RASĀYAN J. Chem.
Vol. 7 | No.3 |214 – 218 | July – September | 2014
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

EQUILIBRIUM UPTAKE AND SORPTION DYNAMICS FOR THE RETRIEVAL OF DIVALENT MANGANESE FROM AQUEOUS SOLUTION USING *MORINGA OLEIFERA* BARK

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ABSTRACT
The objective of this study was to investigate the possibility of using *Moringa oleifera* Bark as an alternative adsorbent for the removal of Mn (II) ions from aqueous solutions. The effect of various parameters influencing the Mn (II) adsorptions such as pH, Contact time, dose of Adsorbent and initial metal ions concentrations have been studied. The data obtained from the batch processes have been used to fit in Freundlich and Langmuir isotherm equations. This method is quite feasible, economic and time saving. The optimum contact time found is equal to 360 min. The optimum dosage is equal to 0.9 gram. The percentage of removal is ranging between 80% - 85%. The equilibrium data fitted very well to Langmuir and Freundlich models.
Keywords: Adsorption, *Moringa oleifera* Bark, Manganese (II), Isotherms, Adsorption kinetics.

INTRODUCTION

Heavy metals are known for their toxicity, tendency to bio-environmental threat and further more they are not susceptible to bacterial or degradation processes which result in increase in concentrations and possibly exceed waterways and sediments upon continuous exposure to substances containing heavy metals. This is a dangerous issue for humans, who are at the top of the food chain, as these metals are accumulated through the food chain. Metals of major concerns are Cadmium, Nickel, Copper, Mercury, Lead, Chromium, Manganese, Zinc and Aluminium[1]. The removal of metal ions like Mn (II) ion from aqueous solution is serious problem in many countries[2].Manganese is one of the most difficult elements to remove from surface waters. Manganese (Mn) is an essential element present in all living organisms and is naturally present in rocks, soil, water, and food. Manganese is the second most abundant metal in nature. Exposure to high oral or ambient air concentrations of Mn can result in elevations in Mn tissue levels and neurological effects[3].Heavy metals in the environment are of great concern due to their recalcitrance and consequent persistence. Manganese has variety of applications in ceramics, dry battery cells, electrical coils and many alloys. In addition to the disposal of untreated discharge from the above applications into water, another major source of pollution of Mn is burning of coal and oil. Exposure to manganese causes neurotoxicity, low hemoglobin levels and gastrointestinal accumulation. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is imperative to search for multifarious methods to reduce water pollution. Many methods available for the removal of trace metals from water namely chemical precipitation, ion exchange, electrochemical treatment, coagulation, solvent extraction and membrane process. But these techniques have limitations and often are neither effective nor economical especially for the removal of heavy metals at low concentrations. Adsorption offers the advantages of low operating cost, minimization of volume of chemical and biological sludge to be disposed, high efficiency in detoxifying effluents and no nutrient requirement[4].Adsorption is a fast and reversible uptake of the heavy metals with micro organisms or biomass. Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments[5]. Numerous biological low-cost adsorbents have been tested for the removal of toxic metal ions from aqueous solutions over the last two decades. The objective of this work is to study the utilization of *Moringa Oleifera* Bark as adsorbent to remove Mn (II) ion from an aqueous solution.

EXPERIMENTAL

Preparation of Adsorbent

Moringa Oleifera Bark (MOB) was collected from a local farm. It was cut in to small segment and dried in sunlight until almost all the moisture evaporated. Then it was ground to get desired particle size of 100 to 200 micron. It was then soaked 2 hours in 0.1M NaOH solution to remove the lignin contents. Excess alkalinity was then removed by neutralizing with 0.1 N HCl. The MOB was then washed several times with distilled water till the washings are free from color and turbidity. The washed MOB was kept in oven and dried at 200^0 C for 24 hrs and stored in desiccators for the further study.

Preparation of Solutions

All the reagents used were of AR grade. Stock Manganese ions solution (1000 mg/L) was prepared by dissolving 19.791 gm of A.R. grade $MnCl_2$in 1000 ml distilled water. The solutions of lower concentrations were prepared by dilution of appropriate volume of stock solution.

Adsorption Isotherms

Equilibrium adsorption isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir and Freundlich isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the Correlation coefficients.

Freundlich Adsorption Isotherm

The Freundlich isotherm is an empirical equation used to describe heterogeneous system. The sorption data of Manganese (II) ions onto MOB was also fitted to Freundlich isotherm, in the following linear form-

$$Log\ qe = log\ K_f + 1/n\ log\ Ce \qquad (1)$$

Where, *qe* is the amount of metal ions adsorbed per gram of adsorbent (mg/g). Ce is the equilibrium concentration of metal ions in solution (mg/L). K_f and *1/n* are Freundlich Constants, indicating the Adsorption Capacity and Adsorption Intensity respectively.

Straight lines were obtained by plotting *log qe* against *log Ce*, which show that sorption of Manganese ions obeys Freundlich isotherm well. The $K_f$and *1/n* values were calculated from intercept and slop of the plot respectively and presented in Table 1. The Correlation coefficient R^2>0.996 and the values of n were higher than 1.0, indicating that adsorption of Mn (II) ions on MOB follows the Freundlich isotherm. The value of ‘r’ indicated the type of the isomer to be either unfavorable (r >1), linear (r =1) favorable (0< r <1). The value of ‘r’ was obtained as 0.048. This confirmed that the bark used is favorable for adsorption of Mn (II) ion under the condition used in this work.

Langmuir Adsorption isotherm

The Langmuir isotherm is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Linear form of Langmuir equation is-

$$1 / qe = 1/ b\ Q_0 X\ 1/Ce + 1/Q_0 \qquad (2)$$

Q_0 and *b is* Langmuir constants related to the capacity and energy of sorption respectively. A plot of *qe* versus *C*e should indicate a straight line of slope 1/ b $Q_0$and an intercept of 1/ Q_0. The values of *Qo* and b and Correlation coefficient obtained from the Langmuir model are shown in Table-1. The Correlation coefficient R^2>0.997suggests that adsorption of Mn (II) ions onto MOB follows the Langmuir isotherm. The maximum monolayer capacity Q_0 obtained from the Langmuir is 9.009mg/g. In order to observed whether the adsorption is favorable or not, a dimensionless parameter 'r' obtained from Langmuir isotherm is $r = (1+ b \times Cm)^{-1}$

Table-1: Isothermal Constants

Freundlich Constants			Langmuir Constants			
K_f	1/n	R^2	Q_0	b	r	R^2
8.318	0.625	0.996	9.009	0.100	0.048	0.997

Where 'b' is Langmuir constant and Cm is maximum concentration used in the Langmuir isotherm.

First order kinetics

The rate of adsorption of Mn (II) on *Moringa olifera* Bark was studied by using the first order rate equation proposed by Lagergren.

Pseudo Second Order Model

The time data of metal ion fitted to Pseudo second order kinetics. Pseudo second order model showed that, Rate constant K_2 is almost constant at different initial concentration which is shown in Table 2.This indicate that adsorption of Mn (II),on *Moringa olifera* Bark obey Second Order Kinetics.

Elovich Model

Adsorption of Mn (II), on *Moringa olifera* Bark is shown. A linear relationship is obtained between the amounts of Mn (II) concentration. As the Table-2, Shows that the value varied as a function of Mn (II) concentration. As the concentration of Mn (II) increases from 20 mg/L. Value of α increases and β decreases. This favored the adsorption phenomenon.

Table-2: Kinetics model value for adsorption of Mn (II) on *Moringa olifera* Bark

Concentration	1^{St} Order			Pseudo Second Order			Elovich Model		
	K_L	q_e	r^2	q_e	k_2	r^2	α	β	r^2
220 mg/L	0.2049	3.5	0.997	3.5	0.340	0.990	1.291	0.900	0.996

Effect of pH

The solution of pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions. The effect of pH on the removal of Manganese ion using MOB as an adsorbent was studied with initial pH range from 2 to 8. The pH affects the solubility of Manganese ion to a great extent. The pH of the aqueous solution is the controlling factor in the adsorption process hence it become necessary to determine at what pH, maximum adsorption will takes place. The maximum removal efficiency was 85% at 8.0 pH value (Figure-1).

Effect of contact time

The effect of Contact time on the amount of Mn (II) ions adsorbed was investigated by using various initial concentrations of Mn (II) ions with 0.5 gram MOB at pH 8.0. The effect of Contact time and metal ions concentrations on the percent removal of Mn (II) by MOB is shown in Fig.-II. The result indicates that removal of Mn (II) ions increases with increase in Contact time and equilibrium was attained in about

360 min. The extent of removal of Mn (II) by MOB was found to increase, reach a maximum value with increase in contact time (Figure-2).

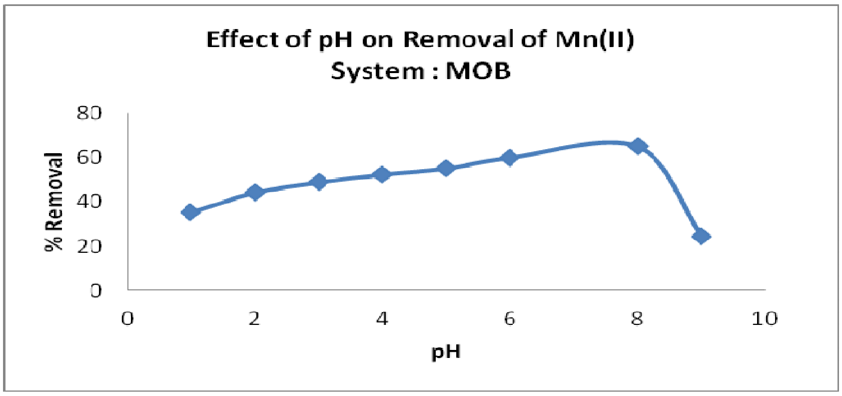

Fig.-1: Effect of pH

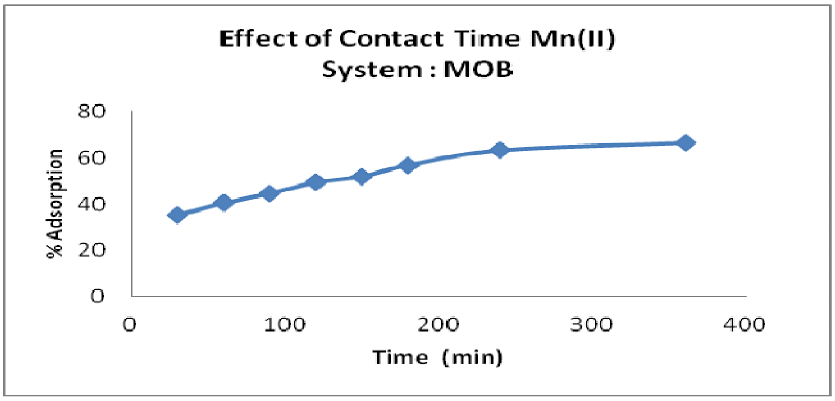

Fig.-2: Effect of Contact Time

Effect of Adsorbent Dose

The effect of the amount of adsorbent dose on the rate of uptake of Manganese ions is shown in Fig.-III. It can be seen that, the rate of the removal of Manganese ions increases with an increases in the amount of adsorbent dose. This may be due to the increase in availability of surface active sites resulting from the increased dose of adsorbent, especially at higher doses. The amount of adsorbent dose varies from 200mg/200ml to 1000mg/200ml. The retrieval efficiency is maximum at dose of 900 mg/200ml which observed Mn (II) ion up to 85% (Figure-3).

CONCLUSIONS

1. The present work is attempt for the systematic studies of removal of Manganese (II) from aqueous solution using low cost adsorbent prepared from*Moringa Oleifera*Bark.
2. From the Experimental Findings, It has been observed that the adsorbent material can be used successfully for removal of Manganese (II) from aqueous solution.
3. The maximum removal efficiency was observed up to 85% for Biosorbent prepared from *Moringa oleifera* Bark at the optimum values of parameters.
4. Due to high efficiency for removal of Mn(II) ion, the treated *Moringa oleifera* Bark is an ideal adsorbent for removal of Mn(II) ion from aqueous solutions.
5. The result reveals that at pH =8.0, percentage removal of Manganese (II) ion is maximum.

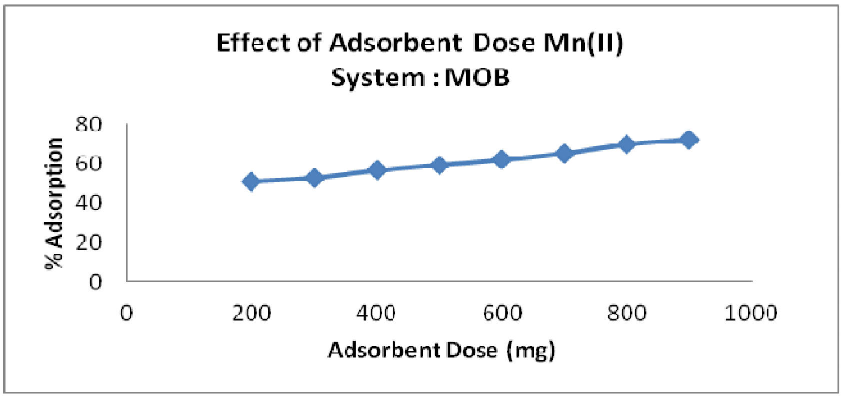

Fig.-3: Effect of Adsorbent dose

ACKOWLEDGEMENT

The authors are thankful to Dr. D. V. Atkare Principal Mahatma Fule Mahavidhyalaya.Warud for providing the necessary facilities for these investigations.

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[RJC-1133/2014]