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Removal of Cr(VI) from aqueous solution by using modified eggshells

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Abstract

In this study the removal of chromium (VI) from aqueous solutions by using modified Eggshells (Eg-Fe) was investigated. The effects of pH, concentration of Cr(VI), Eg-Fe dosage and contact time on the removal process were studied.

The results demonstrate that the chromium concentration and pH of solutions are the predominant factors affecting the removal of Cr(VI), it was observed that the removal capacity significantly decreased at pH value more than 6.5. While the removal efficiency exhibit a decreased tend with increasing of Cr(VI) concentration, while Eg-Fe dosage and contact time were not significantly influential.

The optimal removal conditions were achieved at: pH 6.0, contact time was 120 minutes, while the best dose of the Eg-Fe started from 1.0 g, whereas the removal efficiency reached 82%.

Keywords- Eggshells, iron, removal, adsorption, chromium, aqueous solution,

Introduction

Various industrial processes have become a significant threat to the environment due to the continuous generation of waste [1], some of this waste is non-biodegradable, highly toxic, and carcinogenic. Therefore the International environmental protection agencies adopted a specific approach that involves applying measures to source-reduce the production of pollutants at the source and developing effective technologies for the safe removal of existing waste or modify its physical and chemical properties to eliminate its toxicity and convert hazardous compounds into environmentally friendly materials [2,3].

Even with the significant variety of environmental contaminants, heavy metals are a critical class released from industrial activities that can harm human health even at low concentrations.

Chromium is classified as one of the most toxic metals [4], it exists in two stable oxidized states: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The distribution of chromium in the environment depends on its reducing properties and pH value of medium [5]. (Cr(VI) is classified as highly toxic, carcinogenic and causes severe damage to the liver and kidneys. while (Cr(III)) is much less toxic and stable. [6-8].

Chromium enters into the environment through various industrial processes such as metal plating, tanning, manufacture of dyes, magnetic tapes, photographic materials and others [9].

Several methods for chromium removal from aqueous solutions have been employed including techniques such as ion exchange and membrane filtration [10]. Researchers have also developed methods such as sedimentation, flotation, and biological treatment [11]. However these techniques may exhibit limited efficiency in the presence of high salt concentrations in samples [12,13]. Materials such as activated carbon and alumina have been extensively utilized as active surfaces for adsorbing toxic material. However, these methods exhibit limited efficiency and removal capacity due to non-selective or the influenced by interference.

The use of materials such as clays and calcium carbonate as natural materials is highly preferred in the field of pollutants removal due toe availability and cost-effective which are effective in removing pollutants due to their high surface area [14,15], which enhance adsorbing efficiency.

The continuous increase in industrial activities which generate large amounts of pollutants has prompted researchers to conduct and develop low-cost materials. In recent years the use of natural materials has increased for treating wastewater contaminated with hazardous compounds.

The development of low-cost and available materials that achieve high removal efficiency has become a priority for researchers [16,17]. Recent studies have focused on utilizing waste materials which are randomly discarded to effectively remove various toxic ions. Eggshells are a source of solid waste with huge quantities discarded without control. Recently research has shown the uses of eggshells in various industrial and pharmaceutical applications [18-21]. It consists of approximately 94% ($CaCO_3$) [22], which is a rich source of natural calcium.

Several studies have been conducted on the use of eggshells as an adsorbents material, due to their porosity, which contains between 7,000 and 17,000 surface pores [23, 24]. These characteristics establish eggshells as an effective material for removal various ions from wastewater due to high adsorption capacity [22,24-26], its particular effective for nitrates, whereas high removal capacity reached up to 95% has been observed[27,28].

Recently researchers have developed highly efficient processing techniques that utilize modified materials as selective adsorbents which are based on chemical adsorption onto surfaces containing active sites that bind to the compounds to be removed [29].

This study investigates the development of an effective adsorbent material using eggshells loaded with iron Eg-Fe for the selective removal Cr(VI) ions. The effects of pH, adsorbent dosage Eg-Fe, initial Cr(VI) concentration, and contact time on the efficiency of chromium removal from solutions have been evaluated.

Materials and Methods

Materials

All Reagents used in this study were analytical grade, K_2CrO_4 (Aldrich); Ethanol C_2H_5OH, (Winlab); $(NH_4)_2Fe(SO_4)_2$(Riedel-De Haen); NaOH (Merck); HNO_3 (Merck); DPC, $C_{13}H_{12}N_4O$ (Merck).

Chromium (VI)

A 1000 mg L^{-1} stock solution of Cr(VI) was prepared by dissolving 3.73 g of potassium chromate (K_2CrO_4, p.a., Aldrich) in distilled water. The solution was diluted in a 1000 mL volumetric flask and stored in a amber bottle to ensure stability.

Preparation of eggshells

Residual materials were removed from the eggshells by hand, followed by boiling in deionized water for one hour to eliminate any remaining matter. The eggshells were then rinsed with ethanol and deionized water, after dried overnight at room temperature the eggshells were crushed with a grinder.

Synthesis of modified eggshells Eg-Fe

The modified eggshells Eg-Fe were prepared as follows: 25 g of eggshells were placed in a conical flask containing 50 mL of deionized water and shaken for one hour followed by filtration. Then 50 mL of 0.75 mole L^{-1} ammonium ferrous sulfate solution was added slowly to the eggshells while stirring continuously for one hour.

1.0 mole L^{-1} NaOH was added very slowly while stirring continuously for four hours. The mixture was filtered, and the filtrate was washed with 1000 mL of deionized water, dried at room temperature for 24 hours. The specifications of the Eg-Fe were as follows: Iron content (168.18mgg^{1}), density1.44 mg L^{-1}, stability (pH 4.0 to pH 8.0) and color orange as showed in figure 1).

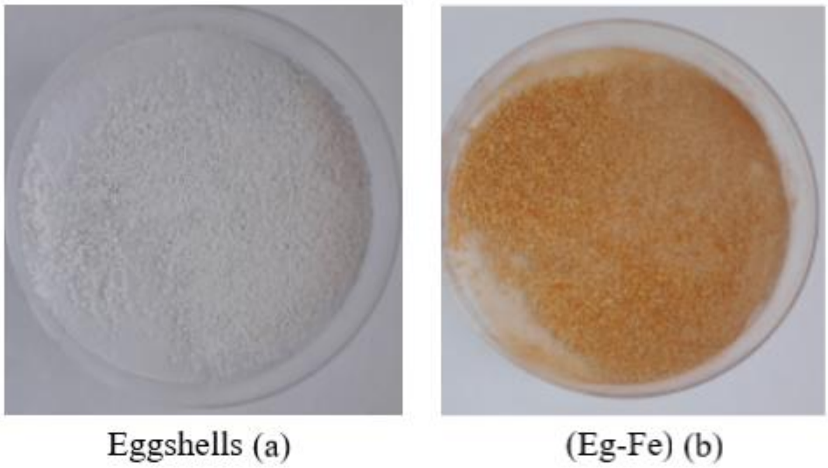

Figure 1: The color of eggshells (a; before) and (b; after) modification

Results and discussions

Effect of pH value

In this study the influence of pH on the removal of Cr(VI) was investigated in the range of pH 4.0 to pH 8 .0, while all other factors were constant (Cr(VI) concentration 10 mg/L; Eg-Fe mass 1.0 g; contact time 60 min; shake speed 150 rpm; and temperature (room temperature). The pH of the solution was adjusted using (NaOH) and (HNO_3). The results are shown in Figure 2. It was observed that the adsorption capacity increased with increasing pH from 5.0 to 7.0, then decreased with further increases in pH. This can be attributed The pH of a solution is a crucial factor in the existence and mobility of chromium in the environment [30-32], where the Cr(VI) exists in its highest concentration as an anion at neutral pH, whereas at acidic conditions it reduced to Cr(III).

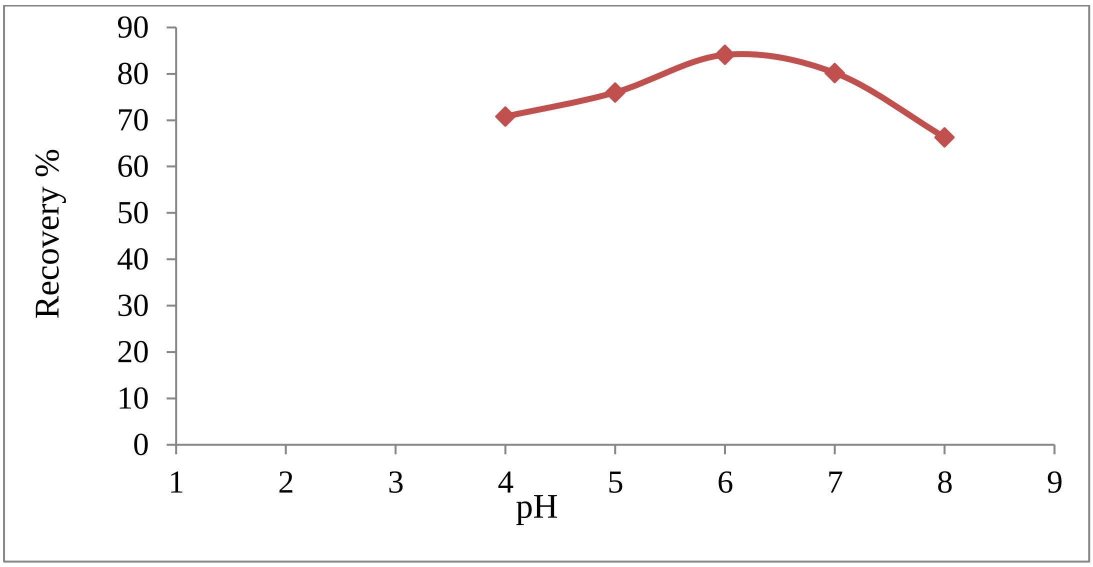

Figure 2: Effect of pH value in the removal process

The results in figure 2 indicated that the removal of Cr(VI)) was significantly influenced by pH of solution, whereas the optimal performance and acceptable removal efficiencies were achieved within weak acid to neutral conditions.

This behavior is consistent with the known environmental chemistry of Cr(VI) and its removal mechanism by iron hydroxide-modified sorbents. In aqueous system Cr(VI) species exists as anions species ($HCrO^-$).

The results demonstrated that the maximum removal efficiency was achieved at pH 6.0 the high removal efficiency at pH 6.0 may be due to two reasons:

- The chemical adsorption results from the strong electrostatic attraction between the positively charged iron hydroxide surface and the anionic $HCrO_4^-$.
- At the pH less than 6.0 the chemical reduction occurs, where Cr(VI) is reduced to Cr(III) by Fe(II) ions or any residual organic matter remaining from the eggshell, the Cr(III) ions are immobilized through the precipitation as insoluble $Cr(OH)_3$

Effect of Eg-Fe dosage

The weight of Eg-Fe is an important parameter that governs the adsorption efficiency in the batch adsorption system. The effect of different doses of Eg-Fe (0.5, 1.0, 2.0, 3.0, and 4.0 g, respectively) was studied while all other factors were constant, whereas the pH value was 6.0, concentration of Cr(VI) (10 mg L^{-1}), temperature (room temperature) and contact time (1 h). The results in figure 3 showed that the adsorption capacity increased with increasing in the dose of the Eg-Fe, the maximum removal was observed at 2.0 g, the adsorption capacity continued to increase with further dose increases. The increase in the adsorption capacity typically increases with the increase in surface area of the adsorbent and the availability of more adsorption sites with the increase in dose of Eg-Fe.

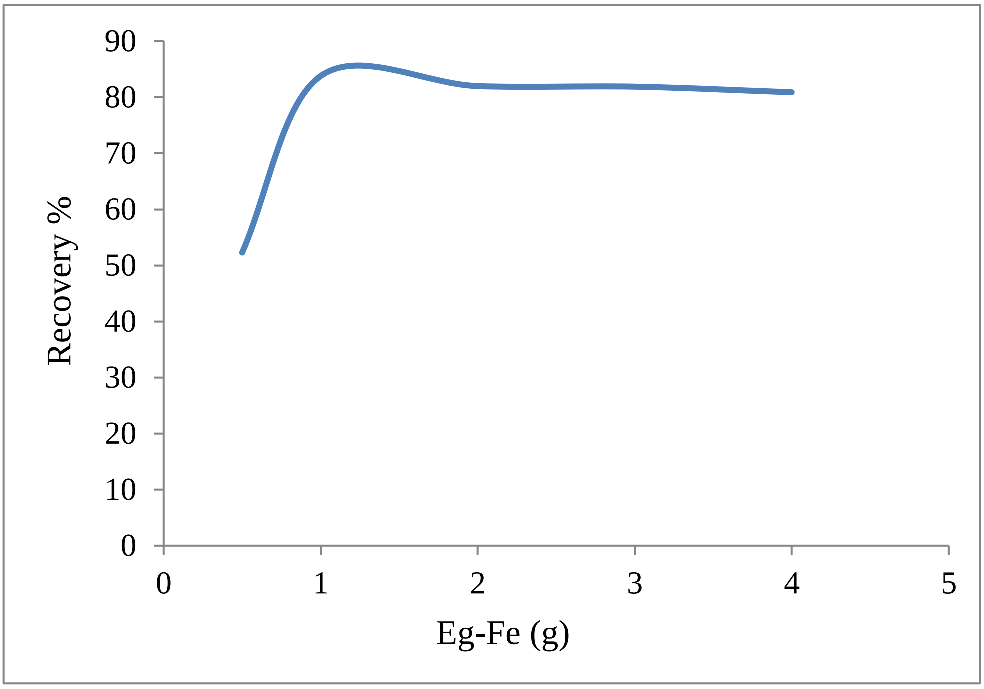

Figure 3: Influence of Eg-Fe dose on removal efficiency

Effect of initial concentration of Cr(VI)

Experiments were conducted to examine the effect of the initial Cr(VI) concentration on adsorption capacity. The Cr(VI) concentration ranged from 10 to 100 mg L^{-1} at pH 6.0, with all other factors held constant; the E-Fe mass was (2 g), contact time (1h), stirring rate (150 rpm), and the temperature of the solution (room temperature). Figure 4 shows that the Cr(VI) removal rate increased from 33% with an initial concentration of 100 mg L^{-1}, while at a lower initial concentration of 10 mg L^{-1}, the binding sites had a greater chance of adsorption of chromium it reached to 79%.

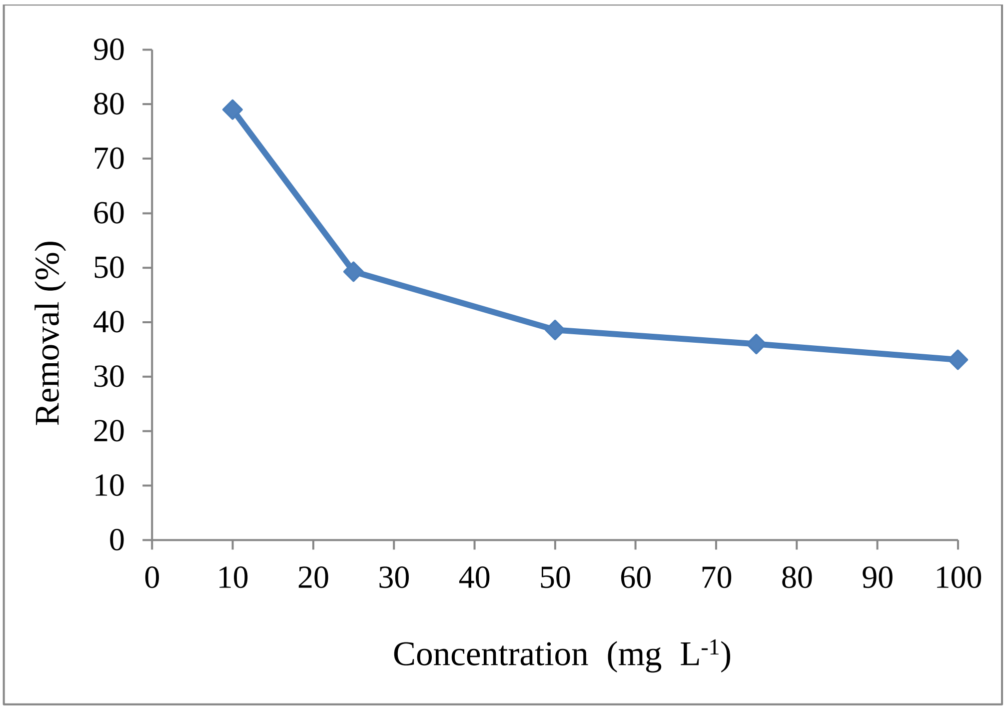

Figure 4: Effect of Cr(VI) concentration on the removal process

Effect of contact time

The adsorption study was conducted at different contact times while all other variables were constant: adsorbent dosage (2.0 g), Cr(VI) concentration (10 mg L^{-1}), pH 6.0, and temperature (room temperature). The results showed that the adsorption efficiency increases with increased with contact time, the removal reaching to 82% after 2.0 hours as shown in figure 5. The adsorption rate then stabilized over time it may due to the iron reaching equilibrium as the Eg-Fe pores became saturated with Cr(VI).

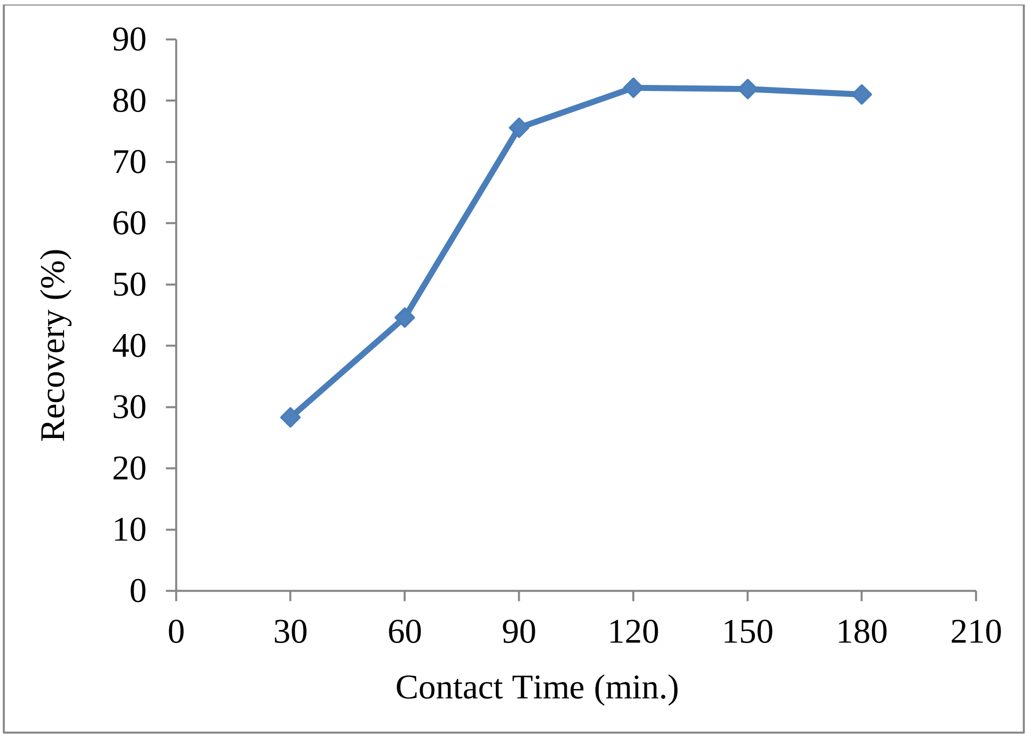

Figure. 5. Effect of contact time on the removal of Cr(VI) by Eg-Fe

Real water samples

The removal of Cr(VI) from tap water was investigated to confirm the efficiency of the eggshells Eg-Fe.

Two real water samples were investigated. The total dissolved solids (TDS) concentrations in sample 1 were 897 mg L^{-1}, while in sample 2 were 109 mg L^{-1}. Different concentrations of Cr(VI) were added to the samples as shown in Table 1.

Table 1: Recovery removal of Cr(VI) by using Eg-Fe in spiked real water samples

Sample	Added (mg L^{-1})	Removed	Recovery
1	10.0	8.3	83 %
2	10.0	8.8	88 %

The results in Table 1 showed that the removal of Cr(VI) by Eg-Fe in sample 2 was unaffected by presence of dissolved salts. However in sample 1 the high concentration dissolving salts slightly reduced the efficiency of Eg-Fe, this decrease may attributed to the presence of naturally ions in the water.

Conclusion

This study demonstrated the practicality of modifying eggshells for use as a selective adsorbent for Cr(VI). The influence of pH on removal efficiency was initially investigated to determine the optimal aqueous condition for subsequent experiments. Furthermore the effects of contact time, Eg-Fe dosage, and Initial Cr(VI) concentration were evaluated.

The results showed that pH is the primary factor influencing removal efficiency, with pH 6.0 as the optimal condition, while the Eg-Fe dosage less than 1.0 gram exhibited minimal impact on the removal process. The

Cr(VI) removal was affected by initial concentration, where the results showed a significant decrease in removal efficiency at concentrations exceeding 15 mg L^{-1}.

This method demonstrates that it is highly effective in the selective removal of Cr(VI) through chemisorption process. It is suggested that the performance of this method can be further enhanced by employing a low-detection-limits analytical technique such as ICP-MS.

References

1. J. Qin , H. Cao, Y. Xu, F. He, F. Zhang and W. Wang, Efficient removal of Cr(III) by microbially induced calcium carbonate precipitation, R. Soc. Chem., 15 : 4, (2025) 2840-2849.
2. M. S. Ayilara and O. O. Babalola, Bioremedition of environmental wastes: thr role of microorganisms, Front. Agron., 5 (2023) 1-15.
3. G. Y. Al-Kinidi, Evaluation the Solidification/Stabilization of Heavy Metals by Portland Cement, J. Ecol. Eng., 20 :3 (2019) 91-100.
4. M. S. Samuel, E. Selvarajan, R. Chidambaram, H. Patel and K. Brindhadevi, Clean approach for chromium removal in aqueous environments and role of nanomaterials in bioremediation: Present research and future perspective, Chemosphere, 284 (2021) 131368.
5. J. Kotsa and Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 107: 3 (2000) 263-283.
6. S. S. Wise, A. L.Homes, L. Liou, R. M. Adam and J. P. Wise, Hexavalent chromium induces chromosome instability in human urothelial cells, Toxicol. Appl. pharmacol., 296 (2016) 263-283.
7. V. K. Gupta, A. K. Shrivasrava and N. Jain, Biosorption of chromium(VI) from aqueouse solution by green aglae spirogyra species, Wat. Res. 35 : 17 (2001) 4079-4085.
8. J. P. wise, J. L. Young, J. Cai and L. Cai, Current understanding of hexavalent chromium [Cr(VI)] neurotoxicity and new perspectives, Environ. Inte. 158 (2022) 1-18
9. A. Kowalik-Klimczak, M. Lozynska, M. Zyck, C. Schadewell, T. Fiehn, B. Wozniak and M. Flisek, Valorisation of tannery waste to recover chromium with a view to reusing it in industrial practise. Membranes, 14 (2024) 1-12.
10. B. Shang, S. Wang, L. Lu, H. Ma, A. Liu, A. Zupanic and Y. Yu, Poultry eggshell-derived antimicro bial materials: Current status and future perspec tives, J. Environ. Manag., 314, (2022) 115096.
11. A. Maslon and J. Czarnota, Efficiency of Brick Dust and Powdered Ceramsite in the Phosphorus Re moval from Wastewater, J. Ecol. Eng., 21:2 (2020) 116346.
12. A. El Nemr, A. El-Sikaily, A. Khaled and O. Abdelwahab, Removal of toxic chromium from aqueous solution, wastewater and saline water by marine red alga *pterocladia capillacea* and its activated carbon, Arab. J. Chem., 8 (2015) 105-117.
13. X. Luo, H. Lang and W. Wang, Experimental study on the effect of salinity change on Fe and Cr removal from estuary water, E3S Web Conferences, 98 (2019) 1-4.
14. S. Tan, C. Cheng, Z Wang, H. Li and Y.Zhao Efficient removal and stepwise recovery of various heavy metals from water by using calcium carbonate with different activity, Sep. Purif. Technol., 345 : 5 (2025) 129142.

15. Z. Wang, Y. Zhao, T. Wen and T. Zhang, Efficient Cd(II) Removal from Aqueous Solution Using Mechanically Activated CaCO3: Removal Pathway and Mechanism,Water, Air, Soil Pollut., 233:9 (2022) 11270.
16. Y. Cheng, H. Dong and T. Hao, $CaCO_3$ coated nanoscale zero-valent iron (nZVI) for the removal of chromium(VI) in aqueous solution, Sep, Purif, Technol., 257 :15(2021) 117967.
17. D. O. Profeta, M. A. da Silva, D. N. Faria, D. F. Cipriano, J. Freitas, F. Soares, T. M. Lima, S. C. Vasconcelos and M. K. Piete, Zeolite/calcium carbonate composite for a synergistic adsorption of cadmium in aqueous solution, Next Mater., 6 (2025) 100493.
18. A .P.Chakraborty, Chicken eggshell as calcium supplement tablet, . Int. J. Ind. Eng. Manag. Sci, 1:5 (2016) 45-49.
19. M. Gaonkar, A. P. Chakraborty, Application of eggshell as fertilizer and calcium supplement tablet. Int.J. Innov. Res. Sci. Eng. Technol., 5 :3 (2016) 3520-3525.
20. N. K. Kinayturk, B. Tunali and D T. Altug, Eggshell as a biomaterial can have a sorption capability on its surface: A spectroscopic research, R. Soc. Open Sci., 8 (2021) 210100.
21. S-C Chang, H-C Hsu, S-K Hsu, Y-K Chang and W-F Ho, Synthesis of hydroxyapatite from eggshell powders through ball milling and heat treatment, J. Asian eram. Soc., 4 (2015) 85-90.
22. L. Castellinin, A. Giordana, M. Malsndrino, L. Operti, G. Cerrato, Sustainablt synthesis of hydroxyapatite-containing composites from eggshells, for soil amendment applications, RSC Sustain., 4 : 1 (2025) 262-268.
23. R. G. Saratale, Q. Sun, V. S. Munagapati, G. D. Saratale, J. Park and D-S Kim, The use of eggshell membrane fo the treatment of dye-containing wastewater: batch, kinetics and reusability studies, Chemosphere, 281 (2021) 130777.
24. W. J. Stadelman, D Newkirk. and L Newby, Egg Science and Technology. CRC Press, Boca Raton, FL, USA. (2017).
25. K. Annane, W. Lemlikchi, S. Tingry, Efficncy of eggshell as a low-cost adsorpent for removal of cadmium: Kinetic and isotherm studies, Biomass Conv. Bioref., 13 (2023) 6163-6174.
26. S. Hajji, T. Turki, M. Hajji and N. Mzoughi, Application of response surface methodology for optimization of cadmium ion removal from an aqueous solution by eggshell powder, Chem. Res. Chin. Univ. 34 (2018) 302–310.
27. Z. H. Al-Agili, Removal of nitrate from aqueous solution by bio-calcium from Iraqi eggshells, J. Ecol. Eng. 24 : 9 (2023) 10-18.
28. A. H. Jendia, S. Hamzah, A. A. Abuhabib and N. M. El-ashgar, Removal of nitrate from groundwater by Eggshell biwaste, water Supp., 20 : 7 (2020) 2514-2529.
29. N. BenIssa, M. Lawar and Y. Elhebshi, Adsorption of thiocyanate from aqueous solution on the Ion exchange resin loaded AgCl as a hybrid selective resin, Int. J. Eng. Res. Gen. Sci, 11:2 (2023) 6-12.
30. J. Scancar and J. Anal. RA critical overview of Cr speciation analysis based on high performance liquid chromatography and spectrometric techniques, J. Anal. At. Spectrom., 29 (2014) 427–443.
31. M. Saraiva, P. Jitaru and J. J. Sloth, Speciation analysis of Cr(III) and Cr(VI) in bread and breakfast cereals using species-specific isotope dilution and HPLC-ICP-MS, J. Food Comps. Anal., 102 (2021) 103991.
32. S. Zhu, J. Chen, Y. Zhu, B. Zhang, J. Jia, M. Pan, Z. Yang, J. Cao and Y. Shen, Influencing factors of hexavalent chromium speciation transformation in soil from a northern china chromium slag site, Molecules 30 (2025) 3-20.