Research Article
Open Access

Regeneration study of adsorbents loaded with zinc metal ions from contaminated water

Abstract

Regeneration of adsorbents is very important from the environmental as well as economical point of view. It allows reuse of adsorbents multiple times and recovery of heavy metals from spent adsorbents, thus lowering the processing costs of separation and facilitating safe disposal of the adsorbents. Desorption is the simplest, cheapest and commonly used technique for regeneration and metal recovery. In the present study, zinc ions were desorbed from mango leaf powder using HCl, HNO_3, NaOH and distilled water as desorbing agents. HCl showed the best elution efficiency (94.7%) followed by HNO3 (89.5%). NaOH and distilled water showed very low elution efficiency (<10%). Regeneration allowed adsorbent to be used for 3 consecutive adsorption cycles with only 11% loss in adsorption efficiency and 16.6% loss in desorption efficiency. Adsorption and desorption isotherms resulted in adsorption hysteresis.

Keywords: desorption, regeneration of adsorbents, mechanism, elution efficiency, hysteresis

Volume 7 Issue 5 - 2023

Achla Kaushal
Chemical Engineering Department, Delhi Skill and Entrepreneurship University, India

Correspondence: Dr. Achla Kaushal, Faculty, Chemical Engineering Department, Guru Nanak Dev Rohini Campus, Delhi Skill and Entrepreneurship University, Delhi, India, Tel +919811200429, Email achla001@hotmail.com

Received: October 07, 2023 | **Published:** October 23, 2023

Introduction

Regeneration of adsorbents is as important as separation of contaminating metal ions by adsorption in terms of waste management and environmental remediation. It presents a possibility to recover heavy metals in concentrated form from waste water, reuse of adsorbents up to a few cycles resulting in lowering of costs of separation. There are various means of regeneration and recovery of adsorbed heavy metal ions such as desorption, ion exchange, thermal treatment, bio regeneration and microwave irradiation etc. Of these techniques, desorption is the most commonly used technique to regenerate adsorbents and recover metal ions. This is done by desorbing or eluting metal ions from the used adsorbent with the help of desorbing agents which should be cost-effective, non-polluting and non-damaging to the adsorbent. Inorganic and mineral acids such as HCl, HNO_3, H_2SO_4 and H_3PO_4 are commonly used for regeneration studies as metal removal is found to be quite high at low pH. NaOH, EDTA, NaCl and distilled water are commonly used for comparison.[1–5]

A number of studies have been carried out on recovery of heavy metal ions from agricultural adsorbents and regeneration of adsorbents e.g. banana pith,[6] Spagnum Moss Peat,[7] Medicago sativa,[8] cassava waste,[9] Ceiba pentandra hulls,[10] areca nut shell,[11] rice husk,[12] Mucilaginous Leaves,[13] and sago waste.[14] Operating conditions in wastewater purification process are quite harsh, resulting in damage to the adsorbent surface and hence loss in its elution efficiency.[15] A series of experiments were carried out with different desorbing agents of different strengths. This helped in selecting the best desorbing agent to achieve the maximum elution efficiency and reusability of the adsorbent with least damage to its surface and loss in its efficiency after experiments. The equilibrium data is analysed with the help of equilibrium models for adsorption isotherms. Adsorption equilibria is attained when the rate of adsorption of a molecule on a surface is equal to the rate of desorption. Models to study the adsorption isotherm are *Langmuir isotherm, Freundlich isotherm, Temkin Isotherm, Brunauer- Emmett- Teller (BET) isotherm, Dubinin–Radushkevich (DRK) isotherm etc.*

In the present study, HCl, HNO_3 and NaOH were used as desorption agents or eluents to recover zinc from the contaminated mango leaf powder as adsorbent. Distilled water was also used for comparison. Experiment was carried out with different concentrations of desorbing agents ranging between 0.01 and 1.0 mol/L to determine the optimum value of the concentration for maximum desorption of Zn (II) ions adsorbed on the surface of MLP. Determination of optimum concentration of desorbing agents very useful in economical processing of wastewater treatment. The batch experiment was carried out for three successive adsorption-desorption cycles. Adsorption isotherms were obtained for both adsorption and desorption processes. Although the adsorption-desorption phenomenon is reversible, yet a part of the equilibrium data was different over a part of the isotherm, resulting in hysteresis phenomenon. Effect of contact time on desorption was also studied.

Materials and method

Batch adsorption

10 mg Zn metal chips (AR) were dissolved in a few drops of conc. HCl. Stock solution was prepared by diluting it with distilled water to a volume of 1 litre. This solution was further diluted by adding distilled water to obtain various concentrations in the range 10-100 mg/L. Mango tree leaves collected from local area were washed, dried and crushed to 200 mesh size. This crushed powder was washed thoroughly to get rid of the colour and other impurities. It was then dried for 6 hours at 60°C in a hot air oven and stored in air tight container. This dried powder was used in the range 1-10 g/L to calculate the % removal of Zn ions from the solution. Adsorption of zinc ions was carried out batchwise in the '*Orbital*' constant temperature variable speed flask shaker. 12 Erlenmeyer flasks were used for batch experiments at a time at 20°C and 150 rpm for 100 minutes in the pH range 2-8. After the batch experiment, the solutions in flasks were filtered with *Whatman filter paper no. 40*. The filtrate was analysed for the concentration of zinc ions with the help of *CHEMITO AA201* Atomic Absorption Spectrophotometer (AAS) using air-acetylene flame. % removal of zinc ions from the contaminated solution at the end of batch experiment was calculated as

% Removal = $[(C_i - C_o)/C_i]*100$, where C_o represents the final zinc ion concentration (mg/L) in the solution and C_i represents the initial zinc ion concentration (mg/L) in the solution.

©2023 Kaushal. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and build upon your work non-commercially.

 Copyright: ©2023 Kaushal

The equilibrium adsorption capacity (mg adsorbate/g adsorbent) was calculated as

$q_e = [(C_i - C_e)V]/m$, where V is the volume of the solution (L), C_e is the equilibrium concentration (mg/L) and m is the mass of the adsorbent (g) used.[16]

Batch desorption

Zinc loaded adsorbents taken from the above batch adsorption experiment were further studied for desorption. Batch desorption was carried out in the '*Orbital*' flask shaker holding Erlenmeyer flasks (100 ml each) containing 50 mL of the elution agent (HCl, HNO_3, NaOH and distilled water) and 5 mg zinc loaded adsorbent at a time at 20°C and 150 rpm for one hour. The concentrations of the elution agents (HCl, HNO_3, NaOH) used were 0.01, 0.1 and 1.0 mol/L each. Equilibrium was attained in 30 mins. The solutions were filtered with *Whatman filter paper no. 40* at the end of the batch experiment and filtrate was analysed for concentration of zinc ions in *CHEMITO AA201* Atomic Absorption Spectrophotometer (AAS) using air-acetylene flame. The elution efficiency Ƞ was calculated as

$$Ƞ = (m_1/m_2)*100$$

Where m_1 and m_2 are the mass (mg) of zinc in the solution before and after the experiment. Mango leaves powder, MLP collected from filtration was dried to be reused in a new adsorption cycle. Adsorption-desorption cycle was carried out up to three cycle with the regenerated adsorbent.

Results and discussion

Effect of desorbing agents on desorption

Results showed that of HCl, HNO_3, NaOH (used in the concentrations range 0.01 to 1.0 mol/l) and distilled water used as desorbing agents, for zinc ion 0.1 mol/l HCl is the most efficient desorbing agent giving elution efficiency 94.7% for zinc ions. 0.1 mol/l HNO_3 also showed a reasonably good elution efficiency of 89.5%. Elution efficiency shown by 0.1 mol/l NaOH and distilled water are 8.8% and 3.4% respectively Figure 1.

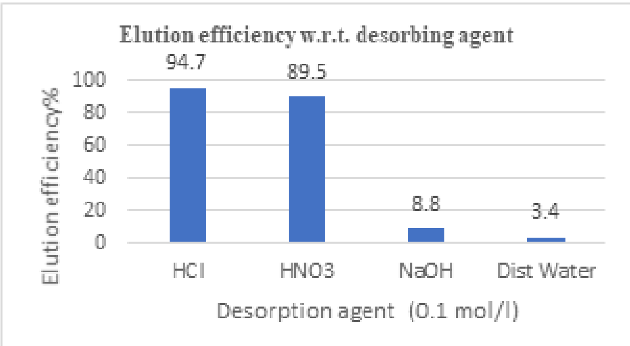


Figure 1 Elution efficiency w.r.t. desorbing agent.

The % metal removal from zinc loaded adsorbents was found to be quite high at low pH. This was due to the fact that under acidic conditions, proton concentration in the solution is high, resulting in less solubility of metal ions. The adsorbent surface is covered completely by the H^+ ions (protons) present in the solution, which replace the cations (Zn^{+2}) present on the adsorbents. As the process proceeds, protons replace more and more cations from the adsorbent surface, leaving it fully protonated and regenerated for new adsorption cycle. The adsorption capacity of adsorbents was retained using caustic soda regeneration carried out as an intermediate step after desorption. Concentrated metals can be recovered from the solution by using conventional techniques.[16] NaOH showed very low elution efficiency, hence poor recovery of zinc. This might happen due to deprotonation of coordinating ligands, resulting in difficulty in detachment of metal ions from the adsorbent surface. Distilled water as desorbing agent showed the least elution efficiency, rendering it unfit as a desorption agent.

Effect of concentration of desorbing agent on zinc desorption

To find out the optimum value of concentration of the desorbing agent, elution efficiency was calculated for different concentration of HCl ranging from 0.01 to 1.0 mol/l. Results showed that the elution efficiency was maximum (94.7%) for 0.1 mol/l HCl. For 0.01 mol/L, the elution efficiency is only 62.5%. Higher concentration of HCl damaged the surface of the adsorbent, hence lowering its efficiency. Therefore, 0.1 mol/l was found to be the optimum concentration for desorbing zinc ions from the contaminated samples Figure 2.

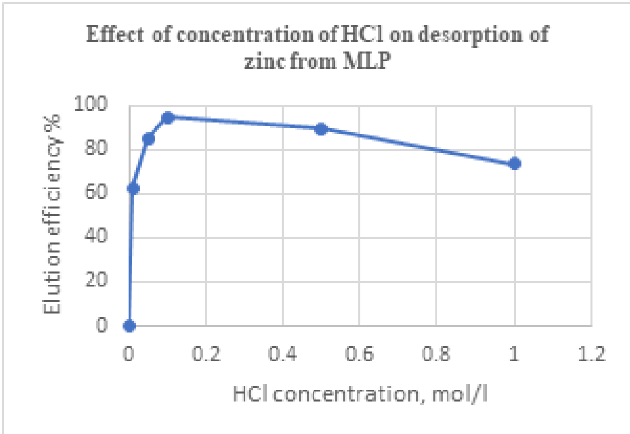


Figure 2 Effect of concentration of HCl on desorption of zinc from MLP.

Effect of desorbing time on lead desorption

In wastewater treatment, equilibrium time is an important parameter to decide the economy of the process. To determine the equilibrium time, the elution efficiency for zinc ions was calculated after every 10 mins as shown in Figure3. It was observed that the desorption was very rapid for first 10 mins, but slows down gradually. Desorption equilibrium is attained in 30 min. No further change in concentration was not observed with time.

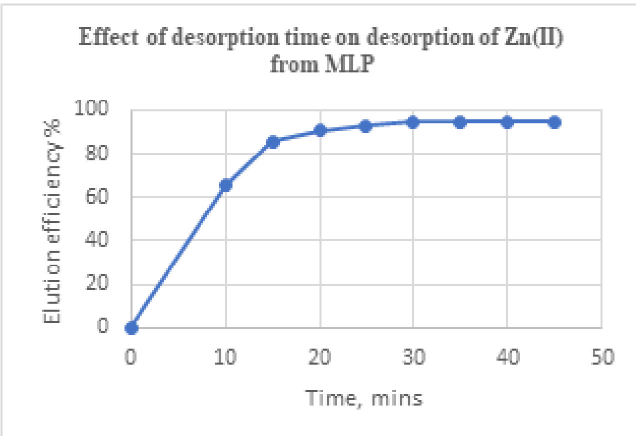


Figure 3 Effect of desorption time on desorption of Zn(II) from MLP.

Citation: Kaushal A. Regeneration study of adsorbents loaded with zinc metal ions from contaminated water. *Int J Hydro.* 2023;7(5):189‒192.
DOI: 10.15406/ijh.2023.07.00356

As discussed in section 3.1, cations are replaced from the adsorbent surface by the protons of the acidic solution, depleting cations from its surface.

Successive cycles adsorption and desorption of Zn (II) on MLP

Regeneration of adsorbent is an important step for an economical process. Three successive cycles of adsorption and desorption of Zn (II) were carried out batch wise to study the reuse of MLP for Zn (II) removal and recovery from waste water Figure 4. Caustic soda regeneration was carried out as an intermediate step after desorption to retain the adsorption capacity of adsorbents. After each successive adsorption-desorption cycle, the efficiency of MLP decreased a little. After three successive adsorption–desorption cycles, the adsorption of Zn (II) by the MLP decreases by 12% and desorption of Zn (II) decreases by 16.6%, respectively. MLP was found to be reusable up to three successive adsorption-desorption cycles for Zn (II) adsorption with slight losses in its initial adsorption/desorption efficiency.

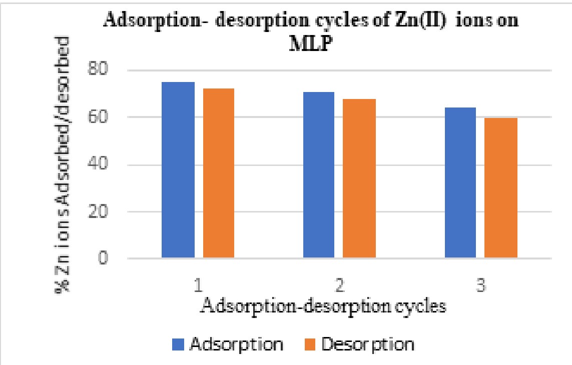
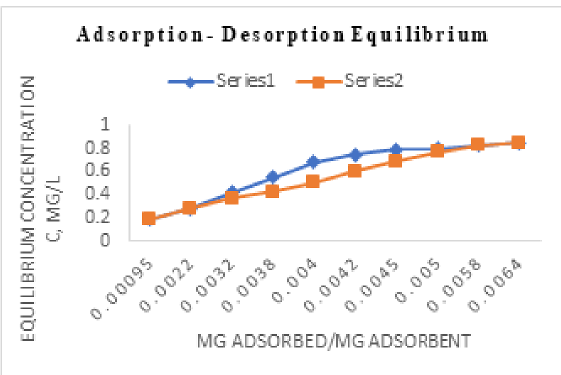


Figure 4 Adsorption- desorption cycles of Zn (II) ions on MLP.

Adsorption hysteresis

The equilibrium curves for adsorption of zinc on the adsorbent and for desorption of the zinc with an initially higher concentration were plotted Figure 5. The curves were plotted using data obtained experimentally. A reversible adsorption-desorption phenomenon was obtained, except that the equilibrium data is different over a part of the isotherm, resulting in hysteresis phenomenon. It results either from shape of openings of capillaries and pores of the adsorbent or due to the wetting of adsorbent by the adsorbate. The desorption equilibrium curve was below the adsorption equilibrium curve.



Series 1: Equilibrium data for adsorption

Series 2: Equilibrium data for desorption

Figure 5 Adsorption- Desorption Equilibrium.

Conclusion

Mango leaf powder as adsorbent showed favourable results in desorption and significant recovery of Zn (II) from contaminated water. Regeneration and reuse of mango leaf powder as adsorbent showed promising results for three consecutive adsorption-desorption cycles. There was no apparent damage to its surface and a loss of less than 17% was observed in its elution efficiency in three cycles. Desorption was very fast in the beginning and equilibrium was reached in 30 minutes. Elution efficiency of 94.7% was achieved with 0.1mol/l HCl and 89.5% with 0.1mol/l HNO_3 at 20^0C. Distilled water and NaOH showed poor elution efficiency, hence cannot be recommended to be used as desorbing agents. Hence, Mango leaf powder can be recommended as a good adsorbent for removal and recovery of zinc ions even at low temperatures.

References

1. Shishebore MR, Afkami A, Bagheri H. Salicylic acid functionalized silica-coated magnetite nanoparticles for solid phase extraction and preconcentration of come heavy metal ions from various real samples. *Chemistry Central Journal.* 2001;5(41):1–10.
2. Quan X, Liu X, Bo L, et al. Regeneration of acid orange 7-exhausted granular activated carbons with microwave irradiation. *Water Research*. 2004;38(20):4484−4490.
3. Sarode DB, Jadhav RN, Khatik VA, et al. Extraction and leaching of heavy metals from thermal power plant fly ash and its admixture. *Polish Journal of Environmental Studies*. 2010;19(6):1325–1330.
4. Jeyakumar SRP, Chandrasekaran V. Desorption and reutilization studies of copper and lead ions by activated carbons prepared from ulva fasciata sp. *International J of Scientific Research*. 2013;2(6):60–63.
5. Qing-zhu L, Li-yuan C, Jing Z, et al. Lead desorption from modified spent grain. *Transactions of Nonferrous Metals Society of China.* 2009;19(5):1371–1376.
6. Low KS, Lee CK, Leo AC. Removal of metals from electroplating wastes using banana pith. *Bioresource Technology*. 1995;51(2–3):227–231.
7. Ho YS. *Adsorption of heavy metals from waste streams by peat*. Ph.D. Thesis, University of Birmingham, Birmingham, UK. 1995.
8. Gardea-torresdey JL, Gonzalez JH, Tiemann KJ, et al. Phyto filtration of hazardous cadmium, chromium, lead and zinc ions by biomass of Medicago sativa (Alfalfa). *Journal of Hazardous Materials.* 1998;57(1–3):29–39.
9. Abia A, Horsfall Jr M, Didi O. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Technology*. 2003;90(3):345–348.
10. Rao MM, Rao GPC, Seshaiah K, et al. Activated carbon from Ceiba Pentandra Hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solution. *Waste Management*. 2007;28(5):849–858.
11. Geetha A, Sivakumar P, Sujatha M, et al. Adsorption of Cr(VI) and Pb(II) from aqueous solution using agricultural solid waste. *J of Environ Sci Eng.* 2009;51(2):151–156.
12. El-Said AG, Badawy NA, Abdel-Aal AY, et al. Optimization parameters for adsorption and desorption of Zn(II) and Se(IV) using rice husk ash: kinetics and equilibrium. *Ionic.* 2011;17(3):263–270.
13. Edokpayi JN, Odiyo JO, Msagati TAM, et al. A novel approach for the removal of Pb(II) Ion from wastewater using mucilaginous leaves of *Diceriocaryum Eriocarpum* plant. *Sustainability.* 2015;7:14026–14041.
14. Quek SY, Wase DAJ, Forster CF. The use of sago waste for the sorption of lead and copper. *Water SA*. 1998;24(3):251–256.

15. Mishra SP. Adsorption–desorption of heavy metal ions. *Current Science.* 2014;107(4):601–612.
16. Kaushal A, Singh SK. Critical analysis of adsorption data statistically. *Applied Water Science*. 2017;7(6):3191–3196.

Citation: Kaushal A. Regeneration study of adsorbents loaded with zinc metal ions from contaminated water. *Int J Hydro.* 2023;7(5):189–192. DOI: 10.15406/ijh.2023.07.00356