SCAVENGING OF MANGANESE (II) ION FROM AQUEOUS SOLUTIONS BY ADSORPTION ON GRANULATED SEED CHARCOAL OF PHASEOLUS LUNATUS FRUIT SHELL

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ABSTRACT

*The objective of this study was to investigate the possibility of using Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell (**GSCPLFS**) 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 effect of pH, Contact time, Adsorbent concentrations and initial metal ion concentrations have been studied. The data obtained from the batch processes have used to fit in Freundlich and Langmuir isotherm equations. Adsorption isotherm (Langmuir and Freundlich) and kinetics model were studied. This method is quite feasible, economic and time saving. The optimum contact time found is equal 360 min. The optimum dosage is equal to 0.9 gram. The percentage of removal is ranging between 80% - 85%.*

Keywords: Adsorption, GSCPLFS, Manganese (II), Batch adsorption process, Adsorption kinetics.

Introduction:

Heavy metals are known for their toxicity, tendency to bio-environmental threat and, furthermore 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. 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 is the second most abundant metal in nature. Mn(II) are essential micronutrients for organisms and plants. However, they become toxic at higher levels. 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. Among the 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. Numerous biological low-cost adsorbents have been tested for the removal of toxic metal ions from aqueous solutions over the last two decades. Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments[5].

MATERIALS AND METHODS:

Preparation of Adsorbent

The adsorbent *Phaseolus lunatus* fruit and seed were collected from pandhari forest situated in between warud and pandhurna. The fruit shell of Phaseolus *lunatus* was first dried at temperature 130^0 C for 6 hours. Then fresh Seed was separated and prepare it for charcoal granules. After that, it was sieved through a fine mesh of 200 micron and washed with distilled water for several time until the leachate was free from any suspended impurities. It was then soaked over a night in 0.1 N NaOH solutions to remove the lignin content, the excess alkalinity was then neutralized with 0.1 N HCl solutions. It was washed with distilled water several times till the washed water become colorless. Then it was kept in muffle furnace at 130^0 C for 6 hours. The adsorbent stored in desiccators for final studies.

Preparation of solutions

All the reagents used were of AR grade.

Mn(II) solution

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 sorption data of Manganese ions onto **GSCPLFS** was also fitted to Freundlich isotherm, in the following linear form

$$\log qe = \log Kf + B \log Ce \qquad (1)$$

Where, *qe* is the amount of metal ion adsorbed per gram of adsorbent (mg/g). Ce is the equilibrium concentration of metal ion in solution (mg/L). *Kf* and *B* 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 *Kf* and *B* values were calculated from intercept and slop of the plot respectively and presented in Table 1. The Correlation coefficient R^2> 0.921and the values of B were higher than 1.0, indicating that adsorption of Mn(II) ions on **GSCPLFS** follows the Freundlich isotherm.

Langmuir Adsorption isotherm

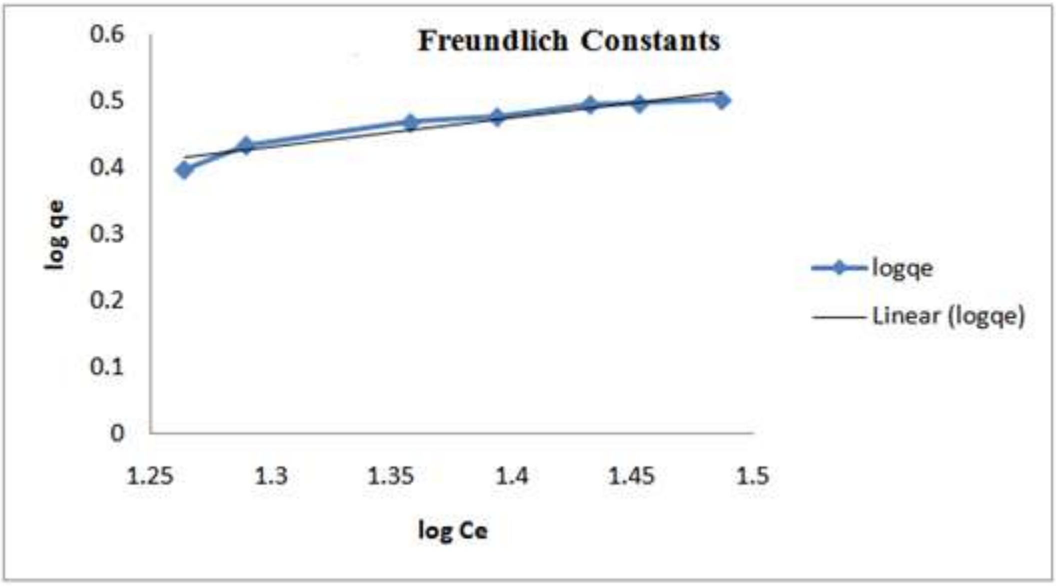
The Langmuir isotherm is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface.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

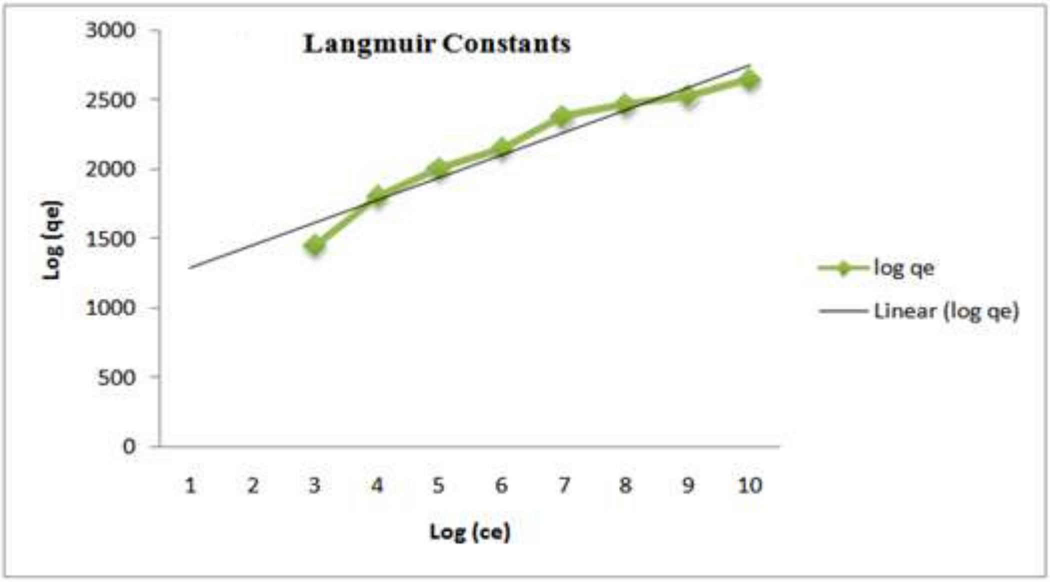
$$1 / qe = 1/ b\, Q_0 \text{ X } 1/Ce + 1/Q_0$$

Q^0 Mg/l and bl/mg *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 Q^0 Mg/l and bl/mg and Correlation coefficient obtained from the Langmuir model are shown in Table 1. The Correlation coefficient $r^2 > 0.935$suggests that adsorption of Mn(II) ions onto **GSCPLFS** follows the Langmuir isotherm. The maximum monolayer capacity Q^0 Mg/l obtained from the Langmuir is 3.374mg/l.

TABLE 1- ISOTHERM CONSTANTS

Mn(II) Concentration	**Freundlich Constants**			**Langmuir Constants**			
Conc.	K_f	B	R^2	Q^0 Mg/l	bl/mg	R	r^2
20mg/L	0.441	7.160	0.921	3.374	0.049	0.34	0.935





First Order Kinetics

The rate of adsorption of Mn(II) on *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (**GSCPLFS**) was studied by using the first order rate equation proposed by Lagergren. It is found that as initial Mn(II) concentration increases, Lagergren rate constant decrease. This indicates that, adsorption does not follow the 1st order kinetics.

Pseudo Second order models :

Pseudo second order model showed that, Rate constant K_2 is almost constant at different initial concentration which is shown in Table 1. This indicates that adsorption of Mn(II). On *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (**GSCPLFS**) obey the 2^{nd} order kinetics. Also the concentration of Mn(II) increasing from 20mg/L to 60 mg/L, equilibrium sorption capacity qe increase.

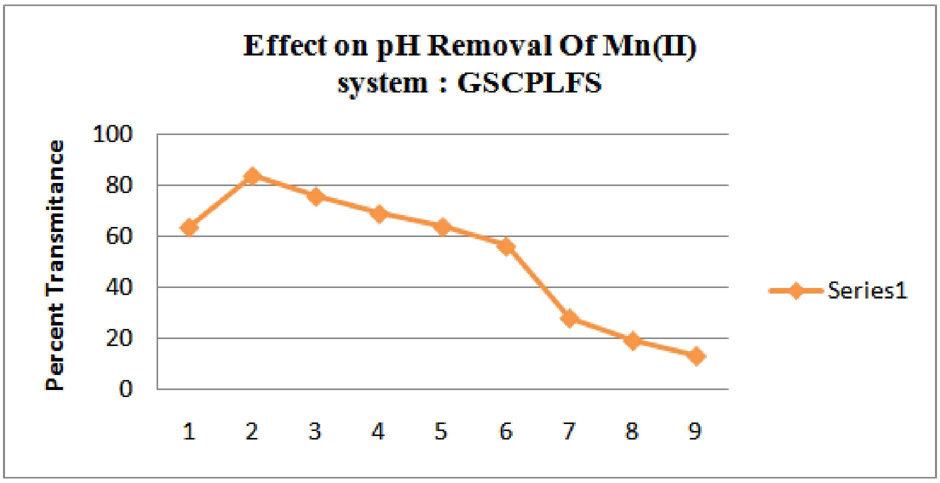
Elovich Model: - Adsorption of Mn(II) on *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (**GSCPLFS**) are shown that value α and β varied as a function of Mn(II) concentration. As the concentration of Mn(II) increases from 20mg/L. to 60mg/L. value of α increase and β decreases. This favored the adsorption phenomenon.

Kinetic model value for adsorption of Mn(II) on *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (GSCPLFS)

Concentration	1st order			Pseudo second order			Elovich		
	K_L	qe	r^2	qe	k_2	r^2	**α**	**β**	r^2
20mg/L	0.0526	10.12	0.992	8.645	0.0018	0.998	0.5642	0.248	0.974
40mg/L	0.0479	14.32	0.945	12.867	0.0016	0.9965	1.207	0.161	0.932
60mg/L	0.0312	19.26	0.943	19.432	0.0017	0.9457	3.874	0.0321	0.984

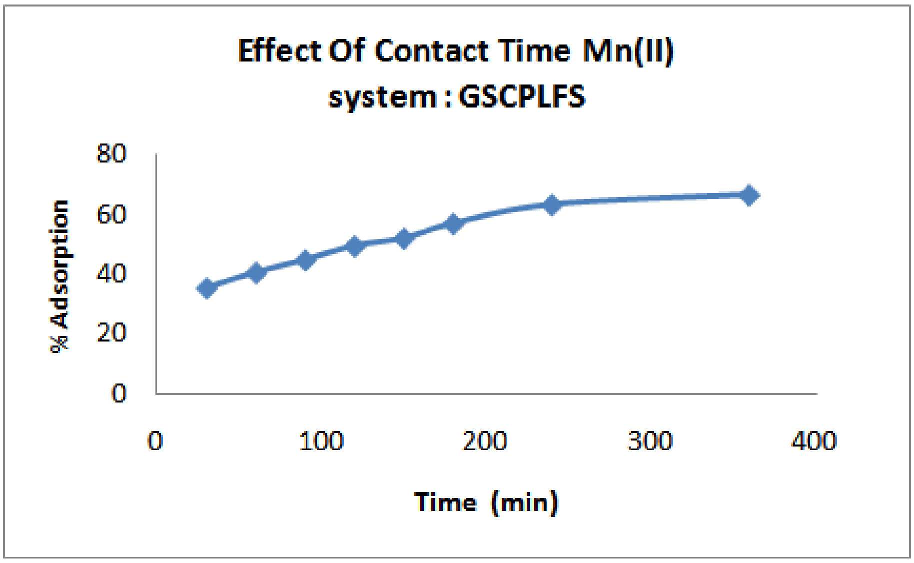
Effect of pH

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. In order to study the effect of pH on the removal of Mn(II) was selected for this purpose. 7 set of 200 ml round bottom flask were collected in which 0.5 gm of Granulated seed charcoal of *Phaseolus lunatus*, was taken and pH of the solution was varied from 1 to 8. Granulated seed charcoal of *Phaseolus lunatus* was shaken in a shaking bottle by taking 200 ml 0.1 M Mn(II) for 3-4 hours. Its initial and final concentration was measured spectrophotometricaly against 540 nm



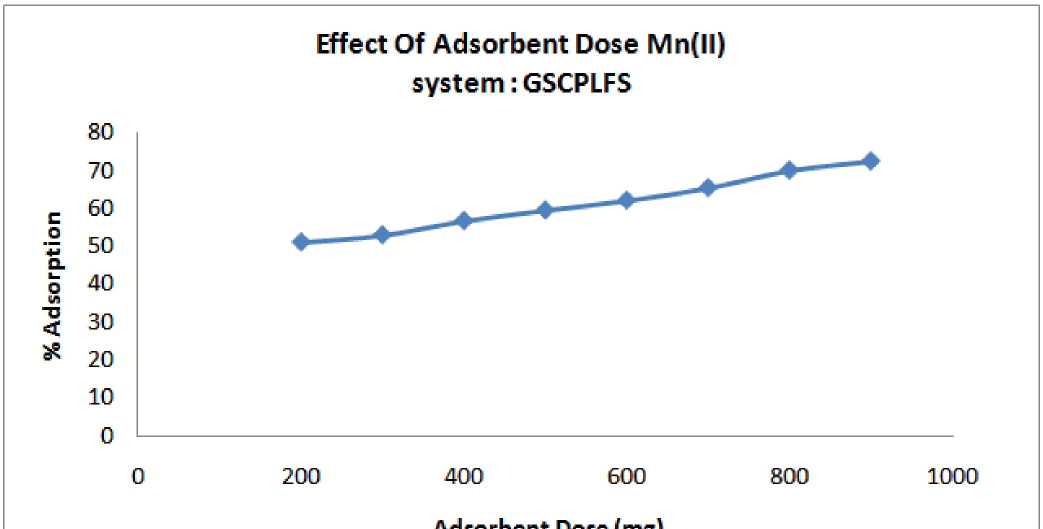
Effect of contact time

The effect of Contact time on the amount of Mn(II) ions adsorbed was investigated by using various initial concentration of Mn(II) ions with 0.5 gram **GSCPLFS** at pH 8.0. The effect of Contact time and metal ions concentrations on the percent removal of Mn(II) by **GSCPLFS** 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 **GSCPLFS** was found to increase, reach a maximum value with increase in 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 is up to 85%.



Conclusion

1) The present work is attempt for the systematic studies of removal of Manganese from waste-water using low cost adsorbent *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (GSCPLFS).
2) The present work on adsorption process is in good agreement with Langmuir & Freundlich isotherm indicating monolayer adsorption process.
3) The adsorption of Mn(II) followed the Pseudo second order model and Elovich model.
4) From the Experimental Findings, It has been observed that the adsorbent material can be used successfully for removal of Manganese from aqueous solution.
5) The maximum removal efficiency was observed up to 85% for Biosorbent prepared from *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (GSCPLFS) at the optimum values of parameters.
6) Due to high efficiency for removal of Mn(II), the treated *Granulated Seed Charcoal of Phaseolus lunatus Fruit Shell* (GSCPLFS) is an ideal adsorbent for removal of Mn(II) from aqueous solutions.
7) The result reveals that at pH 2.0, percentage removal of Manganese is maximum

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