IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 9, Issue 11 Ver. II (November. 2016), PP 48-51
www.iosrjournals.org

Kinetic Study of sorption of Manganese on chitosan

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Abstract: *Manganese is one of the major heavy metal pollutant found in water and wastewater. It is commonly used in non-ferrous alloys, steel making and chemical industries. It causes retardation in growth, eye blindness, fever, muscular fatigue etc. Chitosan was used as a sorbent for the present investigation. The sorption of Manganese (II) on chitosan has been found to be dependent on contact time, concentration, temperature, and pH of the solution. The adsorbents were evaluated for the adsorption capacity using Langmuir and Freundlich adsorption model. The process of removal follows first order kinetics and absorption of heat. The study indicated that due to chemical composition, structure, more adsorption sites, cheap, availability in plenty etc. this substance proves to be efficient adsorbent.*
Keywords: *Adsorption, Manganese Removal, Metal Oxide, Nanoparticles*

I. Introduction

The effluent treatment in developing countries is expensive and major cost is associated with the dependence on imported technologies and chemicals. The indigenous production of treatment techniques and chemicals locally, or using locally available non-conventional materials to treat pollutants seems to be the increasing problem for treatment of effluents. In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pretreatment procedures with suitable biomaterials based on better understanding of the metal bio sorbent mechanism(s) are gaining importance. Activated carbon of agricultural waste products as low cost adsorbents has been reported till now. However, there is an additional cost involved in the processing of the agricultural wastes to convert the same to activated carbon, which is posing economic difficulties necessitating research on alternate adsorbents with equivalent potential of activated carbon. In this paper, attempt has been made to remove Mn (II) from aqueous system by sorption method utilizing treated and untreated low grade chitosan which is commonly a bio sorbent. This investigation deals with the source and characterization of chitosan through IR method, preparation of stocks solution, experimental procedures at different conditions of temperature, PH, particle size and concentration.

II. Sorbent

Low grade chitosan has been used as a sorbent for the removal of heavy metals at different concentrations, temperatures, pH and particle sizes. The structure of chitosan is presented schematically in Figure 1.

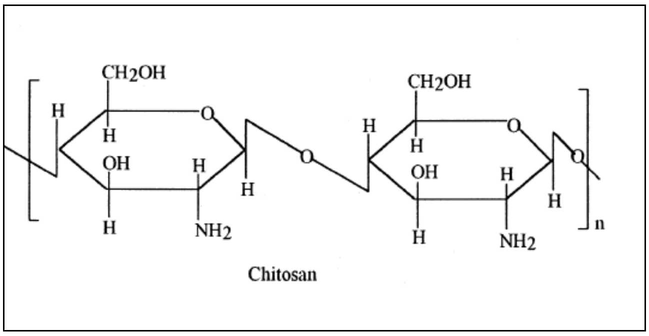

Fig. 1: structure of chitosan

Collection And Preparation Of Sorbent:

Chitosan was obtained from India sea foods, cochi (India) Batch sorption experiments were carried out in temperature controlled shaking machine by agitating 25ml aqueous solutions of sorbates with 1.0 g sorbent in different glass bottles at different conditions of concentrations, temperatures and pH. The pH of different solutions were adjusted with 0.05 M NaOH or HCl by pH meter, systronic 335. The speed of agitation was maintained at 1000 rpm to ensure equal mixing. The progress of sorption was noted after each 20 min. till saturation. At the end of predetermined time interval each 20 min, the sorbate and sorbent were separated by centrifugation at 16,000 rpm and the supernatant liquid analysed by atomic absorption spectrophotometer.

III. Result And Discussion:

Effect Of Contact Time And Concentration

The removal of Mn (II) by sorption on chitosan from aqueous solution increase with time (fig. 2) till equilibrium is attained in 140 min. The fig. show that time of saturation is independent of concentration. It is further noted that the amount of Mn (II) sorbed increases from 2.190 mg.g-1(87.60%) to 5.680 mg.g-1(89.54%) by increasing Mn (II) concentration from 100 mg/l to 250 mg/l. the time-amount sorbed curve is single, smooth and continuous indicating monolayer coverage of Mn (II) on the outer surface of chitosan.

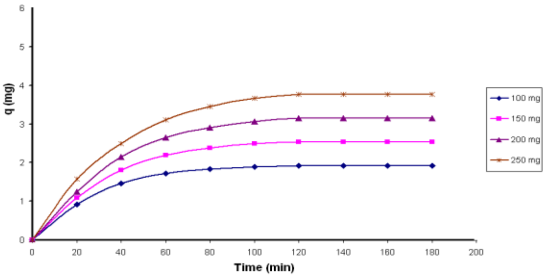

Fig 2: effect of concentration for the sorption of Lead (II) on chitosan;
●100 mg/L, ▪ 150 mg/ L, ◀ 200 mg/L, * 250 mg/L

Sorption Kinetics

The kinetics of sorption of Mn (II) on chitosan was studied using Lagergren equation (yadav et. al. 1987)

Log (qe –q) = log qe- kt / 2.3 ………………….. (1)

Where qe and q are the amount sorbed (mg.g-1) of Mn (II) at equilibrium and at time‘t’ respectively and k is sorption constant. The straight lines obtained from the plots of log (qe-q) against (fig. 4) and different concentrations indicate that the sorption process follows first order kinetics.

Effect Of Temperature:

The amount of Mn (II) sorbed on chitosan increases from 2.190 mg.g-1(87.60%) to 2.3336 mg.g-1 (96.13%) by increasing temperature from 30oc to 40oc indicating the process to be endothermic (fig. 5).

Langmuir Isotherm

The equilibrium data at the different temperatures follow Langmuir equation.

Ce/qe = 1/φ.b + Ce/φ ……………………… (2)

Where Ce mg.L^{-1} is equilibrium concentration of Mn (II) and φ and b are Langmuir constants related to sorption capacity and sorption energy respectively. The value of φ and b (table 4) were determined from the slope and intercept of linear plots Fig. 6. The sorption capacity also increases with temperature suggesting that the active centres available for sorption have increased with temperature.

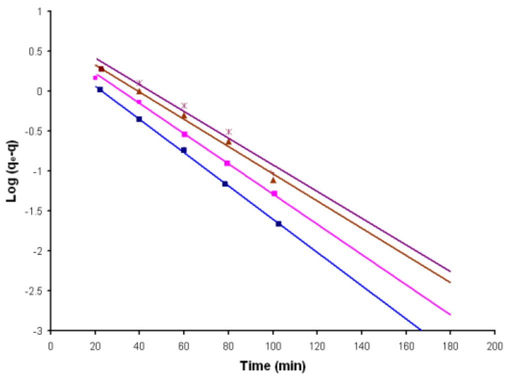

Fig 3: Langergren plot for the sorption of Mn (II) on chitosan;
●100 mg/L, ▪ 150 mg/ L, ◀ 200 mg/L, * 250 mg/L, pH 5, temp 30^{o}c

The change in free energy (ΔG^O), enthalpy (ΔH^O), and entropy (ΔS^O) of sorption have been calculated using following equations.

$$\Delta G^\circ = -RT \ln K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$
$$\Delta H^\circ = RT\,_1T\,_2(T_1 - T_2) \ln k_2 / k_1 \quad \ldots\ldots\ldots\ldots \quad (4)$$
$$\Delta S^o = \Delta H^\circ - \Delta G^{O/} T_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Where K_1 and K_2 are equilibrium constants at temperature T_1 and T_2 respectively.
The negative values of ΔG^o (Table 2) indicate the spontaneous nature of the sorption process. The positive values of ΔH^o at different temperature support the endothermic nature of the process.

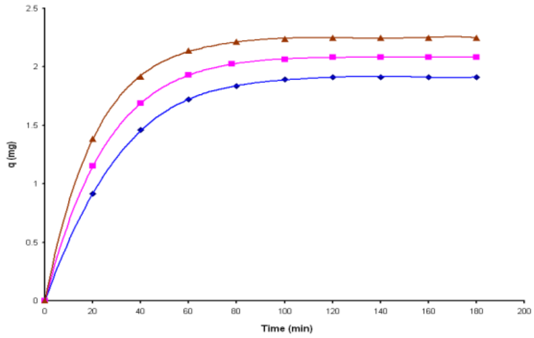

Fig 4: Effect of temperature on the sorption of Mn (II) on Chitosan ● 30°c, ▪ 40°c, ◀ 50 °c

Table 1: Ø values at different temp. and p^H

Temperature (°C)	Ø mg.g-1	p^H	Ø mg.g-1
30	0.7543	2	0.3891
40	1.1865	4	0.6880
50	1.3656	6.5	0.7543

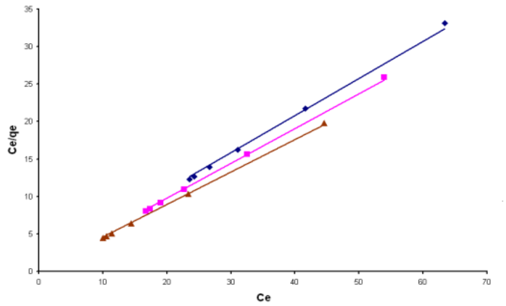

Fig 5: Langmuir isotherm for the sorption of Mn (II) on chitosan; ● 30°c, ▪ 40°c, ◀ 50 °c.

Effect of pH The amount of Mn (II) sorbed on chitosan increases from 1.640mg.g-1 (65.60 %) to 2.190 mg.g-1 (87.60 %) by increasing pH of the solution from 2.0 to to 6.5 (Fig.6). The Sorption capacity Φ, also increase with the increase of pH.

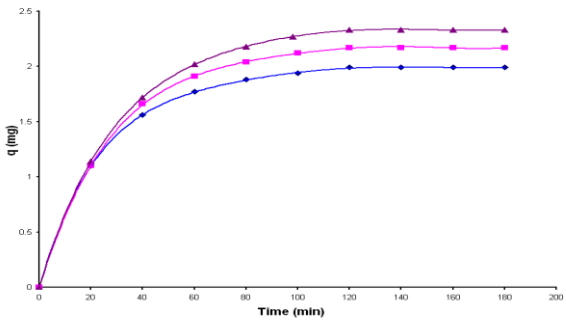

Fig 6: Effect of pH on the sorption of Mn (II) on chitosan; ● 2.0, ▪ 4.0, ◀ 6.5; temp: 30 ° c, conc. 100 mg/l.

Table 2: Thermodynamic parameters at different temperatures

Temperature (°C)	ΔG^o (kcal.mol$^{-1)}$	ΔH^o (kcal.mol$^{-1)}$	ΔS^o (kcal.mol$^{-1)}$
30	-4.96	13.01	19.36
40	-5.12	25.90	34.28
50	-7.26		

IV. Conclusion

From the above observations it is clear that low grade chitosan can be effectively used for the removal of heavy metal ions under investigation from wastewater as it shows significantly high adsorption capacity for removal of Manganese from water as compared to other adsorbents.

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