Original Research Article

Adsorption Analysis of Mn(VII) from Aqueous medium using by Activated Orange Peels Powder

Abstract: Adsorption of Manganese(VII) ions from aqueous solution onto a low cost adsorbent activated orange peels powder has been investigated to evaluate the effects of contact time, initial manganese ion concentration, *p*H, particle size and adsorbent dose on the removal of Mn(VII) systematically. The optimal *p*H value for Mn(VII) removal by the orange peel was found to be 2. The maximum removal efficiency was found 71.3% at *p*H 2. Equilibrium study was examined by the Langmuir and Freundlich isotherm equation.

Keywords: Adsorption isotherms, Activated Orange peels powder, Mn(VII) ion, effluent treatment.

Introduction

Industrial and agricultural wastes pollute water with heavy metals, which reach tissues through the food chain[1]. Heavy metal wastewater exists in various industries such as metal finishing, electroplating, plastics, pigments and mining, which threatens to the environment and human lives severely. Therefore it is urgent to remove those toxic heavy metals from waste water. Several treatment methods have been suggested, developed and used to remove heavy metals from waste water. These methods[2-7] include chemical precipitation, ion exchange, cementation, coagulation and flocculation and membrane processes. However, these techniques have been reported to be very expensive. So, we need heavy metals removal processes which are expected to be simple, effective and inexpensive.

In recent years, a lot of studies have been reported on locally available and various low cost adsorbents[8-17] such as saw dust, tea factory waste, wheat straw, pine needles, soya cake, activated tamarind kernel powder, neem leaves, *Acacia nilotica* leaf powder, *Ziziphus jujuba* leaf powder, sugar industry waste etc. Adsorption is one of the most useful, economically viable methods. This paper reports the potential of orange peels as adsorbent for removal of Mn(VII) from waste water.

Manganese is essential trace nutrient in all known forms of life. Manganese poisoning, however, has been linked to impaired motor skills and cognitive disorders. Higher levels of exposure to manganese in water are associated with increased intellectual impairment and reduced intelligence quotients in school-age children. The adsorption capacities of Activated Orange peels powder at room temperature have been estimated using equilibrium studies. Effects of various parameters like metal ion concentration, adsorbent dosage, *p*H, contact time and particles size have been studied.

Orange peel is abundant in soft drink industries and usually treated as wastes .It is mostly composed of cellulose, pectin, hemi-cellulose, lignin, chlorophyll pigments and other low relative molecular mass hydrocarbons.

Experimental

Preparation of adsorbent:

Orange peels were collected from juice corners of Jodhpur. The collected orange peels were washed with deionised water for several times to remove water soluble impurities, dust and surface adhered particles. The washed leaves were dried in a hot air oven at 85^0C for 48 h. Dry orange peels leaves were crushed in a mechanical grinder ground in ball mill and the resulting crumbs were sieved to different particle size 100, 150, 200, 250 and 300 µm. Orange peels powder of different particle size was activated separately by heat treatment and with concentrated Sulphuric acid. Finally, the products obtained were stored in glass bottle for further use.

Preparation of Mn(VII) solution:

A stock solution of Mn(VII) was prepared by dissolving 2.876 g of 99.3% of $KMnO_4$ in 1 liter double distilled water to obtain 1000 mg L^{-1} stock solution. For further requirement of experiment the other solutions of strength 50-300 mg L^{-1} of Mn(VII) were prepared with the help of stock solution. The *p*H of solutions was adjusted with 0.1 N H_2SO_4 and 0.1 N NaOH solutions as per the requirement and *p*H was measured by *p*H meter.

Adsorption Experiment:

Adsorption experiment were studied in batch mode as function of contact time (20, 40, 60, 80, 100) minutes, biomass dosages (2, 4, 6, 8, 10) g L^{-1}, metal ion concentration (50, 100, 150, 200, 250) mg L^{-1}, pH (2-6) and particle size (100, 150, 200, 250, 300) µm. The batch adsorption was carried out in 100 mL borosil flask, required quantity of bio-sorbent was added to 60 mL of metal ion solution and the mixture was agitated on rotor at 200 rpm.

After complete experiment was carried out at room temperature. After completion of every set of experiments the residual was separated by filtration using Whatmann filter paper no. 42 and only 25 mL of each sample was stored for residual Mn(VII) analysis.

After completion of experiment, the concentration of residual Mn(VII) ion was directly measured by atomic adsorption spectroscopy.

Equation (1) is used to determine the percentage adsorption of metal (Ø, in %) by adsorbent.

$$Ø = \frac{C_o - C_e}{C_o} \times 100 \quad \text{---(1)}$$

Where C_0 is initial metal ion concentration and C_e is the concentration of metal ion after adsorption.

Adsorption isotherm

According to Langmuir theory, the saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad \text{---(2)}$$

the above eq^n 2 can be rearranged by following linear form

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{1}{q_{max}} C_e \quad \text{---(3)}$$

Where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of metal ion adsorbed (mg g^{-1}), q_{max} is q_e for a complete monolayer(mg g^{-1}) and b is sorption equilibrium constant(mg^{-1} L). A graph of C_e versus C_e/q_e should indicate a straight line of slope $1/q_{max}$ and an intercept of $1/bq_{max}$ as shown in Fig.1.

Freundlich has shown that if the concentration of solute in solvent at equilibrium C_e(mgL^{-1}) is raised to the power of m, the amount of solute adsorbed being q_e, then C_e^m/q_e is a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation in the form of logarithm of both sides as shown in Fig. 2.

$$\log q_e = \log K_f + m \log C_e \text{ ---(4)}$$

An adsorption isotherm is characterized by certain constant, These constant values express the surface properties and affinity of the sorbent and can also be used to compare bio-sorptive capacity of biomass for different metal ions. Out several isotherm equations, two have been applied for this study,i.e. the Freundlich and Langmuir isotherms.

RESULT AND DISCUSSION

Effect of contact time on adsorption:

The adsorption of Mn(VII) ions into orange peels was studied by varying the contact time from 20-100 minutes and by maintaining other parameters constant i.e. adsorbent dose 8 g L^{-1}; metal ion concentration 150 mg L^{-1}; particle size 150 µm and *p*H 3. The maximum removal efficiency of activated orange peels powder was found at 80 min. Figure 3 shows that the removal of metal ion increases up to 80 min. and then the percentage removal from aqueous solution becomes constant as 69.5% .

Effect of adsorbent dose on adsorption:

The experiments were carried out ,with the change in adsorbent dosages from 2 g L^{-1} to 10 g L^{-1} in the test solution while keeping the initial ion concentration (150mg L^{-1}), and *p*H 3 at 80 minutes constant time intervals. The percent adsorption is increased with adsorbent dosage, Because increased dosages are responsible for increasing surface area, owing to increase in the total number of adsorption sites as shown in Fig.4.

Effect of concentration on adsorption

The adsorbate concentration between adsorbent and adsorbate species play an important role in the process of removal of pollutants from water and wastewater by adsorption at a particular temperature and *p*H. In high concentration range, the fractional adsorption is low.

The effect of metal ion concentration on adsorption was analysed over the metal ion concentration range from 50-250 ppm and maintaining of the conditions as constant i.e. particle size 150µm,*p*H 3 ; adsorbent dosage 8 g L^{-1},contact time 80 minutes. The removal of the Mn(VII) ions by orange peel decrease with increase in concentration of metal ion solution as shown in fig 5.The occurs because the no.of active sites are fixed in the adsorbent,so when we increase the concentration of metal ion,the competitons within metal ions increase for occupying on the adsorbents.So due to unavailability of adsorbent sites the adsorption decreases.

Effect of *p*H on adsorption:

The removal of metal ions from aqueous solution by adsorption was dependent on the *p*H of the solution since it affected adsorbent surface charge, degree of ionization of the functional groups, and metal ion speciation. Most researchers agreed that the optimal *p*H vary with diverse metal ions. At lower *p*H value, the H^+ ions compete with metal ion for the exchange sites in the system thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions.

The effect of *p*H on adsorption of metal ion Mn(VII) on Activated Orange Peel Powder was analysed over the *p*H range from 2-6 on 150 ppm Mn(VII) solution by particle size 150 µm of adsorbent 8 g L^{-1} at 80 minutes.

As shown in fig 6, removal of Mn(VII) decrease, with increase in *p*H. It shows with decreases in concentration of H^+ ion replacing capacity is decreased. Here Mn(VII) is removed through hydrogen ion exchange method.

Effect of particle size on adsorption:

The experiments were carried out, with change in particle size of adsorbent dosage of Activated Orange Peel Powder from 100-300 µm, and along with maintaining other parameters constant i.e. contact time 80 minutes; adsorbent dose 8 g L^{-1}; metal ion concentration 150 mg L^{-1} and *p*H 3. By decreasing the size of adsorbent, removal efficiency increases as shown in fig 7.because small particle size gives large contact area.

Table:-1. Experimental conditions

Experimental conditions	T(min)	M_s(g L^{-1})	C_o(mg L^{-1})	*p*H	P_s (µm)
Effect of contact time T(min)	**20-100**	8	150	3	150
Effect of adsorbent dosage M_s (g L^{-1})	80	**2-10**	150	3	150
Effect of concentration of Mn(VII) ion C_o(mg L^{-1})	80	8	**50-250**	3	150
Effect of *p*H	80	8	150	**2-6**	150
Effect of Particle Size P_s (µm)	80	8	150	3	**100-300**

Table:-2. Langmuir and Freundlich model parameters estimated from the fitting of experimental point of Mn(VII) adsorption

Langmuir isotherm			**Freundlich isotherm**		
R^2	**q_{max} (mg g^{-1})**	**b (L mg^{-1})**	**R^2**	**K_f (mg g^{-1})**	**m**
0.993	58.5	0.297	0.94	6.722	5.154

Conclusions: The present study shows that the activated orange peels powder is an effective adsorbent for the removal of Mn(VII) from aqueous solutions .Experimental data indicates that the desorption capacity is dependent on operating variables such as adsorbent mass, pH, contact time ,particle size and initial metal ion concentration .The results showed that removal efficiency exceeded 70% from initial concentration of 50 mg L^{-1}.

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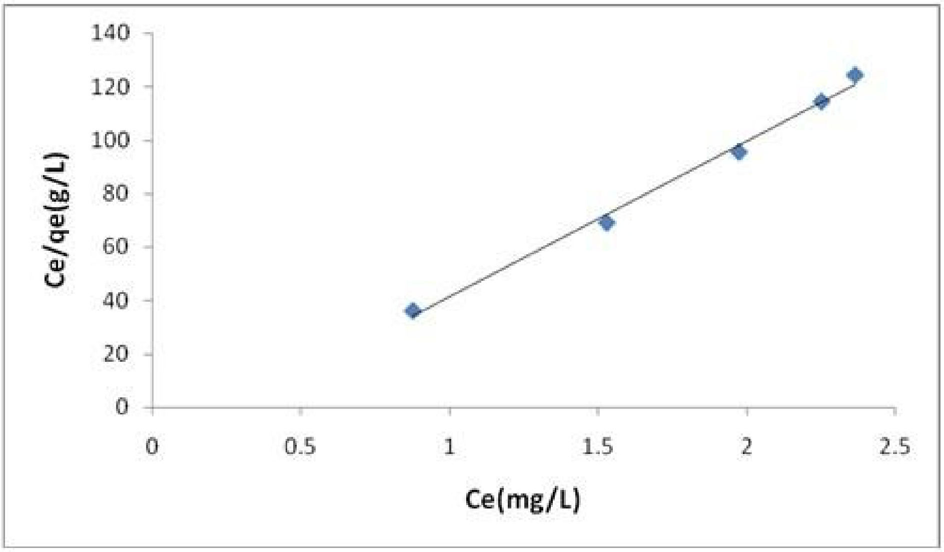


Fig: 1. Langmuir adsorption isotherm

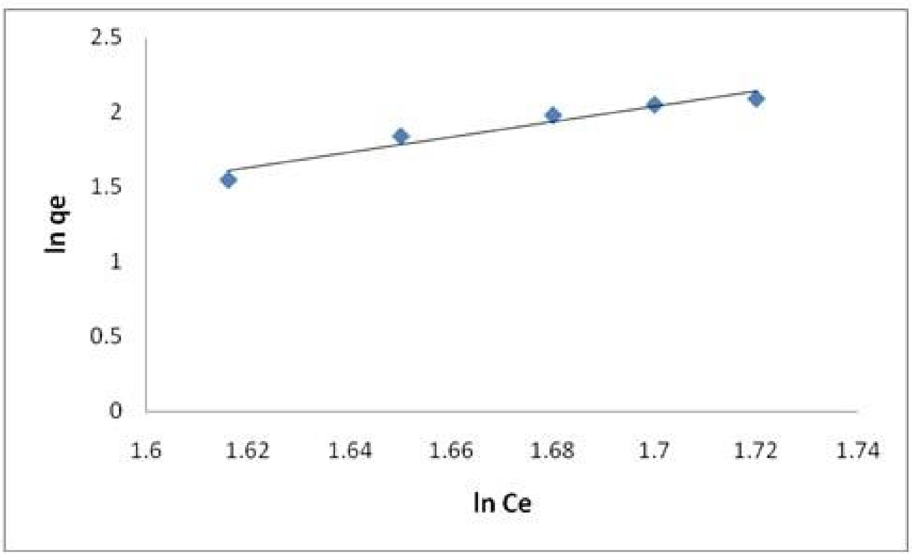
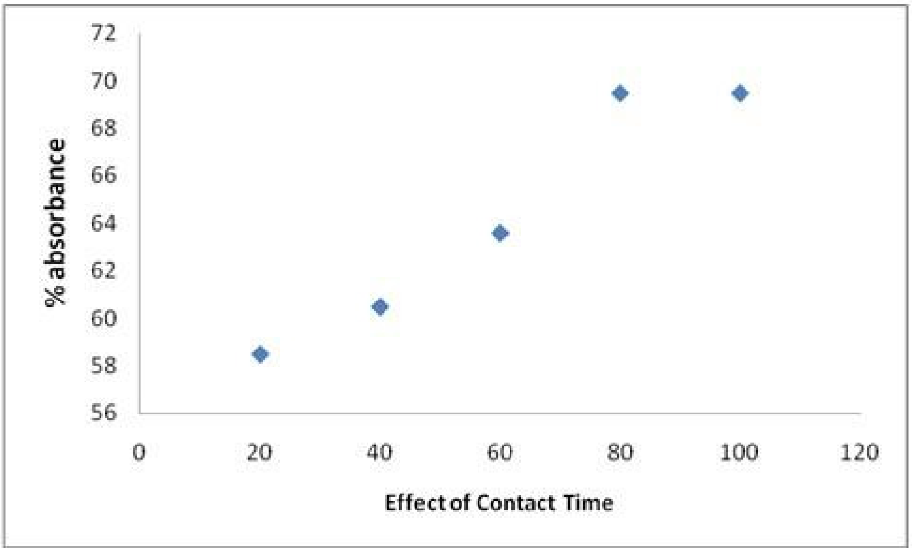
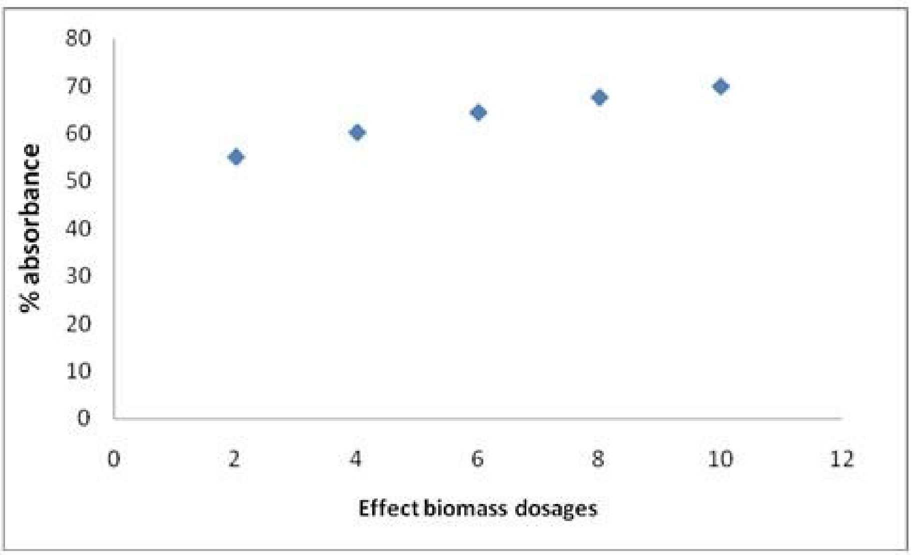


Fig: 2. Freundlich adsorption isotherm



184 **Fig: 3. Effect of Contact Time**



185 **Fig: 4. Effect of biomass dosages**

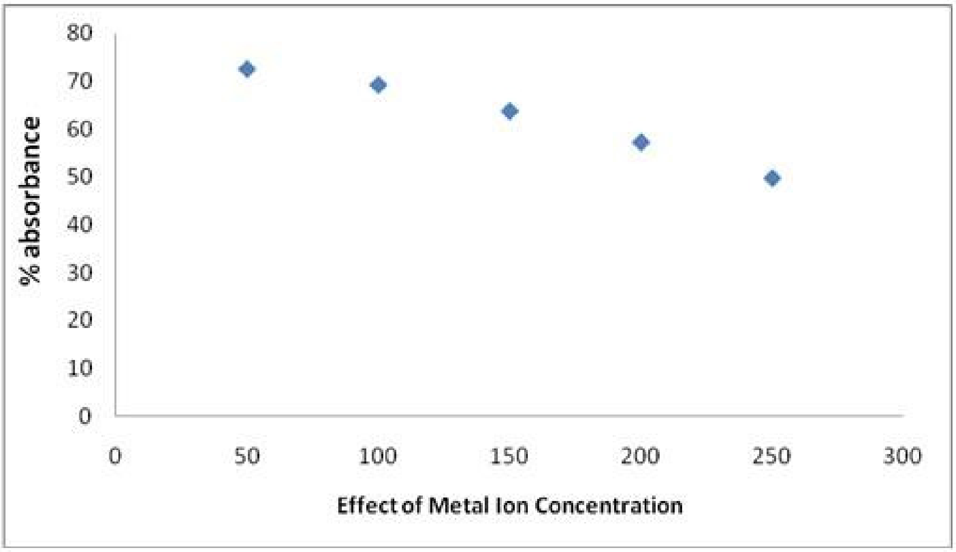


Fig: 5. Effect of Metal Ion Concentration

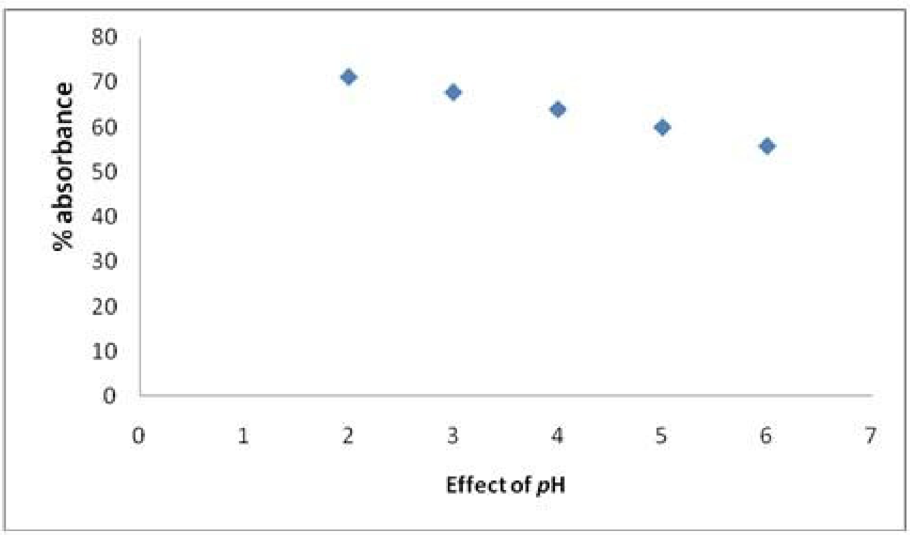
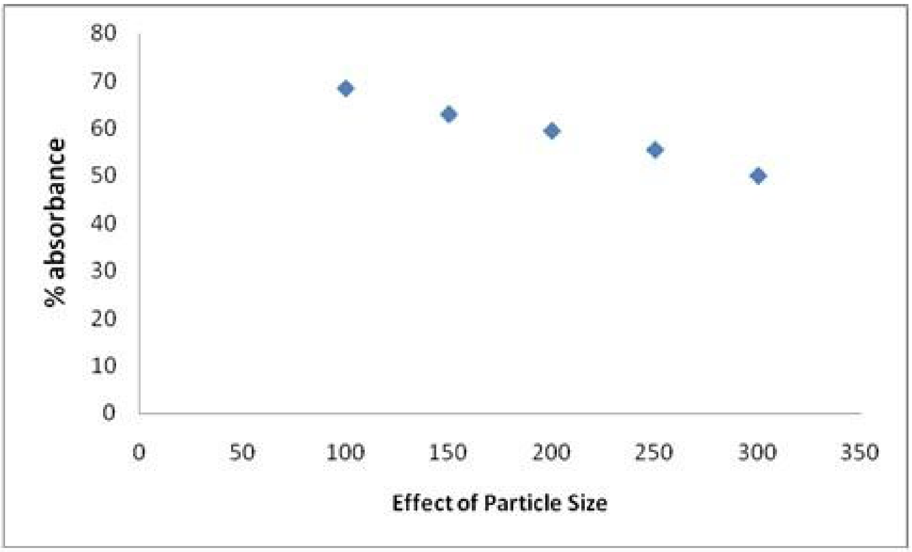


Fig: 6. Effect of *p*H



188 **Fig: 7. Effect of Particle Size**