

Biochar based Nanocomposite derived from Watermelon Rinds as a Novel Adsorbent for Removal of Acid Red 27 Dye: Reusability and Phytotoxicity Assessment

Riti Thapar Kapoor*

Centre for Plant and Environmental Biotechnology, Amity Institute of Biotechnology, Amity University Uttar Pradesh, Noida - 201313, Uttar Pradesh, India

Abstract: Water pollution emerges as a pressing global problem due to rise in population, urbanization, industrialization, and agricultural intensification. Dye contamination in water resources is a serious threat for environment and public health, thus effective strategies are needed to solve the problem. The watermelon fruit rind wastes were used as a raw material for synthesis of biochar nanocomposite for Acid red 27 (AR27) dye removal from aqueous solution. Adsorption has gained attention as a promising technique for AR27 dye removal due to its simplicity, flexibility, cost-effectiveness, and ease of operation etc. The batch study was executed to analyze performance of synthesized watermelon fruit rind biochar (WMR) and MnO₂/WMR biochar nanocomposite as sorbent for AR27 dye elimination from aqueous medium. Experimental findings reported that MnO₂/WMR biochar nanocomposite increased AR27 dye elimination in comparison to WMR biochar. AR27 dye removal (80 mg L⁻¹) was recorded 85% at pH 5 by 0.3 g MnO₂/WMR biochar nanocomposite. Reusability test reported that WMR biochar and MnO₂/WMR biochar nanocomposite can be used up to five consecutive cycles. Thus, application of MnO₂/WMR biochar nanocomposite is a renewable resource with high AR27 dye adsorption efficiency, thus can be applied for dye polluted wastewater treatment and environment protection.

1. Introduction

Water is a vital resource for sustaining ecosystem and health of human-beings. Changes in climate conditions, urbanization, population growth, industrial and agricultural activities have put unprecedented pressure on the natural water resources [1]. The shortage of water and production of agro-industrial wastes have become serious problems specifically for global food system. It has been predicted that worldwide demand for water will rise up to 40% by the year 2050, due to economic development, and intensification of agricultural activities [2]. In food, textile, plastic, pharmaceuticals, cosmetic industries, dyes are utilized in huge amount. Dyes are highly toxic, non-biodegradable with complex structure which pose serious threats on aquatic life and health of human-beings. The industries consume huge amount of water and release dye contaminated wastewater with heavy metals, salts and other

*Corresponding author email: ritit Kapoor@gmail.com

toxic chemicals without any proper treatment [3]. These pollutants lead to eutrophication, reduced dissolved oxygen levels, high turbidity, ultimately adversely affecting the usability of water resources. Amaranth azo dye or Acid red 27 is an anionic dye and highly soluble in water which is applied in food, textile, cosmetics and pharmaceuticals industries. However, AR27 dye is very toxic and has shown respiratory problems, skin allergies, genotoxicity, cytotoxicity, mutagenicity and endocrine disruption etc. [4]. Application of AR27 dye has been banned in the United States and also in some other countries. Several procedures such as coagulation, reverse osmosis, ozonation, oxidation and electrochemical treatment procedures have been used for removal of synthetic dyes from aqueous solution [5]. However, high cost, complexity, use of chemicals and sludge generation are the major drawbacks of the conventional methods. Adsorption is considered as an appropriate method because of its simple procedure, economical, easy operation, high efficiency, and eco-friendly nature [6]. The global production of watermelon fruits was 99.7 million tons in the year 2023 [7]. The watermelon fruit rind is considered as agricultural wastes, which accounts around 40% of the whole weight of the watermelon fruits and mostly discarded in the environment which may lead to environmental pollution [8].

In the present study, abundantly available watermelon rind wastes were used as a raw material for the synthesis of biochar and nanocomposite. Modification of the watermelon fruit rind (WMR) biochar surface area with manganese oxide (MnO_2) nanoparticles generates novel MnO_2 /WMR biochar nanocomposite as an effective catalyst with high surface properties for AR27 dye elimination. The neem (*Azadirachta indica*) leaf extracts were applied as a stabilizing agent for synthesis of MnO_2 nanoparticles. Application of plant extracts act as capping agents assists in forming uniform shape of the nanocomposite particles [9]. The nanocomposites can be easily produced in moderate conditions without chemical reagents for their stabilization, which makes the process economical and eco-friendly. The synergistic effects of biochar and nanoparticles have shown high efficiency for pollutants removal from wastewater. To the best of our knowledge, reports on MnO_2 /WMR nanocomposite production for AR27 dye elimination is not available. Therefore, nanocomposite was prepared by combining WMR biochar to support MnO_2 nanoparticles and neem leaf extracts were also added as stabilizing agent for AR27 dye sorption. The effect of WMR biochar and MnO_2 /WMR nanocomposite treated AR27 dye wastewater was assessed on growth variables of wheat seeds. Therefore, present investigation highlights the development of efficient nanocomposite as an adsorbent from watermelon rind wastes and neem leaves for AR27 dye removal from aqueous solution and can be used at large scale for achieving sustainability.

2. Materials and methods

2.1 Watermelon rind biochar synthesis

Watermelon fruit rind wastes were collected from local vendor and cleaned with tap water, then by deionized water for removal of contaminants. Then, Watermelon rind wastes were kept under sunlight for fifteen days to remove excess moisture and cut into small pieces. For biochar production from WMR, pyrolysis was conducted in pyrolysis reactor at 500°C for 3 h.

2.2 Neem leaves extract preparation

Leaves of neem (10 g) were properly rinsed, kept for boiling in deionized water at 100°C for 15 min. Then, extracts were centrifuged at 10,000 rpm for 10 min, then filtrate was taken for further use.

2.3 Preparation of MnO_2 /WMR nanocomposite

The 2.5 g WMR biochar was added in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ solution (0.1 M) and 20 ml of neem leaves extracts was also mixed and continuously stirred up to half an hour. The mixture pH was kept at pH 11 by 1M KOH and after stirring at 70 rpm kept for one day at room temperature. After filtration, solid was washed by deionized water then with ethanol and dried at 40°C, then for 3h placed at 200°C for calcination and synthesized MnO_2/WMR adsorbent was applied in further studies [10].

2.4 Batch experiments

Impact of various factors such as pH (3-11), exposure time (20-120 min), adsorbent dose (0.15-0.90 g), AR27 dye concentration (20-120 mg L^{-1}), speed of agitation (25-150 rpm), temperature (25-50°C) was analyzed on AR27 dye elimination by WMR biochar and MnO_2/WMR nanocomposite. Acid red 27 dye solution of different concentrations (20, 40, 60, 80, 100, 120 mg L^{-1}) were taken in 6 different flasks. Adsorbent (WMR biochar or MnO_2/WMR nanocomposite) amount 0.15, 0.30, 0.45, 0.60, 0.75, 0.90 g was added, respectively. Optical density was assessed with UV-vis spectrophotometer ($\lambda_{\text{max}} = 520 \text{ nm}$), AR27 dye elimination (%) was analyzed with given equation:

$$\text{AR27 dye removal (\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

Here, C_0 = initial and C_t = final AR27 dye concentrations.

2.5 Reusability test

WMR (0.60 g) and MnO_2/WMR (0.30 g) were added in 80 mg L^{-1} AR27 dye solution in separate flasks, placed for 80 and 40 min at $25 \pm 2^\circ\text{C}$, respectively inside shaking incubator. After centrifugation, filtrate absorbance was assessed to observe AR27 dye uptake by WMR and MnO_2/WMR . The WMR and MnO_2/WMR having AR27 dye was kept at 50°C for 6h to increase dye sorption efficacy, sorbent was washed with 1 N HCl, then NaOH and kept for 45 min at 180 rpm, then optical density of desorbing solution was analyzed. WMR and MnO_2/WMR were separated and washed with distilled water for desorbing solution, elimination and placed at 50°C up to 4 h [11]. The process was repeated for 5 times, and desorption percentage of AR27 dye was assessed with given equation:

$$\text{Desorption (\%)} = \text{AR27 dye desorbed} / \text{AR27 dye absorbed} * 100 \quad (2)$$

2.6 Phytotoxicity assessment

The impact of AR27 dye prior and after treatment of WMR biochar and MnO_2/WMR nanocomposite were assessed on wheat seeds (*Triticum aestivum* var. K-402). Four different test tube sets were arranged containing distilled water, AR27 dye solution, AR27 dye solution treated with WMR biochar or MnO_2/WMR nanocomposite and ten seeds were soaked up to 5 h. After that, seeds were transferred onto petridishes kept inside seed germinator at $24 \pm 1^\circ\text{C}$ in 12 h light up to two weeks. Germination of wheat seeds, length of seedling, fresh and dry weight, vigour index were analyzed with following ISTA procedure [12].

2.7 Statistical analysis

Experiments were executed in triplicate by using randomized block design and mean of treatment was analyzed with DMRT at $p < 0.05$.

3. Results and Discussion

3.1 Batch study

Batch experiments were executed to assess effects of pH, exposure period, dye concentration, adsorbent dose, speed of agitation and temperature on AR27 dye removal from aqueous medium with WMR and MnO₂/WMR nanocomposite. A pH is crucial variable which affects solubility of dye, adsorbent properties, ionization and speciation of dye, and dye sequestration on surface of adsorbent [13]. The effect of pH in range from 3 to 11 on AR27 dye adsorption was carried out with WMR and MnO₂/WMR biochar nanocomposite. Rise in pH from 3 to 5, AR27 dye elimination efficacy enhances 86 and 91% by WMR or MnO₂/WMR at pH 5 (Fig 1a). However, further rise in pH from 5 to 11, sorption percentage of AR27 dye was reduced. It may be because of the repulsive forces between AR27 dye anions and negative sorbent surface at high pH. Effect of exposure period on AR27 dye removal was observed at 20, 40, 60, 80, 100 and 120 minutes. During initial exposure time, fast AR27 dye sorption was recorded finally attained equilibrium, later significantly reduced (Fig. 1b). Highest 74 and 94% AR27 dye uptake was recorded at 80 and 40 min by WMR and MnO₂/WMR, respectively. Impact of various doses of WMR and MnO₂/WMR (0.15-0.90 g) were also analyzed for AR27 dye removal. With increase in adsorbent amount, significant rise in AR27 dye elimination was reported, it may be due to availability of adsorption sites [14]. The 0.30 g of MnO₂/WMR reflected maximum 85% AR27 dye removal (Fig. 1c). Effect of various concentrations of AR27 dye (20 – 120 mg L⁻¹) was assessed and it was recorded that with rise in AR27 dye initial concentration, elimination efficacy of dye was reduced [15]. High AR27 dye (80 mg L⁻¹) elimination efficacy 88 and 95% were recorded with WMR and MnO₂/WMR, respectively (Fig. 1d). The AR27 dye removal was enhanced with increase in speed of agitation (25-150 rpm). With rise in speed of agitation, AR27 dye molecules and WMR or MnO₂/WMR biochar nanocomposite interaction was enhanced, it may be due to increase in dispersion degree of WMR and MnO₂/WMR in dye solution. The 100rpm speed was favourable and it exhibited 89 and 92% AR27 dye removal by WMR and MnO₂/WMR, respectively (Fig. 1e). Effect of temperature (25-50°C) was studied on AR27 dye sorption onto WMR and MnO₂/WMR biochar nanocomposite (Fig. 1f). Elimination of AR27 dye was enhanced by temperature rise, as highest 63 and 69% elimination was recorded with WMR and MnO₂/WMR at 40°C temperature, respectively. With rise in temperature, AR27 dye molecules mobility enhances towards active sites of adsorbent.

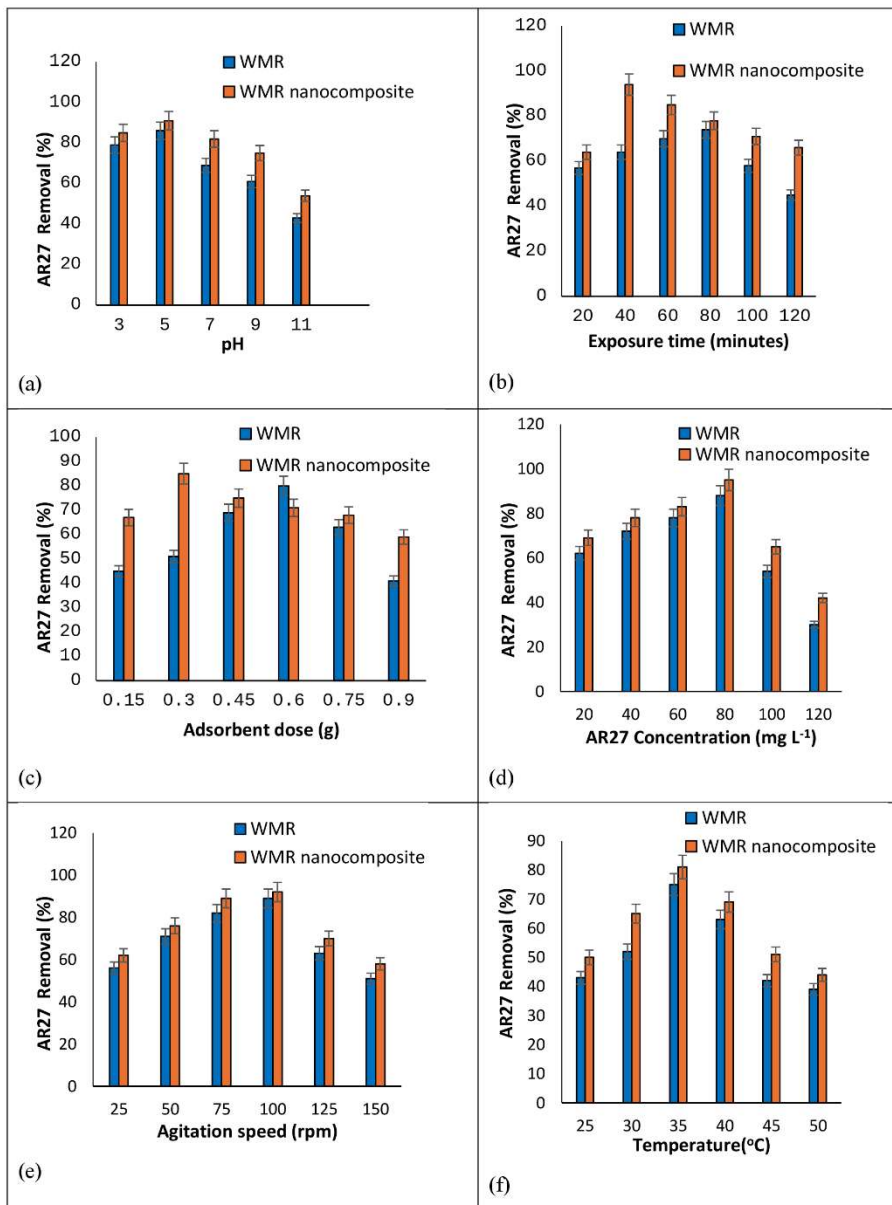


Fig. 1. Impact of (a) pH (b) exposure time (c) dose of adsorbent (d) concentration of AR27 dye (e) agitation speed (f) temperature on AR27 dye elimination in batch experiments.

3.2 Reusability test

The adsorbent recycling plays a significant role in assessing feasibility of prepared material (Fig. 2). Reusability of sorbent can reduce cost, energy consumption used for

synthesis of adsorbent materials and reduce pollution, thus makes the process feasible and environmentally- benign [16]. Recycled WMR and MnO₂/WMR nanocomposite exhibited 81, 65, 54, 42 and 31% and 89, 71, 62, 53 and 44% AR27 dye removal capacity up to five successive cycles, respectively.

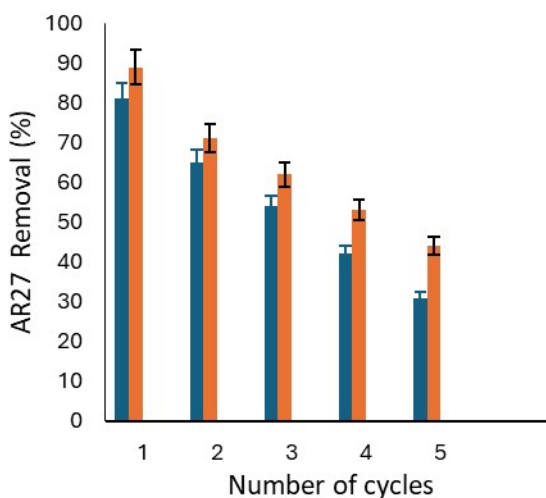


Fig. 2. Acid red 27 dye removal by WMR and MnO₂/WMR nanocomposite up to five consecutive cycles.

3.3 Assessment of phytotoxicity

Impact of AR27 dye was analyzed before or after WMR biochar and MnO₂/WMR nanocomposite treatment on seed germination and growth variables of weed seeds. In control, maximum 92% germination was recorded, while 11% with AR27 dye solution (80 mg L⁻¹). Length of radicle and plumule, fresh and dry weights, and vigour index of wheat seeds exhibited given trend: control > AR27 dye solution treated with MnO₂/WMR > AR27 dye solution treated by WMR biochar > AR27 dye solution (Table-1).

Table 1. Impact of WMR biochar and MnO₂/WMR nanocomposite treated AR27 dye solution on growth variables of wheat.

Treatment	Germination (%)	Radicle length (cms)	Plumule length (cms)	Fresh weight (g)	Dry weight (g)	Vigour index
Control	92 ± 0.40 ^a	2.76 ± 0.05 ^a	11.37 ± 0.11 ^a	8.85 ± 0.18 ^a	2.93 ± 0.03 ^a	12999.6
AR27 dye solution	11 ± 0.82 ^c	0.71 ± 0.01 ^c	2.53 ± 0.03 ^c	3.19 ± 0.07 ^c	0.59 ± 0.01 ^c	356.4
WMR biochar treated	74 ± 0.41 ^b	1.58 ± 0.01 ^b	6.37 ± 0.14 ^b	6.18 ± 0.02 ^b	1.88 ± 0.01 ^b	5883

AR27 dye solution						
MnO ₂ /WM	86 ± 0.71 ^b	1.95 ±	8.28 ± 0.06 ^b	7.89 ± 0.41 ^b	2.17 ± 0.02 ^a	8797.8
R biochar nanocompo site treated AR27 dye solution		0.01 ^b				

Data are mean ± sem of 3 replicates. Letter on data reflects variation in treatment at $p < 0.05$ significant level according to ANOVA.

4. Conclusion

This investigation clearly highlights that WMR biochar and MnO₂/WMR nanocomposite function as propitious adsorbent for AR27 dye elimination from aqueous medium. The prepared adsorbents can be used up to five cycles for AR27 dye removal. Phytotoxicity tests showed that WMR biochar or MnO₂/WMR nanocomposite treated AR27 dye contaminated water can be reused for irrigation purposes. Therefore, present study reveals that valorization of waste biomass into valuable adsorbent boosts circular economy, AR27 dye elimination from aqueous medium with biochar-based nanocomposite assists in addressing environmental challenges.

References

1. S. Rezania, N. Darajeh, P.F. Rupani, A. Mojiri, H. Kamyab, M. Taghavijeloudar, Recent advances in the adsorption of different pollutants from wastewater using carbon-based and metal-oxide nanoparticles. *Appl. Sci.* **14(24)**,11492 (2024). <https://doi.org/10.3390/app142411492>
2. C.I. Cano-Gómez, C. Wong-Arguelles, J.I. Hinojosa-López, D.B. Muñoz-Márquez, J.E. Wong-Paz, Novel insights into agro-industrial waste: exploring techno-economic viability as an alternative source of water recovery. *Waste* **3(2)**,15 (2025). <https://doi.org/10.3390/waste3020015>
3. M. S. Manzar, G. Khan, P. V. dos Santos Lins, M. Zubair, S.U. Khan, R. Selvasembian, L. Meili, N. I. Blaisi, M. Nawaz, H.A. Aziz, T.S. Kayed, RSM-CCD optimization approach for the adsorptive removal of Eriochrome Black T from aqueous system using steel slag-based adsorbent: characterization, isotherm, kinetic modeling and thermodynamic analysis. *J. Mol. Liq.* **339**, 116714 (2021). <https://doi.org/10.1016/j.molliq.2021.116714>.
4. A.E. Ramírez-Rodríguez, E. Cristiani-Urbina, L. Morales-Barrera, E. Aranda-García, Continuous successive cycles of biosorption and desorption of acid red 27 dye using water hyacinth leaves as an effective, economic, and ecofriendly biosorbent. *Bioprocess Biosyst. Eng* **46**, 183-193 (2023). <https://doi.org/10.1007/s00449-022-02822-9>
5. R. Zhao, P.R. Jin, J.Y. Zhu, Y. Li, G.C. Li, A. Volodine, Y.Y. Liu, J.F. Zheng, B. van der Bruggen, Amino acid-based loose polyamide nanofiltration membrane with ultrahigh water permeance for efficient dye/salt separation. *J. Membr. Sci.* **673**, 121477 (2023). <https://doi.org/10.1016/j.memsci.2023.121477>

6. R.T. Kapoor, M. Rafatullah, M. Alam, M.R. Siddiqui, Fabrication of iron and nitrogen doped magnetic banana fruit peel biochar for sequestration of Eriochrome black T dye: mechanistic insights and reutilization strategy. *Chem. Afr.* (2025a) <https://doi.org/10.1007/s42250-025-01400-2>
7. C. Onyango, W. Nyairo, G.P. Tchieta, V.O. Shikuku, Watermelon rind based adsorbents for the removal of water pollutants: a critical review. *Front. Environ. Chem.* **6**, 1568695 (2025). <https://doi.org/10.3389/fenvc.2025.1568695>
8. X. Rico, B. Gullon, J.L. Alonso, R. Yanez, Recovery of high value-added compounds from pineapple, melon, watermelon and pumpkin processing by-products: an overview. *Food. Res. Int.* **132**, 109086 (2020). <https://doi.org/10.1016/j.foodres.2020.109086>.
9. H. Lu, X. Zhang, S.A. Khan, W. Li, L. Wan, Biogenic synthesis of MnO₂ nanoparticles with leaf extract of *Viola betonicifolia* for enhanced antioxidant, antimicrobial, cytotoxic, and biocompatible applications. *Front. Microbiol.* **12**, 761084 (2021). <https://doi.org/10.3389/fmicb.2021.761084>
10. A.Taha, S. Daffalla, Biochar derived from palm waste supported greenly synthesized MnO₂ nanoparticles as a novel adsorbent for wastewater treatment. *Catalysts* **13**, 451(2023). <https://doi.org/10.3390/catal13020451>
11. R.T. Kapoor, S. Sivamani, Exploring the potential of *Eucalyptus citriodora* biochar against direct red 31 dye and its phytotoxicity assessment. *Biomass Convers. Bioref.* **13**, 8011-8022 (2021). <https://doi.org/10.1007/s13399-021-01681-w>.
12. ISTA, International rules for seed testing; international seed testing association, ISTA Secretariat. Bassersdorf, Switzerland (2008).
13. V. Parimelazhagan, P. Yashwath, D. Arukkani Pushparajan, J. Carpenter, Rapid removal of toxic Remazol brilliant blue-R dye from aqueous solutions using *Juglans nigra* shell biomass activated carbon as potential adsorbent: optimization, isotherm, kinetic, and thermodynamic investigation. *Int. J. Mol. Sci.* **23**, 12484 (2022). <https://doi.org/10.3390/ijms232012484>.
14. D. Vara, S. Jha, S. Bisht, S. Shahabuddin, R. Gaur, Suhas, I. Tyagi, Sustainable bio-based adsorbents for simultaneous and efficient removal of hazardous dyes from aqueous solutions. *Toxics* **12**(4), 266 (2024). <https://doi.org/10.3390/toxics12040266>
15. E. Wang, L. Huang, X. Yuan, X. Zhang, L. Guo, C. Xue, X. Chen, Nutritional, phytochemical and antioxidant properties of 24 mung bean genotypes. *Food Prod. Process Nutr.* **3**, 28 (2021). <https://doi.org/10.1186/s43014-021-00073-x>.
16. R.T. Kapoor, M. Rafatullah, M. R. Siddiqui, M. Alam, Adsorptive potential of coconut fruit shell biochar as low-cost adsorbent for sequestration of rhodamine B dye: kinetics, thermodynamics and phytotoxicity studies. *Biomass Conv. Bioref.* **15**, 24609–24628 (2025). <https://doi.org/10.1007/s13399-024-05688-x>