Proceedings of the 7th International Conference of Recent Trends in Environmental Science and Engineering (RTESE'23)
Canada – June 04 - 06, 2023
Paper No. 142
DOI: 10.11159/rtese23.142

Characterization And Field Application Assessment Of Prosopis Cineraria (L.) For Fluoride Sequestration: A Preliminary Investigation

Soumya Kar[1], Rajiv Gupta[2], Zhi Chen[3]
[1] Department of Civil Engineering
Birla Institute of Technology and Science
Pilani, Rajasthan
India
p2016405@pilani.bits-pilani.ac.in
[2] Department of Civil Engineering
Birla Institute of Technology and Science
Pilani, Rajasthan
India
rajiv@pilani.bits-pilani.ac.in
[3] Department of Building, Civil and Environmental Engineering
Concordia University
Montreal, Quebec
Canada
zhi.chen@concordia.ca

Abstract **–** Endemic fluorosis is a worldwide issue affecting potable water security, necessitating the development of economic and elementary fluoride remediation techniques. Recent studies have focused significantly on chemically and thermally modified bio-sorbents to increase fluoride removal efficiency. The current study investigates the potential of a calcium-rich (Ca), untapped biomass *Prosopis cineraria* (L.) Druce under minimal treatment. Although limited work has explored the remediation of contaminants using the proposed adsorbent in different forms, the usage of *Prosopis cineraria* carbon (PCC) for fluoride elimination from an aqueous solution is unexplored. Characterization and water quality index of PCC were studied to corroborate results for physical fluoride remediation. Confirming its efficacy as a fluoride scavenger, the synthesized PCC could remove between 79.7 and 87% of the fluoride from initial concentrations in groundwater.

Keywords**:** Fluoride**,** *Prosopis cineraria* carbon, water quality index, characterization

1. Introduction

Access for all and safe management of water, sanitation, and hygiene services are crucial for achieving Sustainable Development Goal 6. Global water consumption has expanded at twice the pace of population growth over the previous century, significantly influencing the quality of life [1].

As a result of diminishing and polluted surface waterways, groundwater has emerged as a feasible option for meeting the water requirements of numerous segments of society. In addition to ensuring a nation's food security, groundwater reserves are essential to its economic growth. Although groundwater is often considered cleaner than surface water, it contains dissolved salts and ions due to geological interactions and human activities. Fluoride (F^-) is one such toxicant of concern. The geologic and human sources of F^- are calcareous deposits in aquifers, pesticides, and increased industrial activities.

F^- consumption above and below the thresholds recommended by the World Health Organization (WHO) causes dental and skeletal fluorosis, muscle fiber degradation, low hemoglobin levels, excessive thirst, headaches, skin rashes, depression, gastrointestinal problems, urinary tract issues, nausea, and abdominal pains [2].

The Indian state of Rajasthan is particularly prone to endemic F^- toxicity, with reported concentrations ranging from $\leq$1 mg/l to $\geq$ 20 mg/l [3]. Organically derived and developed biomass/waste materials for removing F^- from an aqueous solution are emerging study dependent on the adsorption phenomena. Ca-based adsorbents are effective at removing F^-

, attributed to the formation of insoluble compounds such as CaF_2 and $Ca_5(PO_4)_3F$, hence eliminating the related health risk of leaching [4], [5].

The proposed adsorbent, *Prosopis cineraria* (common name: Khejri), is a calcium- and phosphorus-rich, untapped organic biomass, which makes it an excellent candidate for Ca-based F^- sequestration. Due to its tolerance to harsh climatic conditions, Khejri forms a vital part of the Indian desert environment, cementing its cultural, economic, and ecological dominance in rural Rajasthan [6].

The effectiveness of *Prosopis cineraria* in removing textile dye, lead, and cadmium from water and wastewater has been the subject of a few investigations [7]–[10]. In contrast, no study has reported Khejri's F^- absorption efficiency. The developed adsorbent, *Prosopis cineraria* carbon (PCC), was characterized using point of zero charges, FTIR, XRD, and FESEM in conjunction with EDX to describe the PCC's structural morphology accurately. An index-based water quality assessment was performed on the collected water samples from the study area. The developed water quality indexes and the after-adsorption surface changes on the PCC corroborated the field applicability of PCC.

2. Materials and Methods

2.1. Preparation of Prosopis cineraria carbon (PCC)

Khejri leaves, stems, and pods were collected locally from Pilani, Rajasthan, India, during the annual tree pruning for maintenance purposes between January to March. After gathering, decaying leaves were physically excerpted. The sample was then thoroughly washed under running tap water. A final wash was done with distilled water to remove the remaining dirt and dried under the sunlight until all the moisture was evaporated. After drying, the leaves were soaked in the 0.1N acetic acid solution for 10 hours. After proper washing until neutral pH, the material was air-dried for another 24 hours, then heated at 300° C in a muffle furnace for 6 hours. The resulting material was grounded, sieved through a 150 µm sieve, and subsequently placed in an airtight container for further use. The reagents used [acetic acid (CH_3COOH), sodium hydroxide (NaOH), potassium nitrate (KNO_3), hydrogen chloride (HCL), F^- test kit (catalog number 1.14598.0002] in the study were of analytical grade, and acquired from Merck. All the solutions were made with deionized water.

2.2. Point of zero-charge and Zeta potential

The point of zero charges is a valuable characterization technique to ascertain the surface affinity of an adsorbent towards a specific pollutant in an aqueous medium. It is also described as the pH of net electrical neutrality [11][12]. For $pH < pH_{pzc}$, the adsorbent has a positive surface charge, while for $pH > pH_{pzc,}$ the adsorbent surface has a net negative charge. Further, the total charge on the surface and the stability of the aqueous solution of PCC was assessed by zeta potential analysis [13].

The PCC's point-zero charge (pHpzc) was determined based on the pH drift method. The experiments were conducted in 100 ml conical flasks containing 25 ml of 0.1M KNO_3 solution. Initially, the pH value was varied from 2 to 12 at intervals of 1, adjusting with 0.1M NaOH or 0.1M HCl, noted for each flask as the initial pH (pH_i). Then 0.2 g of PCC was added to each flask, shaken manually, and kept in the dark for 48 hours. After the fixed duration, the final pH was measured (pH_f). The relation between the initial and final pH was plotted, with pH_i on the x-axis and ΔpH ($=pH_f - pH_i$) on the y-axis. The zeta potential of PCC was measured with a Zetasizer Ver.7.12 (Malvern Instruments Ltd.) with the PCC suspended in distilled water.

Fig. 1 represents the pH_{pzc} curve of PCC. The pH_{pzc} of PCC was determined to be 9, implying appreciable defluoridation within the acidic and neutral range ($pH < pH_{pzc}$). Zeta potential results show that our synthesized adsorbent had a net positive surface charge of +11.41 mV. A positively charged surface attracts negatively charged F^- ions [14]. However, at a higher pH, the surface of the adsorbent changes to negative, impeding fluoride adsorption.

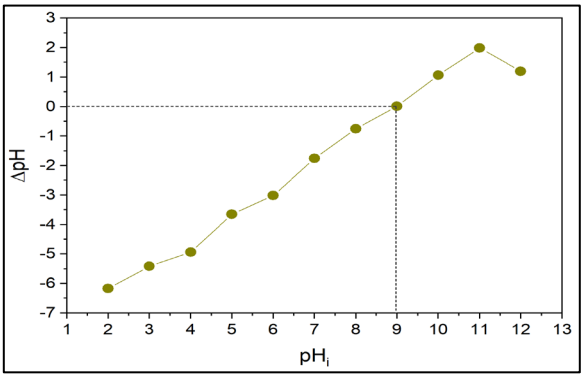


Fig.1: The pzc determination curve

2.3. FTIR

The surface chemistry covering the functional groups and bonds was determined via Fourier-transform infrared spectroscopy (FTIR) spectra acquired using PerkinElmer (Frontier) by mixing samples in KBr and obtaining the spectra in the 400 – 4000 cm^{-1} range. Fig. 2a illustrates a broad range of stretch in the 3800-3000 cm^{-1} region attributed to the water and hydroxyl group [15]. The functional groups of the PCC observed at 1103 cm^{-1}, 1443 cm^{-1}, and 1799 cm^{-1} corresponded to the C-O, S=O, and carboxylate stretching vibration, respectively [10], [16]. The bands at 713 cm^{-1} and 875 cm^{-1} are fingerprints of $CaCO_3$, further confirmed in the XRD analysis (2θ: 29.808° and 43.24°) [17]. The general shift in the absorption bands for pre-and-post-sorption accredits to F^- adsorption onto the PCC [18].

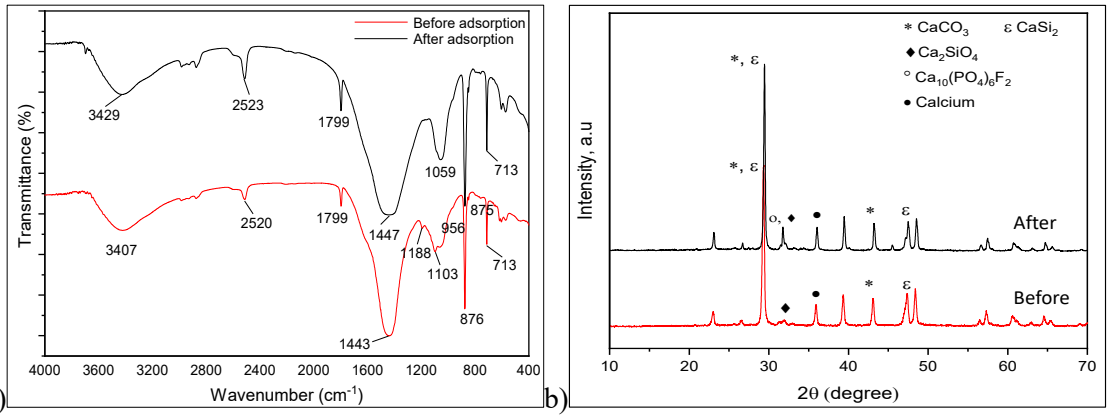
2.4. XRD

X-ray diffraction (Rigaku Miniflex II, CuKa, λ= 1.5406 Å, 30 kV, and 15 mA) was performed within the 2θ range of 10° to 70° with a scanning rate of 2°/min to find the phase composition and probable chemical composition of the prepared adsorbent. The diffraction spectrum was supplemented by the crystallite size calculation using the Scherrer equation.

The XRD phase analysis for 2θ diffraction angles from 10° to 70° is shown in Fig. 2b. Crystalline phases are identified accordingly with the Match Software. The peak obtained at 2θ of 35.95° indicates Calcium (C) (PDF-9012917). The most substantial peak observed at 29.8° could be indexed as $CaCO_3$ and $CaSi_2$. The diffraction peaks observed at 2θ of 43.24° and 47.34° were identified as $CaCO_3$ (PDF- 1010929) and $CaSi_2$ (PDF-1536815), respectively [10], [19]. The peak observed at 31.8° on the unspent PCC could be attributed to the existence of $Ca2SiO_4$ (PDF-1546029). A prominent peak at 31.8° on the loaded PCC acknowledges fluorapatite – $Ca_5(PO_4)_3F$ (PDF- 9006955), confirming defluoridation [20]. Before and after adsorption, the adsorbent's grain size was determined to be 32.27 nm and 45.23 nm at 29.808° and 29.335°, respectively. An increase in grain size substantiates F^- deposition on the PCC surface.

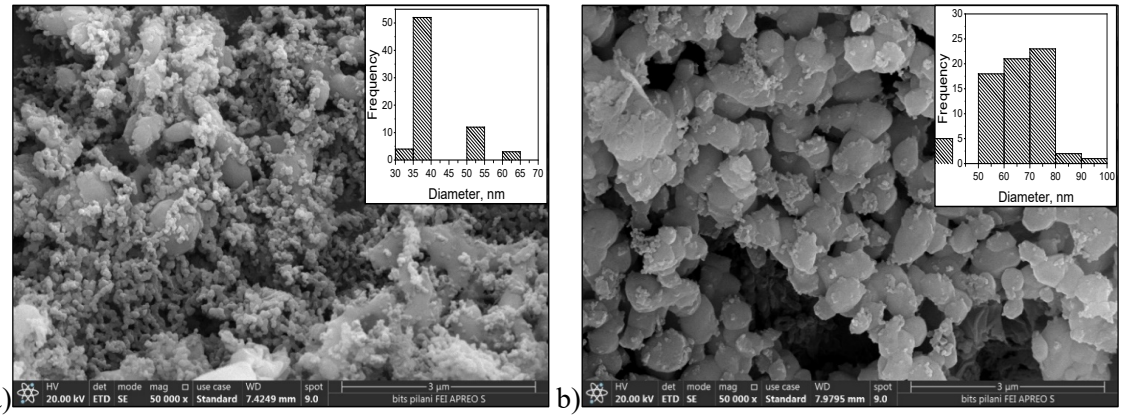
2.5. FESEM, EDX, and EDS dot mapping

The surface morphology of PCC (before & after adsorption) is depicted in Fig. 3a and b. As depicted from the FESEM plan images and insert frequency distribution graph, sorbent particle sizes have increased from 30-40 nm to 50-80 nm for the loaded adsorbent. The presence of F^- in the spent PCC is validated with the EDS elemental mapping, as shown in Fig. 4a. It is to be acknowledged that the particle ranges are approximately in terms of the size determined from the Scherrer equation. A similar discrepancy observed in an earlier study was attributed to small agglomerations of the particles during PCC's synthesis [10]. As observed in Fig. 4b, the main elements in the EDX spectrum data corresponded to Ca, C, O, and P, along with Si and Mg. The detected essential elements have been reported in an earlier study by Nodushan et al. (2020) on *Prosopis cineraria*, including leaves, branches, and stems [21].



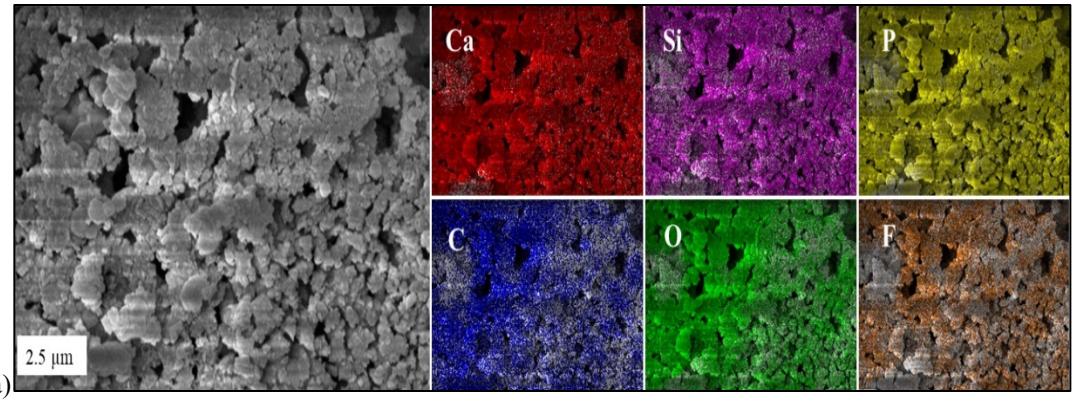
a) b)

Fig.2: a) FTIR spectrum of PCC before and after adsorption b) XRD spectrum of PCC before and after adsorption



a) b)

Fig.3: FESEM images of PCC and Frequency distribution of PCC particles a) before and b) after adsorption



a)

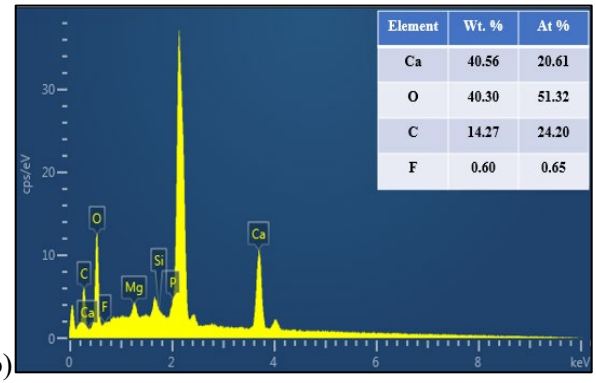
b) 

Fig.4: EDS dot mapping of PCC a) after adsorption b) EDX spectrum of PCC after adsorption

2.6. Evaluation of water quality index

Field groundwater samples were collected from localized villages around the study region and treated with the adsorbents to verify the PCC's field applicability and practical effectiveness. Physio-chemical parameters such as pH, Total dissolved solids (TDS), Total hardness (TH), and F^- were recorded before and after defluoridation. For ease of comprehensibility, the water quality level was represented as a single number, also known as the weighted arithmetic water quality index (WQI). The WAWQI index methodology uses the most measured water quality variables and incorporates those into a mathematical equation [22]. The index is then used to evaluate and classify water quality for domestic usage [23].

The calculation of WAWQI is performed using equation 1:

$$\text{WAWQI} = \frac{\sum_{n=1}^{n} q_n w_n}{\sum_{n=1}^{n} w_n} \quad (1)$$

Where,

n = the number of parameters, q_n = quality rating of the n^{th} parameter, and w_n = relative weight of the n^{th} parameter

$$q_n = 100\left[\frac{V_n - V_{id}}{S_n - V_{id}}\right] \quad (2)$$

where,

S_n = standard value of n^{th} water quality parameter, V_n = observed value of n^{th} water quality parameter, and V_{id} = ideal value of n^{th} water quality parameter

$$W_n = \frac{K}{S_i} \quad (3)$$

Where K = constant proportionality, calculated from equation 4:

$$K = \frac{1}{\sum_{i=1}^{n} \frac{1}{S_i}} \quad (4)$$

$\therefore$ In equation 2, V_{id} is considered as 7 for pH, and $V_{id} = 0$ for the remaining parameters.

The calculated WAWQI values were classified as excellent, good, fair, poor, very poor, inadequate, or unsuitable for human consumption represented in Table 1. The WHO standard values for drinking water quality are as follows: pH – 8.5; TDS – 1000 mg/l; TH – 200 mg/l; and Fluoride: 1 mg/l.

Table 1: Water quality rating as per the WAWQI method

WQI value	Grading	Rating of water quality
0-25	A	Excellent
26-50	B	Good
51-75	C	Fair
76-100	D	Poor
101-150	E	Very poor
Above 150	F	Unfit for drinking purposes

2.7. Field study and evaluated WAWQI

The PCC bio-adsorbent developed was tested with five field groundwater samples collected from the Jhunjhunu district, Rajasthan, India.

The groundwater treatment process maintained the optimum operating conditions of contact time (120 minutes) and dosage (5 g/l). The pH of the collected sample was unaltered to observe PCC performance under neutral conditions. The operating parameters were derived from the isotherm studies (the adsorption process follows the Langmuir-2 and Freundlich's isotherm models).

The physio-chemical parameters of the studied water samples are represented in Table 2. pH was reduced by 4.21% to 12.02% for Villages 1 and 2. Villages 3, 4, and 5 had pH decreases in a similar range at 7.76, 7.45, and 7.72%, respectively. TDS for the village samples decreased by 40.92, 59.53, 49.03, 60.99, and 55 % for the villages sequentially. The recorded TH value increased by 33.33% for village 1. However, a decrease in TH value was observed at 22.857,13.04, 13.04, and 8.64% across villages 2, 3, 4, and 5, respectively. It is further evident from these observations that the PCC synthesized could remove the fluoride in the range of 79.7 to 87 % of its initial concentrations, confirming its potential as an effective fluoride scavenger.

All previously obtained groundwater samples were deemed unfit for consumption with a WAWQI >150, as shown in Fig. 5. The primary contaminant of concern was F^-. While villages 2 through 4 had an F^- concentration beyond the permissible threshold of 1.5 mg/l, only Village 1 had a concentration of F^- within the range of 1 to 1.5 mg/l. Besides lowering the concentration of fluoride, the study's novel adsorbent positively impacted the remaining qualitative parameters. The total WAWQI of the water samples decreased following defluoridation at the optimum dose and duration, keeping pH neutral. The groundwater samples were subsequently put into the good and fair categories following treatment.

Table 2: Physio-chemical parameters observed for water samples before and after treatment.

	Before Treatment	Village 1	Village 2	Village 3	Village 4	Village 5
Water Quality Parameters	pH	8.4	7.83	8.11	8.59	8.29
	TDS (mg/l)	452	598	720	685	856
	TH (mg/l)	120	140	322	230	185
	F^- (mg/L)	1.2	1.53	1.75	2.05	1.91
	After Treatment	Village 1	Village 2	Village 3	Village 4	Village 5
	pH	7.39	7.5	7.48	7.95	7.65
	TDS (mg/l)	267	242	367	267.2	385.2
	TH (mg/l)	160	108	280	200	169
	F^- (mg/L)	0.18	0.31	0.32	0.34	0.25

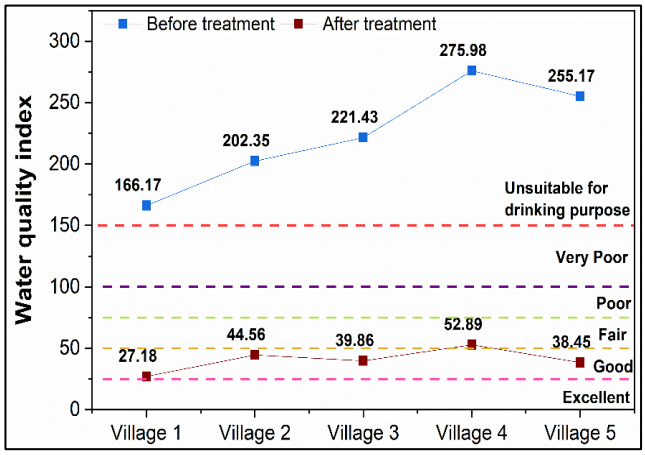


Fig.5: WAWQI of village water samples after treatment with PCC

4. Conclusion

Studies focusing on fluoride remediation have witnessed an increasing trend, with the underlying challenges being the development of low-cost, readily available, and mildly treated high-performing adsorbents. For the current study, the authors evaluated low-cost and readily available calcium-rich biomass, PCC, with a facile synthesis method as an alternative for Fluoride remediation. The synthesized adsorbent was characterized using pHpzc, zeta potential, XRD, FTIR, FESEM, EDS, and EDX.

The PCC surface exhibited a favorable charge distribution and performed best at pH< 9. The negatively charged adsorbate was drawn to the positive adsorbent. The PCC successfully removed fluoride in the 79 to 87% range from the study area's water samples collected from the villages. PCC had no degrading effect on the collected water samples established from the WAWQI values. Further, previously classified as unsuitable for human consumption, water samples were considered potable after treatment. The findings of this study revealed that PCC had effectively adsorbed fluoride from aqueous solutions under neutral conditions. With modified preparation methods, PCC can be combined with additional filter-making raw materials and advanced into low-cost and energy-efficient water filters to achieve fluoride-free water.

Acknowledgments

The authors are grateful to the Department of Science and Technology, Government of India, for supporting the project titled "Conjunctive use of Rainwater and Groundwater to provide safe drinking water with the intervention of Advanced Technology vide Grant No. DST/TM/WTI/2K16/204(G)". The authors further acknowledge Mr. Cuckoo Kochar (President & CEO, DCR Phoenix Group) & the Indian Council of Cultural Relations for the GNDJ initiative (Guru Nanak Dev Ji Academic and Research Initiative).

References

[1] UN, "The Sustainable Development Goals Report 2020," 2020.

[2] 2022 WHO, *Guidelines for drinking-water quality: fourth edition incorporating the first and second addenda. Geneva: World Health Organization; 2022.* 2022.

[3] S. L. Choubisa, "Fluoride distribution in drinking groundwater in Rajasthan, India," *Curr. Sci.*, vol. 114, no. 9, pp. 1851–1857, 2018.

[4] M. Y. Choi, J. I. Lee, C. G. Lee, and S. J. Park, "Feasibility of using calcined patinopecten yessoensis shells for fluoride removal and investigation of the fluoride removal mechanism," *Desalin. Water Treat.*, vol. 233, no. November, pp. 292–302, 2021.

[5] V. Sivasankar, S. Rajkumar, S. Murugesh, and A. Darchen, "Tamarind (Tamarindus indica) fruit shell carbon: A calcium-rich promising adsorbent for fluoride removal from groundwater," *J. Hazard. Mater.*, vol. 225–226, pp. 164–172, 2012.
[6] P. R. Krishnan and S. K. Jindal, "Khejri , the king of Indian Thar desert is under phenophase change," *Curr. Sci.*, vol. 108, no. 11, pp. 1987–1990, 2015.
[7] F. Eshraghi, M. Motavassel, B. Roozbehani, and N. J. H. Fard, "Cadmium Removal from Aqueous Solution by Prosopis Cineraria Leaf Ash Abstract (PCLA)," *J. Environ. Friendly Process.*, vol. 4, no. 1, pp. 4–11, 2016.
[8] V. K. Garg, R. Kumar, and R. Gupta, "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: A case study of Prosopis cineraria," *dye. Pigment.*, vol. 62, no. 1, pp. 1–10, 2004.
[9] R. Natarajan and R. Manivasagan, "Effect of operating parameters on dye wastewater treatment using prosopis cineraria and kinetic modeling," *Environ. Eng. Res.*, vol. 25, no. 5, pp. 788–793, 2020.
[10] A. A. Shahmaleki, M. Motevassel, A. A. Isari, and B. Anvaripour, "An effective approach for the adsorptive removal of lead from an aqueous medium using nano Prosopis Cineraria leaf ash (NPCLA): characterization, operational effects, and recyclability," *Model. Earth Syst. Environ.*, vol. 6, no. 1, pp. 139–149, 2020.
[11] N. K. Mondal, R. Bhaumik, K. Sen, and P. Debnath, "Adsorption of fluoride in aqueous solutions using saline water algae (Rhodophyta sp.): an insight into isotherm, kinetics, thermodynamics and optimization studies," *Model. Earth Syst. Environ.*, no. 0123456789, 2021.
[12] D. E. Villela-Martínez, R. Leyva-Ramos, A. Aragón-Piña, and R. Navarro-Tovar, "Arsenic Elimination from Water Solutions by Adsorption on Bone Char. Effect of Operating Conditions and Removal from Actual Drinking Water," *Water. Air. Soil Pollut.*, vol. 231, no. 5, 2020.
[13] M. K. Indana, B. R. Gangapuram, R. Dadigala, R. Bandi, and V. Guttena, "A novel green synthesis and characterization of silver nanoparticles using gum tragacanth and evaluation of their potential catalytic reduction activities with methylene blue and Congo red dyes," *J. Anal. Sci. Technol.*, vol. 7, no. 1, pp. 1–9, 2016.
[14] N. Hoang Lam, H. T. Ma, M. J. K. Bashir, G. Eppe, P. Avti, and T. T. Nguyen, "Removal of phosphate from wastewater using coal slag," *Int. J. Environ. Anal. Chem.*, vol. 101, no. 15, pp. 2668–2678, 2021.
[15] H. R. Pouretedal and N. Sadegh, "Effective removal of Amoxicillin, Cephalexin, Tetracycline and Penicillin G from aqueous solutions using activated carbon nanoparticles prepared from vine wood," *J. Water Process Eng.*, vol. 1, pp. 64–73, 2014.
[16] H. Granbohm, K. Kulmala, A. Iyer, Y. Ge, and S. P. Hannula, "Preparation and Photocatalytic Activity of Quaternary GO/TiO2/Ag/AgCl Nanocomposites," *Water. Air. Soil Pollut.*, vol. 228, no. 4, 2017.
[17] V. Ramasamy, P. Anand, and G. Suresh, "Synthesis and characterization of polymer-mediated CaCO3 nanoparticles using limestone: A novel approach," *Adv. Powder Technol.*, vol. 29, no. 3, pp. 818–834, 2018.
[18] A. Naga Babu, D. S. Reddy, G. S. Kumar, K. Ravindhranath, and G. V. Krishna Mohan, "Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent," *J. Environ. Manage.*, vol. 218, pp. 602–612, 2018.
[19] S. K. Bux, M. Rodriguez, M. T. Yeung, C. Yang, A. Makhluf, R. G. Blair, J. Fleurial, and R. B. Kaner, "Rapid solid-state synthesis of nanostructured silicon," *Chem. Mater.*, vol. 22, no. 8, pp. 2534–2540, 2010.
[20] B. Thole, "Ground Water Contamination with Fluoride and Potential Fluoride Removal Technologies for East and Southern Africa," *Perspect. Water Pollut.*, 2013.
[21] S. K. H. Nodushan, M. Emtiazy, M. H. Salmani, M. H. Lotfi, and M. E. Zadeh, "Monitoring of Essential and Toxic Elements in Leaves, Branches, and Stem of Prosopis cineraria (as Anti-Inflammatory) Growing in Iran," *Biol. Trace Elem. Res.*, vol. 198, no. 2, pp. 714–720, 2020.
[22] F. García-Ávila, C. Zhindón-Arévalo, L. Valdiviezo-Gonzales, M. Cadme-Galabay, H. Gutiérrez-Ortega, and L. F. del Pino, "A comparative study of water quality using two quality indices and a risk index in a drinking water distribution network," *Environ. Technol. Rev.*, vol. 11, no. 1, pp. 49–61, 2022.
[23] B. Panneerselvam, S. Karuppannan, and K. Muniraj, "Evaluation of drinking and irrigation suitability of groundwater with special emphasizing the health risk posed by nitrate contamination using nitrate pollution index (NPI) and human health risk assessment (HHRA)," *Hum. Ecol. Risk Assess.*, vol. 27, no. 5, pp. 1324–1348, 2020.