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Adsorption Analysis of Mn(VII) from Aqueous Medium by Natural Polymer Chitin and Chitosan

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Batch experiments were carried out for the adsorption of Mn^{7+} ions on to natural polymer chitin and chitosan. Several variables *viz.*, initial adsorbent concen-tration, pH, temperature and contact time were also evaluated. Equilibrium data were fitted to the Langmuir and Freundlich isotherm equation.

Key Words: Adsorption, Chitin, Deacetylated chitin, Mn(VII).

INTRODUCTION

Heavy metals in waste water have emerged as the focus of environmental remedial efforts because of their toxicity and threat to human beings. Due to rapid growth of industrialization and urbanization with new technological advancement, the existing water resources are contaminated by discharging waste water containing organics, colour, heavy metals, *etc*¹. Hence, removal of toxic and heavy metal contaminates from wastewater is one of the most important environmental and economic issues². Many models of adsorption for cations and anions on surface have been developed considering variations in parameters such as pH, adsorbent-adsorbate concentration, time and even ionic strength³⁻⁵. Among the physico-chemical treatment, process of adsorption is found to be highly effective, cheap and easy method and it has inspired the investigators to search for suitable low cost adsorbent.

Manganese is one of the ubiquitous element. It has key role in many enzymatic reactions, so it is regarded as an essential element in mammals. But it is also one of the ion capable of being toxic when present beyond the tolerance level in water bodies.

In recent years considerable attention has been devoted to the study of different types of low cost material such as tamarind kernel powder, guar gum. Herein in present paper, the natural polymer chitin and chitosan were used as adsorption materials for the removal of Mn^{7+} ion.

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EXPERIMENTAL

Chitin is a non-toxic, biodegradable, high molecular weight, naturally occurring polymer of N-acetylglucosamine.

Deacetylated chitin (chitosan) was produced by refluxing it with 40 % NaOH for 3 h. The product was characterized by IR spectrum, which exhibits a strong band appearing as coupled doublet at 3424 cm⁻¹ due to (N-H) stretch of primary amine. The bond at 2931 cm⁻¹ is due to (C-H) stretching. The presence of band at 1640 cm⁻¹, 1155 cm⁻¹ is due to the (N-H) bending vibration of primary amine and (C-O-C) and (C-N) stretching, respectively.

The stock solution of Mn(VII) was prepared by dissolving KMnO₄ in double distilled water. Batch adsorption experiments were carried out at room temperature. Different amounts of adsorbents (1, 2, 3 g/L ...) were agitated with 5 mL Mn(VII) solution of desired concentration. The initial pH of solution was adjusted by digital pH meter (Model 151 R) using either 0.1 N HCl or 0.1 N NaOH. Samples were withdrawn at appropriate interval of time and concentration of Mn(VII) remaining in solution was determined spectrophotometrically (Model 106).

RESULTS AND DISCUSSION

Effect of pH: The variation in the adsorption of Mn(VII) as a function of pH was studied over pH range 2-7 using 50 mL of 10 ppm Mn(VII) solution with adsorbent concentration 2 g/L. Mn(VII) forms stable complex anion in acidic medium. It is evident from Fig. 1a and 1b that maximum removal of Mn(VII) was obtained at pH 3 and 4 for chitin and chitosan, respectively. At lower pH *i.e.*, in acidic medium N atom of N-acetyl (chitin) and amino (chitosan) functional groups present on adsorbent will be protracted and thus the adsorbents behave as an anion exchanger. While at high pH value adsorption decreases, which may be due to the ionic repulsion between anionic sites of adsorbent surface⁶.

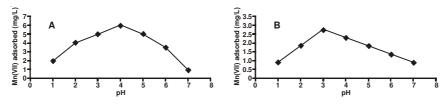
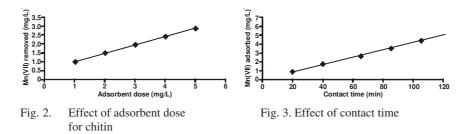


Fig. 1. Effect of pH (A) for chitin (B) for chitosan

Effect of adsorbent dose: Amount of adsorbent used for treatment has been varied. As the amount of adsorbent increases from 1 to 5 mg/L, percentage removal increases because of increased surface area owing to the increases in the total number of adsorption shown in Fig. 2.

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Effect of contact time: Batch adsorption studies were conducted to determine variation in adsorption of Mn(VII) with initial concentration 10 ppm. Equilibrium Mn(VII) concentration was determined at regular time intervals of 20 min for both adsorbents (chitin and chitosan) at their respective optimized pH values. Adsorption increased at initial stages and the process reached at saturation stage at 2 h and thereafter, it remained constant. No considerable increase in sorptive ability of both adsorbent was observed further as shown in Fig. 3.



Adsorption isotherm: Quantification of the adsorption capacity of adsorbent for the removal of metal ions from the solution was studied using Freundlich and Langmuir adsorption equations.

The empirical Freundlich equation based on adsorption on a heterogeneous surface is as follows:

$$q_e = \frac{X}{m} = K_f (C_e)^{1/n}$$

where X is the amount of adsorbate adsorbed and m is amount of adsorbent, C_e is the equilibrium concentration of adsorbate in the solution, K_f is the measure of sorption capacity 1/n is sorption intensity^{7,8}. This equation can be linearized in logarithmic form as follows:

$$\log q_e = \log \frac{X}{m} = \log K_f + 1/n \log(C_e)$$

The plot of $\log q_e$ with $\log C_e$ should yield a straight line and $\log K_f$ and 1/n are calculated from intercept and slope.

The langmuir equation can be described in the following way:

$$\frac{C_e}{(X/m)} = \frac{1}{(bV_m)} + \frac{C_e}{V_m}$$

where V_m is the maximum adsorption density corresponding to monolayer formation on the adsorbent and b is adsorption bond energy99,10 while Ce, X, m have same meaning as in previous isotherm. If the adsorption data follow this pattern, a plot of $\frac{C_e}{(X/m)}$ with C_e should yield a straight line. Adsorption

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data for adsorption of Mn(VII) by adsorbent with different amount of adsorbents were made to fit in both the isotherms as shown in Figs. 4 and 5.

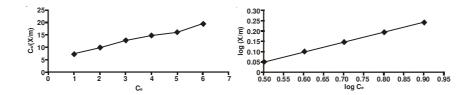


Fig. 4. Langmuir isotherm

Fig. 5. Freundlich isotherm

This study reveals that an optimum contanct period of 2 h is required for maximum removal of Mn(VII) by both adsorbents while pH values differ for both. For chitin the pH = 3 but for chitosan pH = 4. The adsorption occurs in acidic medium and with high amount of adsorbent, it also follows Langmuir and Freundlich isotherm. This method can be used to remove Mn(VII) ions from effluent by using natural polymer, as it affects water bodies and human beings beyond the tolerance level.

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