum dried overnight at 60 ºC.

(ii) CS-NZVI-GO nanocomposite: Chitosan suspension (100 mL) was mixed with 0.1 M $FeSO_4$ solution and stirred for 30 min. To this, 0.2 M $NaBH_4$ solution was added followed by 100 mL of GO suspension and magnetically stirred further to get ternary nanocomposite CS-NZVI-GO. The black coloured product was filtered, vacuum dried at 60 ºC overnight.

(iii) GO-CS-NZVI nanocomposite: Graphene oxide (GO) suspension (100 mL) was mixed with 100 mL of chitosan suspension and stirred for 0.5 h. To this, 0.1 M $FeSO_4$ solution was added and the solution was magnetically stirred further to achieve complete mixing. Afterwards, 0.2 M $NaBH_4$ solution was added to get ternary nanocomposite GO-CS-NZVI. The black coloured product was filtered and vacuum dried at 60 ºC overnight.

(iv) Bare NZVI was also prepared by following similar synthetic procedure to further analyze the effect of ternary modification on dye removal efficiency.

Batch experiments: These as-synthesized ternary nano-composites *i.e.* GO-NZVI-CS, CS-NZVI-GO and GO-CS-NZVI and bare NZVI were employed to treat contaminated water samples to remove toxic anionic dye Congo red. For all experi-ments, 50 mL of dye solution in deionized water was taken, to which 50 mg of composite was added, solution was magne-tically stirred for 0.5 h in direct sun light on terrace (76000 lux), After that the composite was separated with an external magnetic bead owing to magnetic nature of composites. After separation, the UV-VIS spectra of resultant solutions was reco-rded. The wavelength of maximum adsorption of Congo red *i.e.* (λ_{max} 498 nm) was observed. All the experiments were conducted at 38-40 ºC and at pH of dye in water. A similar study was conducted on a mixture of rhodamine B (a cationic dye) and Congo red (an anionic dye) in 1:1 proportion.

The removal efficiency of the synthesized nanocomposites employed was determined using eqn. 1:

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

where, C_o and C_t are the initial and at any time 't' concentration of dye in the solution.

The adsorption efficiency (q_t) (mg/g) is defined as the amount of dye adsorbed by the synthesized nanocomposite at any time 't' and was calculated using eqn. 2:

$$q_t = \frac{C_o - C_t}{W} \times V \qquad (2)$$

where, W is the mass of removal agent (g) and V is the volume of dye solution (L). At equilibrium, when no further decrease in the concentration of dye is observed, henceforth 'q_t' is written as 'q_e' *i.e.* equilibrium adsorption efficiency.

RESULTS AND DISCUSSION

FTIR studies: To explore the structures and possible bindings of components in the ternary nanocomposites, FTIR analysis of GO, CS, bare NZVI and all the ternary composites was done (Fig. 1). A band at 3300-3100 cm^{-1} in the ternary nano-composites can be assigned to O-H stretching frequency. Bands at 1035 and 1026 cm^{-1} in GO and CS, respectively can be attributed due to C-O stretching, whereas the bands at 2118 and 2117 cm^{-1} and at 1376 and 1371 cm^{-1} in GO and CS, respectively can be explained due to CH$_2$ symmetric and asymmetric stretching. A sharp peak at 1718 cm^{-1} on GO can be assigned to C=O stretching due to the oxy functional groups present on GO, which is absent in ternary composites indicating possible bonding with amino groups on chitosan. A peak at 1646 cm^{-1} observed in all the ternary nanocomposites can be attributed to C=O stretching of the possible amide linkage between GO and CS, which was not initially present in either GO or CS [10,21].
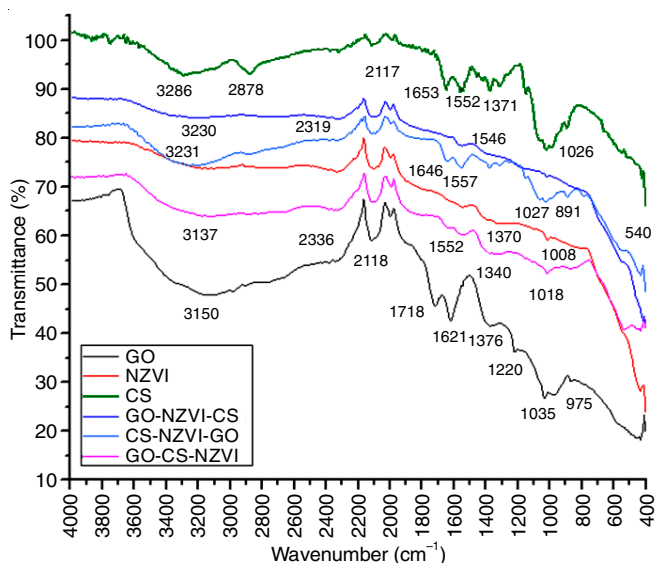

Fig. 1.   FTIR of bare graphene oxide (GO), chitosan (CS), nano zerovalent iron (NZVI), ternary nano composites GO-NZVI-CS, CS-NZVI-GO and GO-CS-NZVI

Morphological studies: The SEM image clearly revealed the spherical nanoparticles of NZVI self aggregated in chain like arrangement in bare NZVI (Fig. 2a). Nanoparticles can be observed densely agglomerated. In ternary nanocomposite GO-CS-NZVI (Fig. 2b), these spherical NZVI particles in chains can still be observed but less aggregated and supported on GO-CS support. This can be clearly visualized that the GO-CS support the reduce self aggregation of chains and hence improves the available surface area for sorption and hence dye removal. Similarly, spherical NZVI particles can be observed in GO-NZVI-CS (Fig. 2d), again in denser aggregation. In CS-NZVI-GO (Fig. 2c) larger sized spherical aggregates of NZVI were present instead of chain like morphology. The results suggested that binding of NZVI particles to GO-CS support improves the morphology and results in increased surface area of ternary nanocomposite.

The elemental distribution of the synthesized nanocomposites was revealed from the EDS analysis. The EDS data also corroborated the fact that presence of GO and CS in modified NZVI resulted in an increased Fe content in all the ternary nano-composites as compared to bare NZVI resulting from binding of the NZVI particles to GO-CS, GO or CS (Fig. 3a-d). Improved Fe content in all the ternary composites could result into better dye removal efficiency of the ternary composites than bare NZVI.

UV-Visible analysis of dye removal: Change in the peak of maximum absorbance of CR dye at λ_{max} 498 nm along with was observed after treatment with various removal agents *i.e.* NZVI, CS-NZVI-GO, GO-NZVI-CS and GO-CS-NZVI. The reaction conditions were kept same for all the removal agents *i.e.* 50 mL of the dye sample was treated with 50 mg of removal agent for a contact time of 30 min (Fig. 4a-c). The study revealed that NZVI exhibited 86% removal of dye, which was observed to be enhanced with all the three modified ternary composites. A maximum of 98% dye removal was observed with ternary nanocomposite GO-CS-NZVI which was followed by 94.3% and 93% removal with GO-NZVI-CS and CS-NZVI-GO, respectively. Equilibrium adsorption efficiency (q_e) was calculated to be 48.15 mg/g. The observation clearly indicates significant enhancement in dye removal efficiency of NZVI after modification with GO and CS. Among ternary nanocomposites, GO-CS-NZVI showed the maximum dye removal efficiency which can be explained due to fact that GO and CS bind together *via* amide linkages between oxy groups of GO and amino groups of CS leading to the formation of GO-CS support, which further binds NZVI particles on to it. Effective binding of NZVI onto the GO-CS support leads to minimized self aggregation of NZVI particles owing to its magnetic nature and hence increased surface area for dye adsorption. Furthermore, the effective binding of NZVI particles to the GO-CS support also reduces its rapid oxidation to its oxides and hydroxides resulting in improved reducing efficiency. In addition, dye samples were also treated with ternary composite GO-CS-NZVI in dark and removal efficiency was compared with that of samples treated in sunlight. The observation revealed dye removal efficiency was significant and similar in dark treated sample also.

A mixture of Congo red (anionic dye) with rhodamine B (cationic dye) dye solution was also treated with all the three ternary composites and NZVI. Similar results were obtained in treatment of mixture of dyes. The removal efficiency of NZVI was enhanced from 90% to a maximum of 98.7% with ternary composite GO-CS-NZVI indicating enhanced removal after modification with GO-CS support. The CS-NZVI-GO
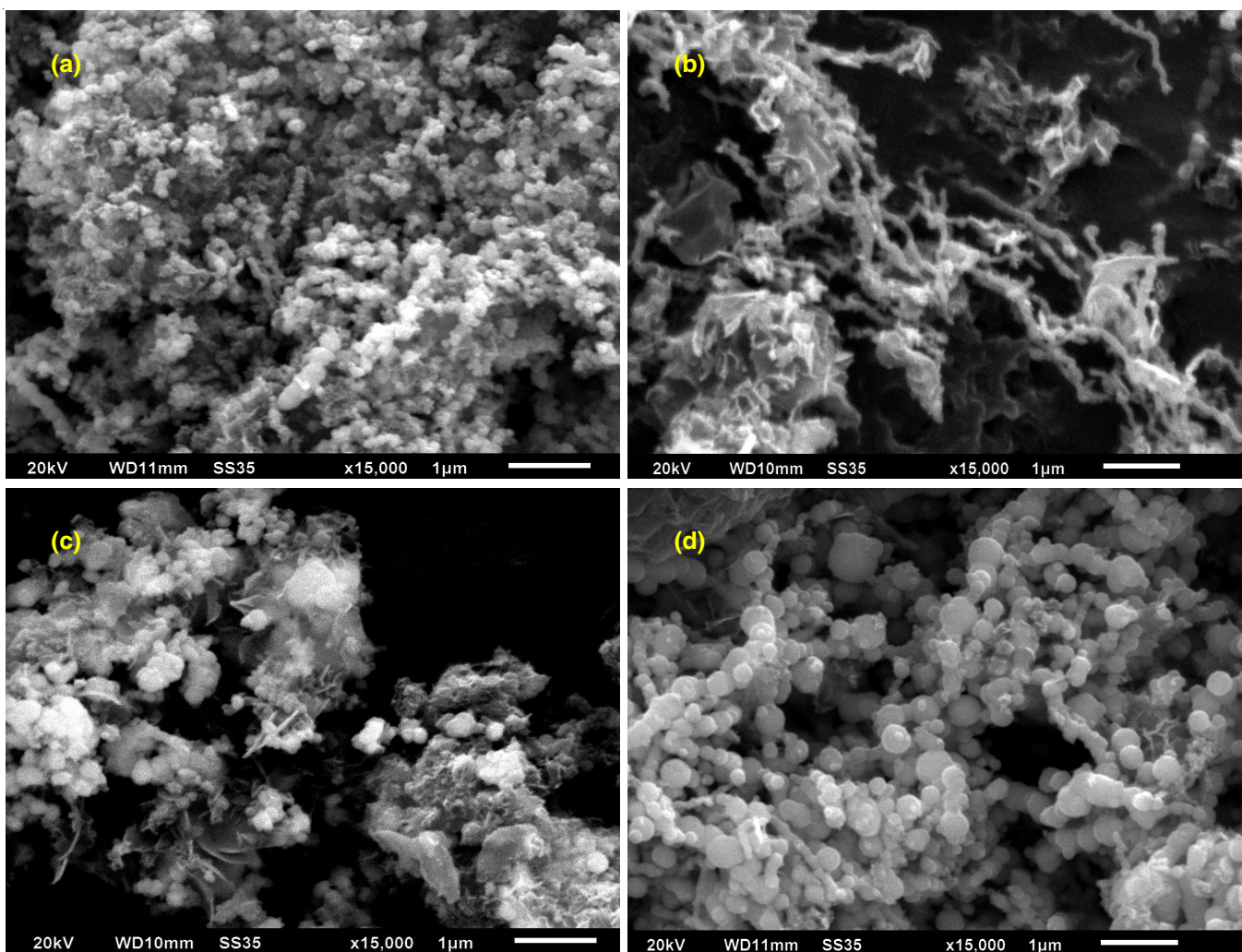
Fig. 2. SEM images of (a) bare NZVI (b) GO-CS-NZVI (c) CS-NZVI-GO (d) GO-NZVI-CS
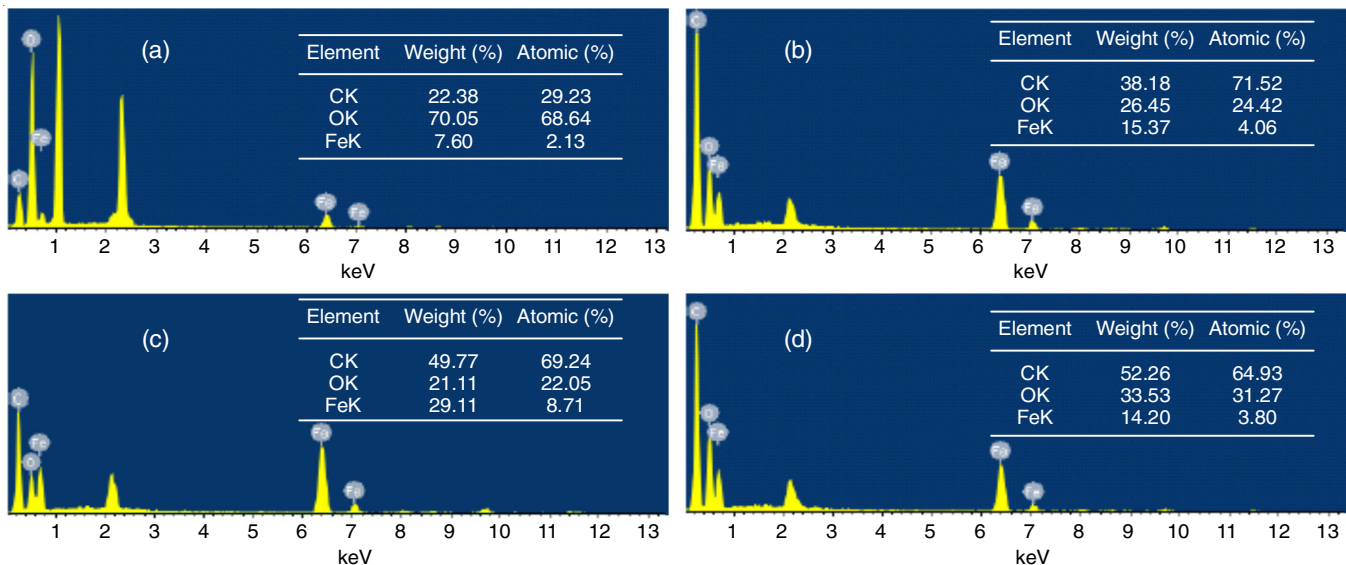

Fig. 3. EDS images and data of (a) bare NZVI, (b) GO-CS-NZVI, (c) GO-NZVI-CS and (d) CS-NZVI-GO

and GO-NZVI-CS also exhibited considerable removal efficiencies of 93.7% and 96%, respectively (Fig. 5a-c). Equilibrium adsorption efficiency (q_e) was calculated to be 79 mg/g. The

observation indicates efficacy of ternary composites in treatment of effluents, which contain mixture of toxic dyes. Dye mixture was also treated further with ternary composite GO-CS-NZVI
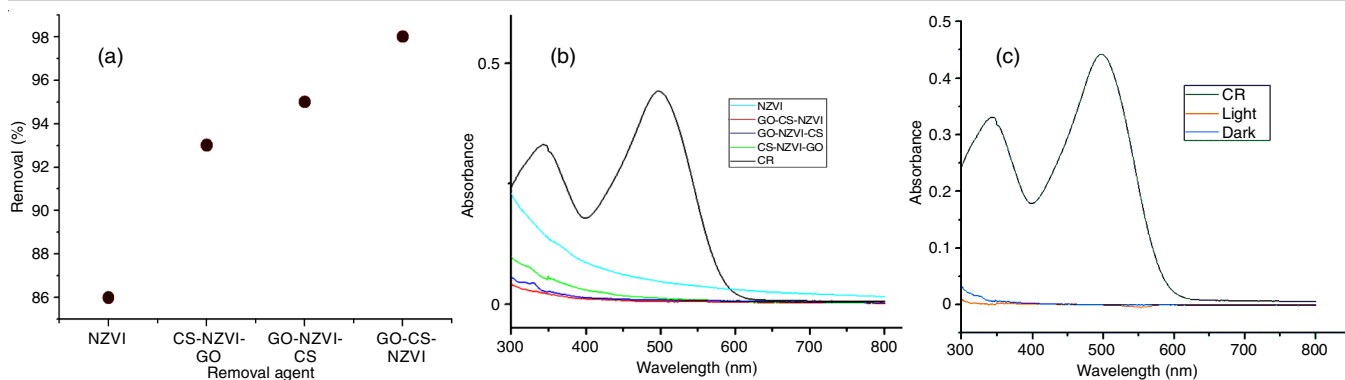
Fig. 4. (a) Comparative % removal of Congo red dye with various removal agents *i.e.* NZVI, CS-NZVI-GO, GO-NZVI-CS and GO-CS-NZVI (b) UV-VIS absorbance peaks of untreated and treated samples of Congo red with various removal agents (c) absorbance peaks of Congo red when treated with ternary composite GO-CS-NZVI in sunlight and dark, reaction conditions- 50 mL of dye solution, dosage of composite -50 mg, contact time-30 min
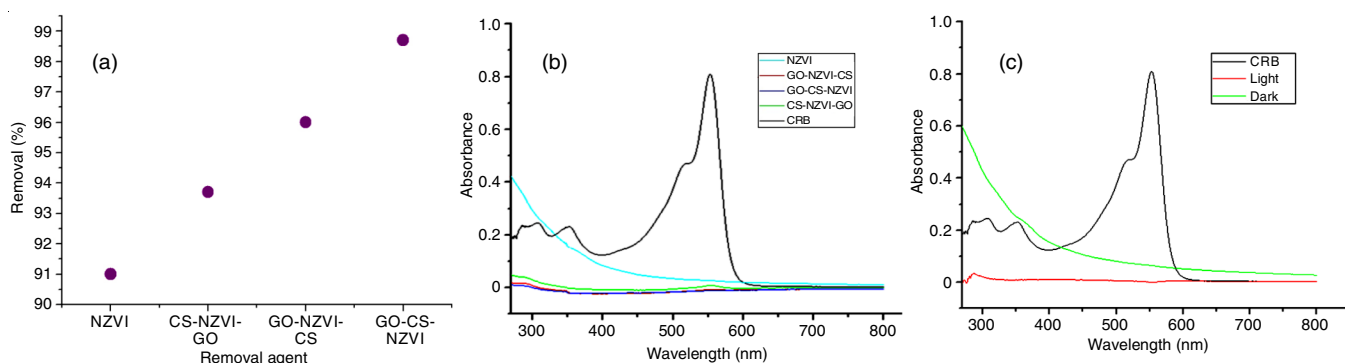

Fig. 5. (a) Comparative % removal of mixture of dyes CR and RB (CRB) with various removal agents *i.e.* NZVI, CS-NZVI-GO, GO-NZVI-CS and GO-CS-NZVI (b) UV-VIS absorbance peaks of untreated and treated samples of mixture of dyes with various removal agents (c) absorbance peaks of dyes mixture when treated with ternary composite GO-CS-NZVI in sunlight and dark, reaction conditions- 50 mL of dye mixture, dosage of composite -50mg, contact time-30 min

in dark by keeping other reaction conditions remain same. The removal efficiency was observed to reduce from 98.7% in sunlight to 87.5% in dark indicative of adsorption of dyes followed by reductive degradation of dyes also.

Comparison studies: The dye removal efficiency of as-synthesized ternary nanocomposites was compared with other adsorbents employed for removal of Congo red dye reported in the literature and study indicated the ternary nanocomposite can be applied as a potential removal agent for Congo red dye contaminated water (Table-1).

Conclusion

In summary, the graphene oxide (GO) and chitosan (CS) modified nano zerovalent iron (NZVI) in the form of a ternary nanocomposite exhibited enhanced dye removal efficiency than bare NZVI under similar reaction conditions. Among three ternary nanocomposites synthesized, the GO-CS-NZVI showed the maximum dye removal efficiency for Congo red dye and also from a mixture of Congo red and Rhodamine B dyes *i.e.* 98% and 98.7%, respectively. This removal efficiency in both the cases was better than bare NZVI, which was observed to

TABLE-1
COMPARATIVE REMOVAL EFFICIENCIES OF DIFFERENT ADSORBENTS
TOWARDS CONGO RED DYE REPORTED IN THE LITERATURE

Adsorbent/catalyst	Removal efficiency (%)	Ref.
Modified commercial zeolite	99.24	[22]
Moringa oleifera seed coated adsorbent	> 90.00	[24]
Ternary metal selenide chitosan microspheres (ZBiSe-CM)	99.63	[23]
Chrysanthemum indicum adsorbent	84.10	[25]
γ-Al$_2$O$_3$-SiCl (nano-γ-Al$_2$O$_3$ covalently bonded to 3-chloropropyltrimethoxysilane)	83.61	[26]
PANi/BiOCl photocatalyst	88.35	[27]
GO-CS-NZVI	98.00	Present study
GO-NZVI-CS	94.30	Present study
CS-NZVI-GO	93.00	Present study

be 86% and 90%, respectively. Comparative analysis of SEM and EDS results revealed the less agglomerated spherical NZVI particles in chain like arrangement supported on the GO-CS support in GO-CS-NZVI as compared to densely aggregated chains in bare NZVI. The study indicated that GO-CS modified NZVI in the form of a easily retrievable ternary magnetic nanocomposite can be suitably employed in treatment of dye contaminated water.

ACKNOWLEDGEMENTS

CONFLICT OF INTEREST

The authors declare that there is noconflict of interests regarding the publication of this article.

REFERENCES

1. Q. Wang, J. Lian, Q. Ma, Y. Bai, J. Tong, J. Zhong, R. Wang, H. Huang and B. Su, *New J. Chem.*, **39**, 7112 (2015);
   https://doi.org/10.1039/C5NJ00987A

2. J. Goscianska, M. Marciniak and R. Pietrzak, *Sep. Purif. Technol.*, **154**, 236 (2015);
   https://doi.org/10.1016/j.seppur.2015.09.042

3. S. Wang, M. Zhao, M. Zhou, Y.C. Li, J. Wang, B. Gao, S. Sato, K. Feng, W. Yin, A.D. Igalavithana, P. Oleszczuk, X. Wang and Y.S. Ok, *J. Hazard. Mater.*, **373**, 820 (2019);
   https://doi.org/10.1016/j.jhazmat.2019.03.080

4. J. Zdarta, T. Jesionowski, M. Pinelo, A.S. Meyer, H.M.N. Iqbal, M. Bilal, L.N. Nguyen and L.D. Nghiem, *Bioresour. Technol.*, **344**, 126201 (2022);
   https://doi.org/10.1016/j.biortech.2021.126201

5. A. Pant, R. Tanwar, B. Kaur and U.K. Mandal, *Sci. Rep.*, **8**, 14700 (2018);
   https://doi.org/10.1038/s41598-018-32911-3

6. M.J.K. Ahmed, M. Ahmaruzzaman and M.H. Bordoloi, *RSC Adv.*, **5**, 74645 (2015);
   https://doi.org/10.1039/C5RA13970H

7. H. Bendjama, S. Merouani, O. Hamdaoui and M. Bouhelassa, *J. Photochem. Photobiol. Chem.*, **368**, 268 (2019);
   https://doi.org/10.1016/j.jphotochem.2018.09.047

8. C. Baslak, G. Arslan, M. Kus and Y. Cengeloglu, *RSC Adv.*, **6**, 18549 (2016);
   https://doi.org/10.1039/C5RA23433F

9. M. Ptaszkowska-Koniarz, J. Goscianska and R. Pietrzak, *Colloids Surf. A Physicochem. Eng. Asp.*, **543**, 109 (2018);
   https://doi.org/10.1016/j.colsurfa.2018.01.057

10. K.C. Lai, B.Y.Z. Hiew, L.Y. Lee, S. Gan, S. Thangalazhy-Gopakumar, W.S. Chiu and P.S. Khiew, *Bioresour. Technol.*, **274**, 134 (2019);
    https://doi.org/10.1016/j.biortech.2018.11.048

11. Y. Zou, X. Wang, A. Khan, P. Wang, Y. Liu, A. Alsaedi, T. Hayat and X. Wang, *Environ. Sci. Technol.*, **50**, 7290 (2016);
    https://doi.org/10.1021/acs.est.6b01897

12. M. Shekofteh-Gohari, A. Habibi-Yangjeh, M. Abitorabi and A. Rouhi, *Crit. Rev. Environ. Sci. Technol.*, **48**, 806 (2018);
    https://doi.org/10.1080/10643389.2018.1487227

13. D.S. Ken and A. Sinha, *Environ. Nanotechnol. Monit. Manag.*, **14**, 100344 (2020);
    https://doi.org/10.1016/j.enmm.2020.100344

14. M. Yusuf, F.M. Elfghi, S.A. Zaidi, E.C. Abdullah and M.A. Khan, *RSC Adv.*, **5**, 50392 (2015);
    https://doi.org/10.1039/C5RA07223A

15. K. Zhang, R. Hu, G. Fan and G. Li, *Sens. Actuators B Chem.*, **243**, 721 (2017);
    https://doi.org/10.1016/j.snb.2016.12.063

16. K. Gul, S. Sohni, M. Waqar, F. Ahmad, N.A.N. Norulaini and M.O. A. K, *Carbohydr. Polym.*, **152**, 520 (2016);
    https://doi.org/10.1016/j.carbpol.2016.06.045

17. P. Arora, A. Fermah, J.K. Rajput, H. Singh and J. Badhan, *Environ. Sci. Pollut. Res. Int.*, **24**, 19546 (2017);
    https://doi.org/10.1007/s11356-017-9571-7

18. S. He, H. Zhu, H. Zhao and Z. Zhu, *RSC Adv.*, **9**, 39945 (2019);
    https://doi.org/10.1039/C9RA07937H

19. W.S. Hummers Jr. and R.E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958);
    https://doi.org/10.1021/ja01539a017

20. M. Thakur, H. Singh, J.K. Rajput and R. Kumar, *Int. J. Environ. Anal. Chem.*, (2021);
    https://doi.org/10.1080/03067319.2021.1873974

21. S. Sheshmani and H.N. Ghamsari, *Int. J. Environ. Anal. Chem.*, **100**, 912 (2020);
    https://doi.org/10.1080/03067319.2019.1645840

22. I.H. Khalaf, F.T. Al-Sudani, A.A. AbdulRazak, T. Aldahri and S. Rohani, *Water Sci. Technol.*, **83**, 1369 (2021);
    https://doi.org/10.2166/wst.2021.078

23. S. Khan, A. Khan, N. Ali, S. Ahmad, W. Ahmad, S. Malik, N. Ali, H. Khan, S. Shah and M. Bilal, *Environ. Technol. Innov.*, **22**, 101402 (2021);
    https://doi.org/10.1016/j.eti.2021.101402

24. J.M. Jabar, Y.A. Odusote, K.A. Alabi and I.B. Ahmed, *Appl. Water Sci.*, **10**, 136 (2020);
    https://doi.org/10.1007/s13201-020-01221-3

25. J. Chukki, S. Abinandan and S. Shanthakumar, *Int. J. Ind. Chem.*, **9**, 305 (2018);
    https://doi.org/10.1007/s40090-018-0160-5

26. M.E. Mahmoud, A.E.H. Abdou, A.K. Shehata, H.M.A. Header and E.A. Hamed, *J. Ind. Eng. Chem.*, **57**, 28 (2018);
    https://doi.org/10.1016/j.jiec.2017.08.004

27. A. Namdarian, A. Goljanian Tabrizi, N. Arsalani, A. Khataee and A. Mohammadi, *J. Ind. Eng. Chem.*, **81**, 228 (2020);
    https://doi.org/10.1016/j.jiec.2019.09.012