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Chelating exchanger for Removal of Calcium(II) and Magnesium (II) ions

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Abstract

The NR/PEO block copolymeric hydrogel can act as chelating exchangers due to the presence of electron donor oxygen atoms of PEO. So they can form metal complexes and can remove metals from aqueous medium. The effect of initial metal ion concentration on the metal ion adsorption capacity was investigated for Ca^{2+} and Mg^{2+} metal ions from aqueous solution. The linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Here from the linear regression coefficient it is found that Freundlich equation was best fit for both the metal ions and the 1/n value is approximately equal to 1 indicating linear adsorption leading to identical adsorption energies for all sites. The adsorption capacity of NR/PEO block copolymer increases with metal ion concentration and this trend is shown by calcium and magnesium. At 0.02M concentration magnesium shows highest adsorption capacity.

Keywords: Hydrogels, chelating exchanger, adsorption, metal ion removal.

Introduction

A wide variety of physical and chemical processes are available for the removal of metal ions from aqueous medium. But most of them are sludge producing or not cost effective. This has led to the use of better materials which are low cost and value added products from easily available sources[1]. Recently swellable polymeric materials have received increased interest due to their ability to complex with metal ions. These materials find applications in various branches of chemistry, chemical technology and biology[2].

Among polymeric sorbents hydrogels incorporated with different chelating groups are found to be promising materials. Hydrogels with polymeric materials are three dimensional network structure capable of absorbing and retaining water due to the large number of hydrophilic groups in the macromolecular structure. They swell and shrink by absorbing and desorbing water[3,4]. Recent examples are the crosslinked polymeric materials containing functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, and sulphonic acid groups[5-10].

A polymer-metal complex is a coordination complex formed between a ligand function anchored on a polymer matrix and a metal ion. The metal ion is attached to the polymeric ligand by a coordinate bond. Polymeric ligand contains coordinating groups or atoms mainly N, O and S. Polymer-metal complex possesses a specific structure since the metal ion is surrounded by a structured polymer chain. These complexes show distinctive properties which are different from their low- molecular weight analogues.

The major advantages of polymeric sorbents are easy loading and reusability.The binding of metal ions by a polymeric sorbent depends on its macromolecular structure, crosslinking density, hydrophilic/hydrophobic balance, functional group attached and the resulting polymer- metal complex stability constants.

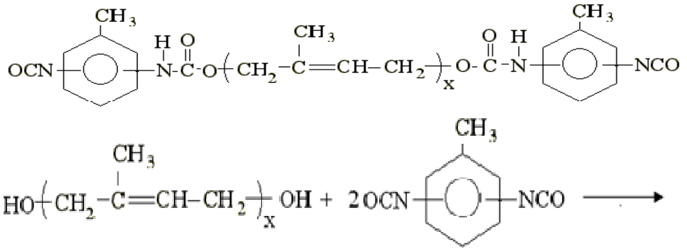
In the present study, an attempt is made to use NR/PEO block copolymer hydrogels as chelating agents for the sorption of Ca^{2+} and Mg^{2+}ions from aqueous medium under noncompetitive conditions.

Material and Methods

Reagents and instruments: Natural crumb rubber (NR) was purchased from Rubber Research Institute of India, Kottayam. Polyethylene oxide (PEO), calcium chloride ($CaCl_2$) and magnesium sulphate ($MgSO_4$) were obtained from Merck. Hydroxyl terminated natural rubber (HTNR) was prepared by the photochemical depolymerisation of natural rubber[14].

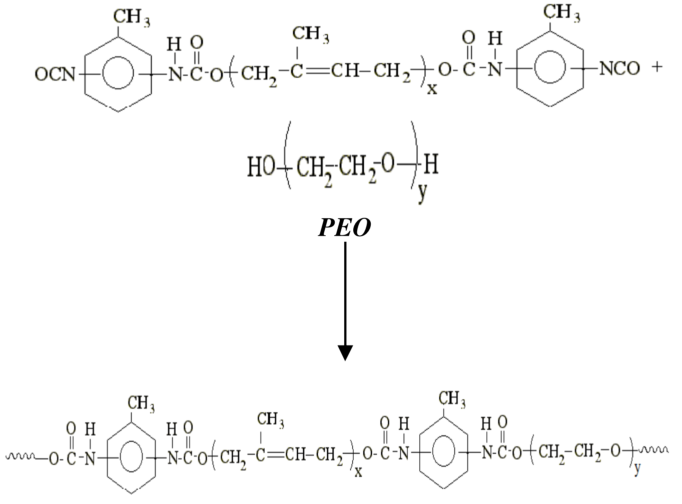
Preparation of NR/PEO block copolymers: Block copolymerisation was carried out using the two-shot method as per standard procedure[14]. Based on this procedure HTNR was first end capped with isocyanate group by reacting with toluene diisocyanate. This was followed by chain extension with PEO.

i. *End capping of HTNR*



End capped HTNR
Schime-1

ii) Chain extension process



NR/ PEO Block copolymer
Schime-2

Determination of Metal Ion Removal Capacity: Non-competitive adsorption of calcium(II) and magnesium (II) ions were carried out at room temperature. The quantitative analysis of metal ion concentration in the aqueous solution was determined by atomic absorption spectroscopy. The removal capacity, qe (mg/g), was calculated from the following equation: $q_e = (C_0\text{-}C_e)V/W$

Where: C_0 and C_e (mg/l) are the initial and equilibrium metal ion concentrations in the adsorption medium, respectively, and V (l) and W (g) are the volume of the metal ion solution used in the adsorption experiment and the weight of the hydrogel, respectively.

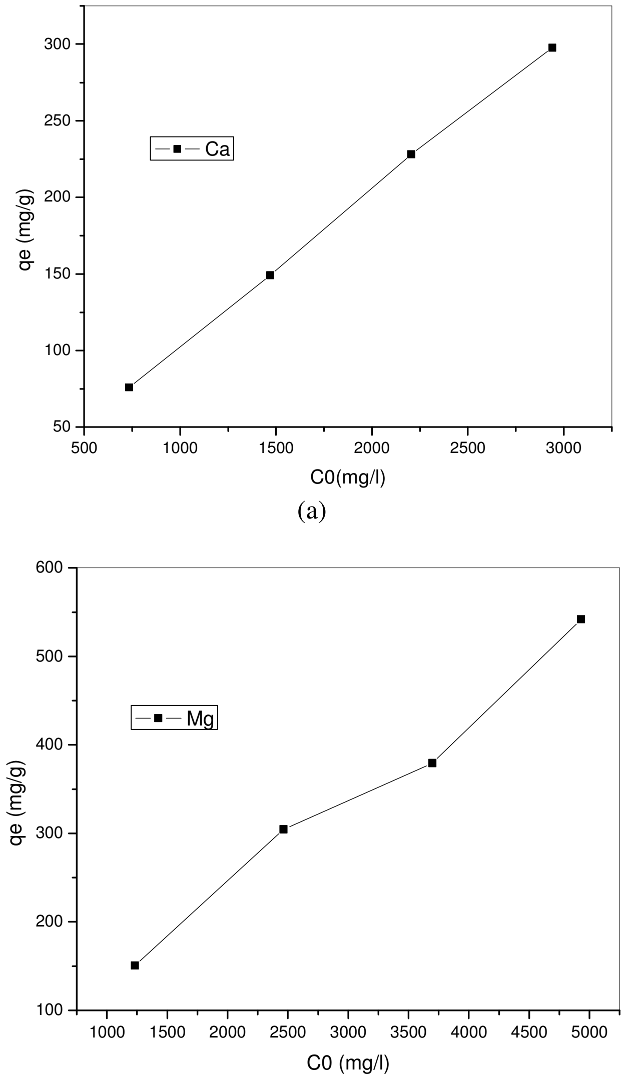
Estimation of the distribution of metal ions: The dispensation ratio of the metal ions i.e., Ca^{2+}, and Mg^{2+} between the polymer phase and the aqueous phase was evaluated at 25^0 C. The experiments were carried out as described above at different concentrations. The distribution ratio, K_d, is defined by the following relationship.

$K_d = ((C_0\text{-}C_e)/(C_e \text{ x } W)) \text{ x } V$

Results and Discussion

Metal ion Adsorption Studies: PEO/NR block copolymers form excellent hydrogels due to the presence of hydrophilic PEO segments and the hydrophobic NR segments. In open chain polyethers such as PEO, many chealating atoms (oxygen atoms) are present. This chealating groups can bind with metal cations by electrostatic interaction. In water, the PEO chains form loose coils which are attached to the hydrophobic NR part. As a result they can form cavities of definite size depending upon the molecular weight of PEO. Due to this coiled structure chealating oxygen atoms are favourably arranged to bind the metal cations and the etheric oxygen atoms can wrap around the metal cations to form single or double helical structures with the metal ions in the centre of a channel- like feature.

Effect of initial concentration: The adsorption experiments were carried out using metal ion concentration ranging from 0.005- 0.02 M. Adsorption isotherms (Figure-1a and 1b) show that the sorption capacity of metal ions increased with concentration. An increase in metal ion concentration accelerates the diffusion of metal ions from solution to the adsorbent surface due to the increase in driving force of concentration gradient. Hence, the amount of adsorbed metal ion increased as the concentration increased from 0.005-0.02M.As the initial metal ion concentration increases more and more metal ions are available for the polymer binding site and adsorption capacity increases.

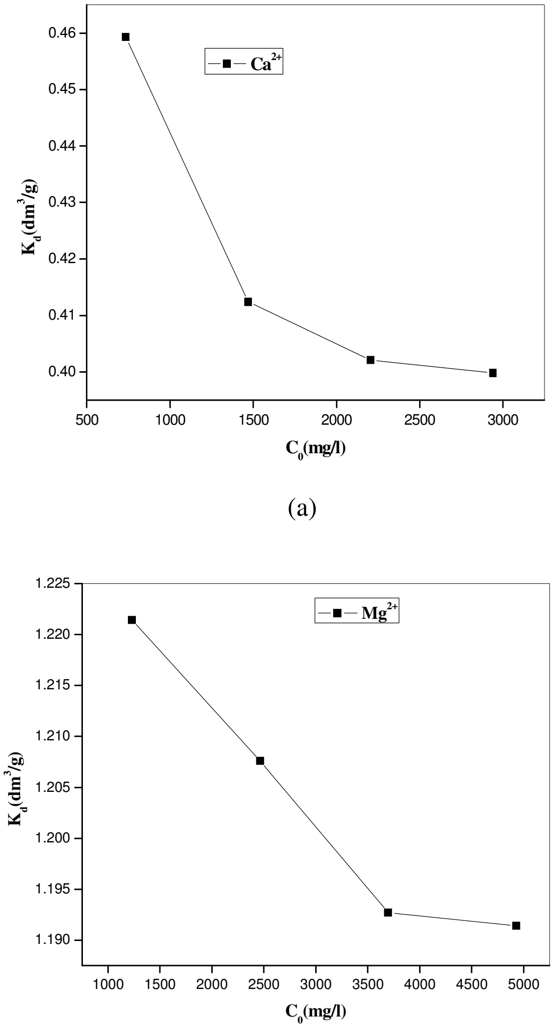


(a)

(b)

Figure-1
Adsorption isotherms of NR/PEO block copolymer for (a) Ca(II) and (b) Mg(II) ion

Distribution ratios of metal ions at different concentrations: Effect of initial metal ion concentration on the amount of metal ions distributed between the two phases can be explained by the data given in Figure-2a and 2b. The data on the distribution ratio as a function of initial concentration indicate that the relative amount of metal ion uptake by the copolymer decreases with increasing concentration metal ions. From the result it reveals that the ion uptake capacity is increased with a decrease in atomic number. The steric influence of the etheric oxygen atoms in the copolymer is probably responsible for their observed low binding capacities for heavier metal ions. The higher value of distribution ratio for Mg (II) may be due to the formation of more stable complex with chelating ligands. Therefore the polymer under study has more selectivity of Mg^{2+} than Ca^{2+} ions which form rather weak complex.



(b)

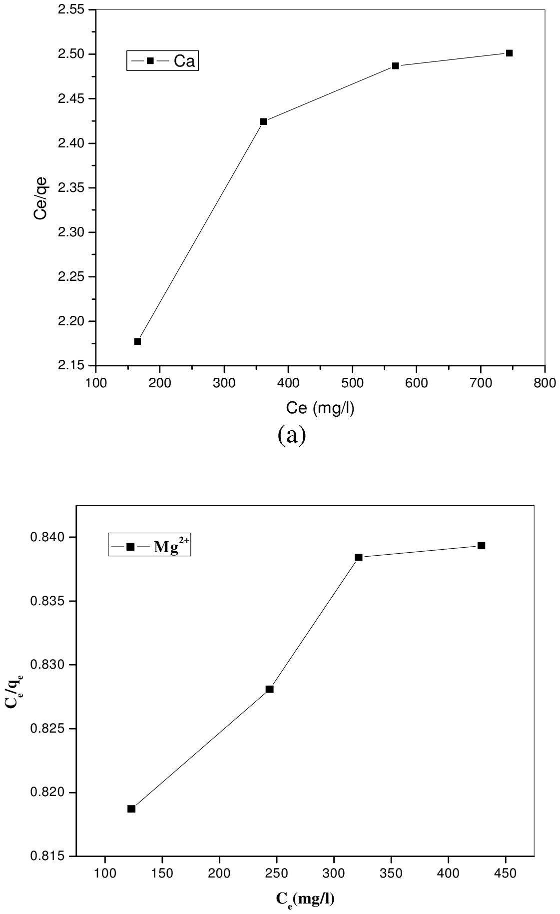
Figure-2

Comparison of distribution ratio of NR/PEO block copolymer for (a) Ca(II) and (b) Mg(II) ion

Adsorption isotherms: In order to have a quantitative explanation of metal adsorption capacity and to find adsorption mechanism effectively, it is useful to utilize mathematical models estimating the metal adsorption. The Freundlich and Langmuir adsorption isotherm models were applied in the present study.

The Langmuir isotherm (Figure-3a and 3b) represents the equilibrium distribution of metal ions between the solid and liquid phases. This model explains the monolayer coverage of metal ions on a homogenous surface without any interaction between adsorbed ions. To get the equilibrium data, initial metal concentrations were varied while the adsorbent mass in each sample is kept unaltered. The linearized Langmuir isotherm is
$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$

where Q_0 and b are the Langmuir constants indicating the capacity and energy of adsorption, respectively. These constants were calculated from the intercept and the slope of the linear plot of C_e/q_e vs. C_e based on experimental data.



(b)

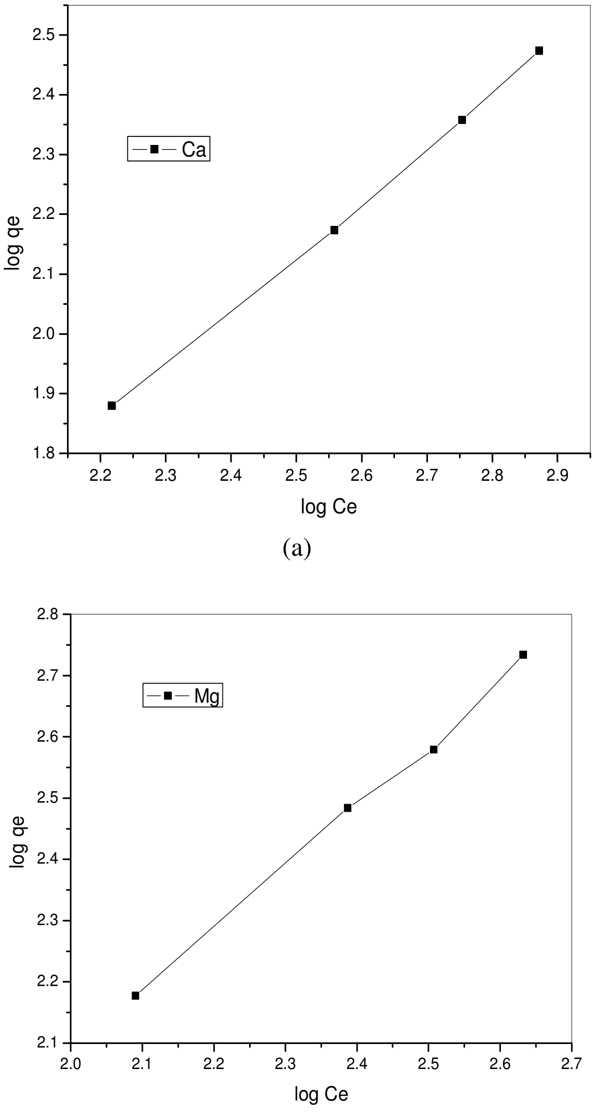
Figure-3

Langmuir isotherm of NR/PEO block copolymer for (a) Ca(II) and (b) Mg(II) ion.

The Freundlich sorption isotherm (Figure-4a and 4b) is widely used for the mathematical description of adsorption, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression incorporating the surface heterogeneity and the exponential dispensation of active sites and their energies. The linearized form of the Freundlich isotherm is

$$\log q_e = \log K + (1/n) \log C_e$$

where K is a Freundlich constant related to the adsorption capacity, and 1/n is related to the adsorption intensity of an adsorbent. The values of K and 1/n were calculated from the intercept and slope, respectively, of the linear plot of log q_e vs log C_e based on experimental data.



(a)

(b)

Figure-4

Freundlich isotherm of NR/PEO block copolymer for (a) Ca(II) and (b) Mg(II) ion

Freundlich isotherm explains monomolecular layer coverage of adsorbent by the solutes. Adsorption is said to be favorable when the Freundlich constant 1/n is between 0.1 and 1 and represented a heterogenous surface structure of the adsorbent. Meanwhile, smaller value of 1/n indicates stronger interaction between the adsorbent and the metal ions, while 1/n equal to 1 implies linear adsorption leading to identical adsorption energies for all sites.

Table-1

Constants of isotherm models for Ca(II) and Mg(II)

Metal ions	Freundlich constants			Langmuir constants		
	K	1/n	R^2	Q_0	b	R^2
Ca^{2+}	1.3575	0.9052	0.9995	1864.121	0.0002	0.8941
Mg^{2+}	1.1628	1.0098	0.9984	13896.28	0.00008	0.8614

Here from the correlation values it is found that Freundlich equation was best fit for all the metal ions and the 1/n value is approximately equal to 1 indicating linear adsorption leading to identical adsorption energies for all sites. From the Langmuir constants it is clear that the energy needed for chelating Mg (II) ion is much lesser than that of Ca (II) ion, so they can easily form complexes with the polymer and adsorption capacity increases.

Conclusion

The NR/PEO block copolymer hydrogel was prepared from PEO having molecular weight 6000.These hydrogels were used for adsorption of Ca(II) and Mg(II) ions under noncompetitive condition. It was found that adsorption capacity increased with initial metal ion concentration. The Freundlich model was used to fit the experimental equilibrium data for both the metal ions. The polymer also showed preference towards Mg(II) ion.

References

1. Ekebafe L.O., Ogbeifun D.E. and Okieimen F.E., *African Journal of Environmental Science and Technology*, **6(7),** 275 **(2012)**
2. Kasgoz H., Kasgoz A., Sahin U., Temelli T.Y. and Bayat C., *Polymer-Plastics Technology and Engineering*, **45**, 117 **(2006)**
3. Ei-Hag Ali, A; Shawky, H. A; Abd El Rehim, H.A; Hegazy, *E.A. European Polymer Journal,* **39,** 2337 **(2003)**
4. Uzum O.B. and Karadag E., *Advances in Polymer Technology*, **00,** 1 **(2011)**
5. Kradag E., Saradin D. and Guven O., *Sep. Sci.Technol.*, **30,** 3747 **(1995)**
6. Fromm K.M., *Coordination Chemistry Reviews*, **252,** 856 **(2008)**
7. Karyn B., Visscher and Harry R., Allock, *Chem. Matter*, **6**, 2040 **(1994)**

8. Kasgoz H., Kasgoz A., Sahin U., Temelli T.Y. and Bayat C., *Polymer-Plastics Technology and Engineering*, **45**, 117 **(2006)**

9. Ei-Hag Ali A., Shawky H.A., Abd El Rehim H.A. and Hegazy E.A.*, European Polymer Journal,* **39,** 2337 **(2003)**

10. Nobuhiro Nishiyama,Yukio Kato,Yuichi Sugiyama, Kazunori Kataoka, *Pharmaceutical Research,***18,** 7 (**2001**)

11. Mathew B. and Pilla V.N.R., *Polymer,* **34,** 2650–2658 (**1993**)

12. Lindsay D., Sherrington D.C., Greig J.A. and Hanckok R.D., *React. Polym.,* **12,** 59 **(1990)**

13. Green R.B. and Hanckok R.D., *Hydrometallurgy*, **6,** 351 **(1981)**

14. Ravindran T., Gopinathan Nair M.R. and Joseph Francis D., *Journal of Applied Polymer Science,* **35,** 1227 **(1988)**