I.A.U
Karaj branch

Application of Magnetized Sawdust Cross-linked by Polyethylenimine for Removal of Zn^{2+} from Aqueous Solution

Avat Ghasemi[*1], Meisam Shabanian[2]

[1]Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

[2]Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), Karaj, Iran

Abstract

The need to elimination heavy metal from aqueous solutions cannot be over emphasized. Very studies have investigated the removal heavy metal from water. In this study a new magnetic nanocomposite of PEI on magnetized Sawdust (SD/MNP/PEI) was prepared. Investigations were conducted to study the adsorption behavior of heavy metal Zn (II) on the SD/MNP/PEI nanocomposite in aqueous medium by varying parameters such as contact time, pH, and initial metal concentration. Zn (II) adsorption was broadly dependent of pH. Isotherm data demonstrate that the Langmuir adsorption model was the best-suited model for this study. The results confirmed the good adsorption capacity of the new magnetic nanocomposite for the removal of Zn (II) from aqueous solutions and its great potential for practical applications.

***Keywords*:** Heavy metal, SD/MNP/PEI, Nanocomposite, Zn (II).

*****Corresponding *author**: *Avat Ghasemi, Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, 1913674711, Iran, Email: Avat.gh@iau-tnb.ac.ir.*

Introduction

Today elimination of the heavy metal contaminated from the environment is very essential and obviously be overemphasized. There is an increasing worldwide concern for environmental protection. Recently, there is increased attention and focus on heavy metals, which are becoming one of the most serious environmental problems due to their hazardous impact and adverse health effects. Year by year hazardous material like heavy metals increases in our environment, due to rapidly increasing population and industrialization along with anthropogenic activities, and natural sources such as weathering of rocks and volcanic activities are the cause for enriching the water reservoirs with heavy metals. Heavy metals such as Zn (II) are known to be highly toxic due to their non-biodegradability [1-5].

According to the World Health Organization (WHO), zinc is one of the most toxic heavy metal. When consumed in large amounts, zinc is difficult for the body to process, which may lead to the accumulation of Zn (II) in various organs and cause serious illness. Due to the toxicities associated with Zn (II), WHO has recommended maximum permissible limit of Zn (II) in drinking water as 3 mg L^{-1}[6]. In order to elimination metal pollutions and reach environmental standards, many conventional methods such as ultrafiltration [7], oxidation [8], coagulation [9], ion exchange [10], precipitation [11], reverse osmosis [12], adsorption on carbon active [13], etc. have been reported in the literature to remove Zinc along with other heavy metals from waste water. Most of these methods are extremely expensive and not applicable, especially when there are in low concentrations.

Compared to alternative technologies, adsorption is still the most attractive and widely considered as one of the most popular method for the removal of heavy metals from the wastewater due to its cheap cost, easy availabilityand insensitivity to toxic substance, biodegradability, simplicity of design/operation with high capacity and favorable rate [14]. Adsorption technology can efficiently remove toxic materials from the liquid phase, and chemical surface treatments of adsorbents can significantly enhance the selectivity and capacity of substrates.

Recently, great attention was paid to magnetization of low cost materials which are considered as promising adsorbents for the removal of different pollutants from wastewater at industrial scale. These adsorbents possess many valuable properties including low cost, chemical stability, extended lifecycles and easy separation by applying an external magnetic field [15]. Also, the adsorption capacity of these adsorbents can be greatly improved by their surface modification with suitable functional groups [16, 17].Many polymers due to their advantages such as chemical stability in harsh environments, including strong acidic, alkaline, salty and oxidizing solutions, high flexibility in the design of structures, properties,feasible regeneration, and thermal durability, have been

prepared for removal applications. Substances that have amine groups at this Structure can easily adsorb heavy metals and chelating with them. Polyethyleneimine (PEI) is a water-soluble chelating polymer, which has a high amine density and accessible primary amine sites on the chain ends, which act as desirable building blocks for the construction of adsorbents. Chelating polymers are some of the most effective adsorbents for remediation of polluted water. They have a good potential for metal ions recovery as they have chelating ligands or anchoring sites with functional groups containing donor atoms such as nitrogen, phosphorus, oxygen or sulfur that can donate electrons to metal ions, thus forming a coordination polymer – metal complex [18, 19].

A common way to increase the stability of PEI on a surface is by chemical cross-linking it. This study was aimed at using a cross-linked PEI attached on magnetic sawdust, as an adsorbent for the removal of Zinc from aqueous solutions. The influence of pH, contact time, initial concentration of Zn (II), and adsorption process isotherms has been investigated.

Experimental

Chemicals

Polyethyleneimine (PEI, Mw = 2000 g mol^{-1}) was purchased from Sigma Aldrich. Other chemical reagents used in this work including ferric chloride hexahydrate (FeCl$_3$.6H$_2$O, 98%), ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O), ammonia solution (25%), epichlorohydrin(EPC), Sodium bicarbonate (NaHCO$_3$), Sodium hydroxide (NaOH), and (Zn(NO$_3$)$_2$.6H$_2$O, 99%) were purchased from Merck. Sawdust was prepared from Poplar tree.

Preparation of SD/ MNP / PEI nanocomposite

Sawdust was sieved pass through a 470 μm Standard Sieve. Nanoparticles-loaded sawdust (SD-MNP) was prepared by modified co-precipitation method [20]. The dried SD-MNP was steeped in epichlorohydrin (5 mL) and NaOH (1.4 M, 10 mL) and stirred for 2 h at 60°C. The obtained raw product was subsequently rinsed with NaOH (1.4 M, 50 mL) and distilled water (50 mL). The epoxidized SD/MNP was added in a solution of NaHCO$_3$ (50 mM, pH 9, 50 mL) and PEI. The reaction system was incubated for 5 h with gentle stirring at 65°C. The grafted nanocomposite was sequentially rinsed with NaHCO$_3$ and distilled water and dried in vacuum at 40°C [21].

Results and discussion

Equilibrium Studies

Each of the batch experiment was carried out by adding 0.2 g of nanocomposite with 50 ml of different concentrations of Zn (II) solution at an agitation speed of about 60 rpm. The residual

concentration of Zn (II) was analyzed after a predetermined interval of time (60 min) until the system reached equilibrium by using atomic absorption spectrophotometer (Varian AA-220). All the reported data are the average of at least triplicate measurements.

Isotherm Studies

For isotherm studies, each experiment was conducted at 25 °C. The removal percentage and the amount of adsorbed metal ion per gram of nanocomposite at equilibrium (q_e, (mg g^{-1})) were calculated using Equations (1, 2), respectively.

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

$$q_e = \frac{V}{M}(C_o - C_e) \qquad (2)$$

Where C_o and C_e (mg L^{-1}) are the initial and equilibrium concentrations of contaminants, respectively. q_e (mg g^{-1}) is the adsorbed amount of adsorbate per unit mass of the adsorbent at equilibrium. V (L) is the volume of adsorption solution, M (g) is the mass of adsorbent [22].

Contact time

Figure 1 describes the effect of Contact time and uptake by SD/MNP/PEI. It is clearly visible from the graph, that amount of uptake, q_t (mg g^{-1}) increased with increased agitation time and after certain period of contact time with the nanocomposite, and it reached to a static value beyond which no further change of uptake was observed reflecting the equilibrium state of the system. The experimental data showed that, the adsorption process was taking place rapidly at initial stage of contact period and after that near the equilibrium point it became slower. The rate of Zn (II) uptake was initially high due to the availability of larger surface area of SD/MNP/PEI for adsorption. With the lapse of time, the surface adsorption sites were occupied. The remaining vacant sites were difficult to be captured by Zn (II) ions due to repulsive forces between adsorbate that is Zn (II) present in solid and bulk phases.
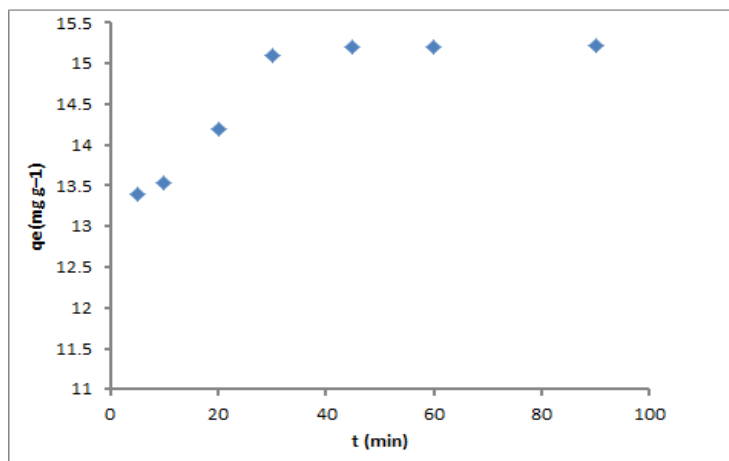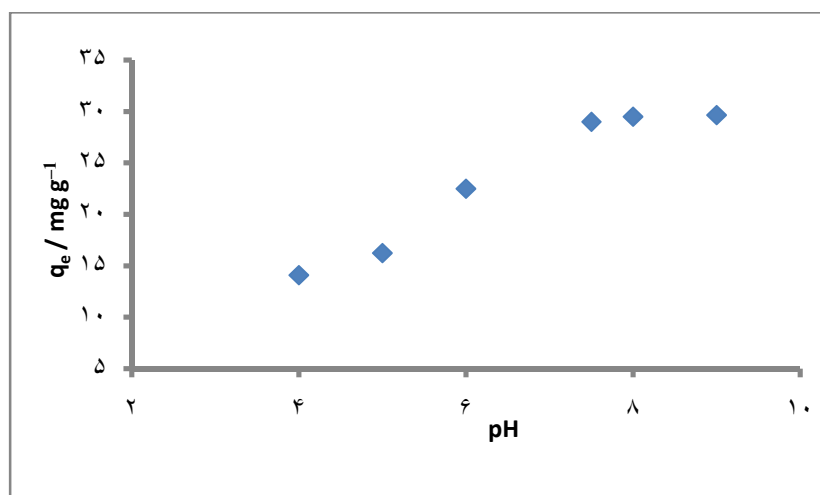
Figure 1. Effect of pH on removal of Zn (II).

pH

In order to study the effect of pH, the solution pH was changed from 4-9 while keeping the other variable constant. Figure 2 describe the effect of pH on removal% of Zn (II) onto SD/MNP/PEI nanocomposite. It was observed that adsorption of Zn (II) ion from the solution was strongly pH dependent. At lower pH of 2-4 range the adsorption was very low and it rapidly increased between pH 5-8. After that with increase of pH, there was no significant increase of removal % of Zn (II) from the solution.

At low pH values, highly protonated amino groups can strongly act with cations via electrostatic forces and high H^+ might compete with Zn (II) for active binding sites [23]. When the pH increased, the protonated degree of the adsorbent and competition of H^+ decreased and amino groups could chelate with Zn (II) easily and strongly, which created increasing adsorption capacity and was in agreement with the zeta potential results [24]. As the pH increases from 4-9, the adsorption surface became less positive and therefore electrostatic attraction between Zn (II) ions and the surface of SD/MNP/PEI was increased resulting greater removal efficiency between pH 6-8. The result depicts that removal% was increased steadily up to pH 7, after pH 8; more or less it was same. Cumulative effect of adsorption and precipitation has enhanced the removal efficiency at higher pH values. Therefore, to ensure true adsorption, all kinetics experiments were carried out at pH 7.

Figure 2. Effect of pH on removal of Zn (II).

Initial Zinc concentration

The adsorption experiments at initial Zinc concentrations from 25 to 125 mg L^{-1} were also performed with 0.2 g SD/MNP/PEI and the results are represented in Figures 3. The results indicate that percentage Zn (II) removal decreases as the initial concentration of Zn (II) was increased. This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. The percentage removal of Zinc was higher at lower initial Zinc concentrations and smaller at higher initial concentrations, which clearly indicate that the adsorption of Zn (II) from its aqueous solution was dependent on its initial concentration.
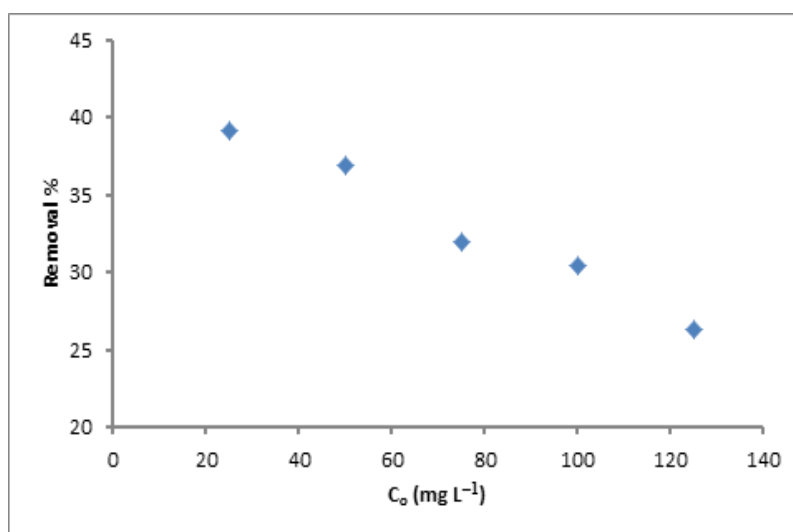
Figure 3. Effect of Initial metal concentration on removal % of Zn (II).

13

Adsorption Isotherm

To obtain the adsorption isotherms and analyze the adsorption model, we conducted the adsorption experiments with various initial Zn (II) concentrations. Adsorption isotherms were obtained by studying the relationship between the equilibrium concentration and the equilibrium capacity. The Langmuir and Freundlich equations were employed to study the adsorption Isotherm of Zn (II) on the SD/MNP/PEI.

Langmuir isotherm assumes monolayer coverage of adsorbate on the outer surface of the adsorbent without interactions. The equation of Langmuir isotherm as follows:

$$\frac{C_e}{q_e} = \frac{1}{(bq_m)} + \frac{C_e}{q_m} \qquad (3)$$

Where q_m is maximum monolayer adsorption capacity (mg g^{-1}) and b is the constant of Langmuir related to the affinity of binding sites, it is a measure of the energy of adsorption.

The degree of appropriate of SD/MNP/PEI drawn toward Zn (II) is predicted from the values of separation factor constant (R_L), which is shown as follows:

$$R_l = \frac{1}{(1+bC_o)} \qquad (4)$$

Where C_o(mg L^{-1}) represented the initial concentration of Zn (II). The Langmuir isotherm constant is represented by b.

The value of R_L revealed that the adsorption of zinc onto the SD/MNP/PEI is favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$), and linear ($R_L = 1$) and unfavorable ($R_L > 1$). The equation of Freundlich isotherm as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (5)$$

In which q_e is the amount of Zn (II) adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of Zn (II) (mg g^{-1}). The n and K_f and are the Freundlich constants related to the intensity parameter and the relative adsorption capacity of the adsorbent.

In this study, the values of R_L were between 0.4 and 0.8 for Zn (II) (Table 1), signifying favorable adsorption of the zinc by SD/MNP/PEI. In the Freundlich isotherms model, values of n in range of 2 to 10, 1 to 2, and 0 represents good, poor, and difficult adsorption characteristics, respectively [25]. As shown in Table 1, the value of n was 1.54 for Zn (II), which means that Zn (II) was adsorbed on the surface of SD/MNP/PEI. This is interpreted as poor adsorption.

The data produced using the Freundlich model and Langmuir model are exhibited in Table 1. Table 1 shows that the R^2 values of the Langmuir model are higher than in Freundlich model, which

suggests that the monolayer adsorption of Zn (II) is on energetically identical sites within the SD/MNP/PEI.

Table 1. Isotherm modeling parameters for the adsorption of Zn (II) and onto SD/MNP/PEI.

Metal ion	Langmuir isotherm				Freundlich isotherm		
	q (mg g^{-1})	b	R_L	R^2	K_f (mg g^{-1})	n	R^2
Zn	35.21	0.0107	0.4 - 0.8	0.99	0.92	1.54	0.98

Comparison of Zn^{2+} removing efficiency

Adsorption capacity is the key-point of each adsorbent material. The adsorption capacity (mg/g) is the amount of the molecule adsorbed per unit mass of the adsorbent at a given gas-phase concentration under equilibrium conditions. The maximum adsorption capacities of different adsorbents for the removal of Zn^{2+} have been compared with the reports in the literature Table 2. The result shows that the nanocomposite was used in this paper, capable competed with another adsorbent.

Table 2. Adsorption capacities of different adsorbents for the removal of Zn^{2+}.

Adsorbent	Adsorption capacity $mg\ g^{-1}$	References
M. spicatum	15.59	[26]
Bagasse fly ash	2.34	[27]
Moss	14.7	[28]
Botrytis cinerea	12.98	[29]
Natural zeolite	2.21	[30]
SD/MNP/PEI	35.21	This paper

Conclusion

The summary of this research is as follows:

a) A new SD/MNP/PEI nanocomposite was prepared by a simple, cost-effective and environmental friendly technique.

b) The adsorption of Zn^{2+}was evaluated using SD/MNP/PEI as an adsorbent and show high efficiency.

c) Langmuir and Freundlich isotherm models were used to validate the adsorption process. The results gained from this study were well described by the theoretical Langmuir. It occurs monolayer.

d) This study has shown that the low coast nanocomposite adsorbent has strong potential in treatment wastewater in the developing world.

e) The most advantage of this absorbent is the ability to do the work in normal conditions such as pH, time and easily separation adsorbent from aqueous media.

This nanocompositealso can be used for other heavy metals. As well as at future works the foundation of PEI can be changed as an effective parameter for adsorbent process.

References

[1]   S.S. Bagali, B.S. Gowrishankar, A.S. Roy, *Engineering*, 3, 409 (2017).

[2]   Z.Z. Chowdhury, S.M. Zain, A. Rashid, K. Khalid, *Orient. J. Chem.*, 27, 405 (2011).

[3]   F.Deniz, A. Karabulut, *Ecological Engineering*, 106, 101 (2017).

[4]   A. Movahedi, A. Lundin, N. Kann, M. Nydén, K. Moth-Poulsen, *Physical Chemistry Chemical Physics*, 17, 18327 (2015).

[5]   S.S. Salih, T.K. Ghosh, *International Journal of Biological Macromolecules*, 106, 602 (2018).

[6]   S. Guo, P. Jiao, Z. Dan, N. Duan, G. Chen, J. Zhang, *Chemical Engineering Journal.*, 317, 999 (2017).

[7]   J. Huang, F. Yuan, G. Zeng, X. Li, Y. Gu, L. Shi, W. Liu, Y. Shi, *Chemosphere*, 173, 199 (2017).

[8]   J.C. Yoo, C. Lee, J.S. Lee, K. Baek, *Journal of Environmental Management*, 186, 314 (2017).

[9]   C.A. Basha, M. Somasundaram, T. Kannadasan, C. W. Lee, *Chemical engineering journal*, 171, 563 (2011).

[10]   O. Tavakoli, V. Goodarzi, M.R. Saeb, N.M. Mahmoodi, R. Borja, *Journal of Hazardous Materials*, 334, 256 (2017).

[11]   M. Ye, G. Li, P. Yan, J. Ren, L. Zheng, D. Han, S. Sun, S. Huang, Y. Zhong, *Chemosphere*, 185, 1189 (2017).

[12]   Y. Li, Z. Xu, S. Liu, J. Zhang, X. Yang, *Computational Materials Science*, 139, 65 (2017).

[13]   I. Villarreal, A.B. Petriciolet, R.M. Valencia, *Journal of Molecular Liquids,* 230, 686 (2017).

[14]   Y. Ma, B. Zhang, H. Ma, M. Yu, L. Li, J. Li, *Science China Materials,* 59, 38 (2016).

[15]   P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, *Science of the Total Environment*, 424, 1 (2012).

[16]   A. Dias, A. Hussain, A. Marcos, A. Roque, *Biotechnology advances*, 29, 142 (2011).

[17]   S. Zhang, H. Niu, Z. Hu, Y. Cai, Y. Shi, *Journal of Chromatography A.*, 1217, 4757 (2010).

[18]   M. Khoobi, T.M. Delshad, M. Vosooghi, M. Alipour, H. Hamadi, E. Alipour, M.P. Hamedani, Z. Safaei, A. Foroumadi, A. Shafiee, *Journal of Magnetism and Magnetic Materials,* 375, 217 (2015).

[19]   D.M. Saad, E.M. Cukrowska, H. Tutu, *Water Science and Technology*, 66, 122 (2012).

[20]   J. Shah, M.R. Jan, S. Jamil, A.U. Haq, *Toxicological & Environmental Chemistry*, 96, 218 (2014).

[21]   J. Ma, C. Wang, Y. Wei, *RSC Advances,* 6, 43648 (2016).

[22]   S. Hassani, A. Ghasemi, M. Fazli, K. Haghbeen, R.L. Legge, *The Canadian Journal of Chemical Engineering*, 93, 2214 (2015).

[23]   M. Amara H. Kerdjoudj, *Talanta*, 60, 991 (2003).

[24]   B. Gao, F. An, K. Liu, *Applied Surface Science*, 253, 1946 (2006).

[25]   Y. Li, K. Sui, R. Liu, X. Zhao, Y. Zhang, H. Liang, Y. Xia, *Energy Procedia.*, 16, 863 (2012).

[26] O. Keskinkan, M. Goksu, A. Yuceer, M. Basibuyuk, *Process Biochemistry*, 39, 2 (2003).

[27] V.K. Gupta, I. Ali, *Separation and Purification Technology*, 18, 131 (2000).

[28] D. Mohan, K.P. Singh, *Water Research*, 36, 2304 (2002).

[29] S. Tunali, T. Akar, *Journal of Hazardous Material*, 131, 137 (2006).

[30] T. Motsi, N.A. Rowson, M.J.H. Simmons, *International of Mineral Processing*, 92, 42 (2009).