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

Vikal Gupta*, Sharda Kumari, Chandresh Virvadiya

Department of Chemistry , Jai Naraian Vyas University, Jodhpur-342001

*E-mail ; vikal_chem@yahoo.co.in

Abstract: Adsorption of Manganese(VII) ions from aqueous solution onto a activated orange peels powder as low cost adsorbent has been investigated. The effects of various parameters such as contact time, initial manganese ion concentration, *p*H, particle size and adsorbent dose on the removal of Mn(VII) have also been studied systematically. The optimal *p*H value for Mn(VII) removal by the activated 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 equations.

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

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 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 found to be very expensive. So, we need effective and inexpensive processes for removal of heavy metals.

In recent years, a lot of studies have been reported on locally available and various low cost adsorbents[8-22] 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. The efforts that already introduced in this field are probably less favourable in terms of economy and public acceptance. Natural renewable resources that have potential to be used as scientific tool are utilized in this research. 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 peels are 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 obtained products were stored in glass bottle for further uses.

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 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 experimenst 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 different experimental conditions were shown in table 1. The batch adsorption was carried out in 100 mL borosil flask. The required quantity of bio-sorbent was added to 60 mL of metal ion solution and the mixture was agitated on rotor at 200 rpm.

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. The concentration of residual Mn(VII) ion was directly measured by atomic adsorption spectroscopy. The percentage of Mn(VII) ion removal was calculated using following equation:

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

Where Ø is adsorption capacity in mg g^{-1}; C_0 and C_e are initial metal ion concentration and metal ion concentration after adsorption.

Adsorption isotherm

i) Langmuir isotherm

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

$$q_e= \frac{q_{\max} bC_e}{1 + bC_e} \qquad \text{---(2)}$$

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

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

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 the maximum adsorption capacity corresponds to complete monolayer coverage on the surface (mg g^{-1}) and b is sorption equilibrium constant(mg L^{-1}). A graph of

C_e versus C_e/q_e gives the straight line of slope $1/q_{max}$ and intercept of $1/bq_{max}$ (Fig.1). It shows the adsorption of Mn(VII) follows Langmuir isotherm model.

ii) Freundlich isotherm

The following empirical equation is used to describe heterogeneous system

$$q_e = K_f C_e^{1/n} \quad \text{---(4)}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is equilibrium concentration of adsorbate (mg L^{-1}), while K_f is the Freundlich constant related to the adsorption capacity and 1/n is the heterogeneity factor. A linear form of the Freundlich equation is obtained by taking the logarithm of equation (4).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \text{ ---(5)}$$

The plot of ln q_e versus ln C_e gives a straight line of intercept ln K_f and slope of 1/n (fig. 2). The Freundlich constants are represented in table 2.

An adsorption isotherm is characterized by certain constants. These constant values express the surface properties and affinity of the sorbent. They can 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:

The adsorption of Mn(VII) ions into orange peels was studied by varying the contact time from 20-100 minutes and 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 minutes. The figure 3 shows that removal of metal ion increases up to 80 minutes and after that percentage removal from aqueous solution becomes constant as 69.5%. Therefore, the contact time 80 minutes is sufficient time for bonding between adsorbate and adsorbent.

Effect of adsorbent dose:

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 other parameters constant i.e. metal ion concentration (150mg L^{-1}); *p*H 3; contact time 80 minutes. The result for adsorptive removal of Mn(VII) with respect to adsorbent doses is shown in fig. 4. The percentage removal of Mn(VII) increases initially and then attains equilibrium after 10 g L^{-1} of adsorbent dose.

Effect of metal ion concentration:

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 other conditions as constant i.e. particle size 150µm; *p*H 3; adsorbent dosage 8 g L^{-1},contact time 80 minutes. The percentage removal of Mn(VII) ions decreases with increase in concentration of metal ion solution as shown in fig 5. This can be explained with fact that adsorbent has a limited number of active sites, which would have become saturated above a certain Mn(VII) ion concentration.

Effect of *p*H:

As one of the most important parameters dominating sorption, initial pH of solution has an impact on the speciation of ions in aqueous solution and electro negativity of binding sites on the surface of adsorbents. Most researchers agree 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.

In acidic solution, a five electron oxidation process occurs:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

In neutral solution, the main process is a three electron oxidation:

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

In strongly alkaline solution, only a one electron process occurs:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

The effect of *p*H on adsorption of metal ion Mn(VII) by activated orange peel powder was analysed over the *p*H range from 2-6 keeping other parameters constant.

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

Effect of particle size:

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 larger 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})**	**n**
0.993	58.5	0.297	0.94	6.722	5.154

Conclusion:

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 research finding reveals that removal efficiency is 71.3% at initial concentration 50 mg L^{-1} with pH 2.

Acknowledgement:

The authors are grateful to U.G.C. for awarding major research project. Sharda Kumari and Chandresh Virvadiya are thankful to the UGC ,New Delhi for the award of Project fellow and UGC- SRF respectively.

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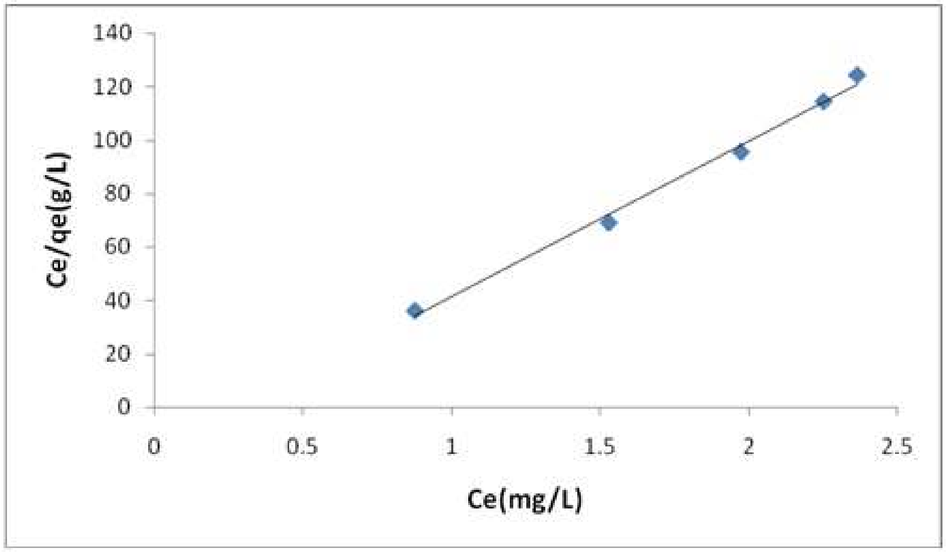

Fig: 1. Langmuir adsorption isotherm

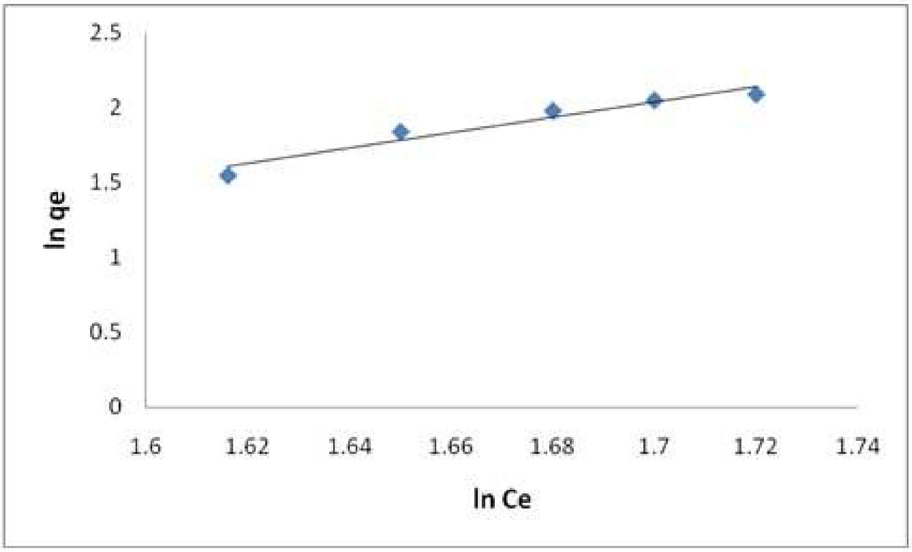

Fig: 2. Freundlich adsorption isotherm

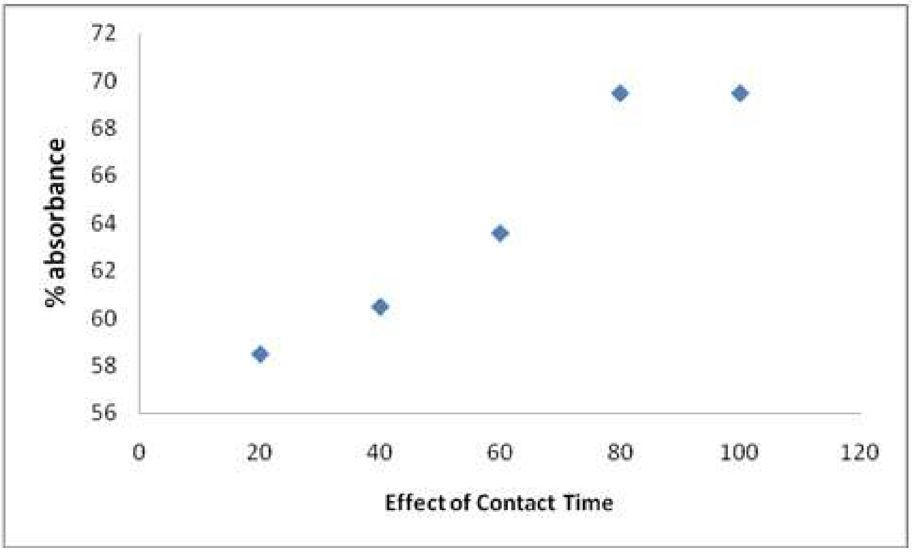

Fig: 3. Effect of Contact Time

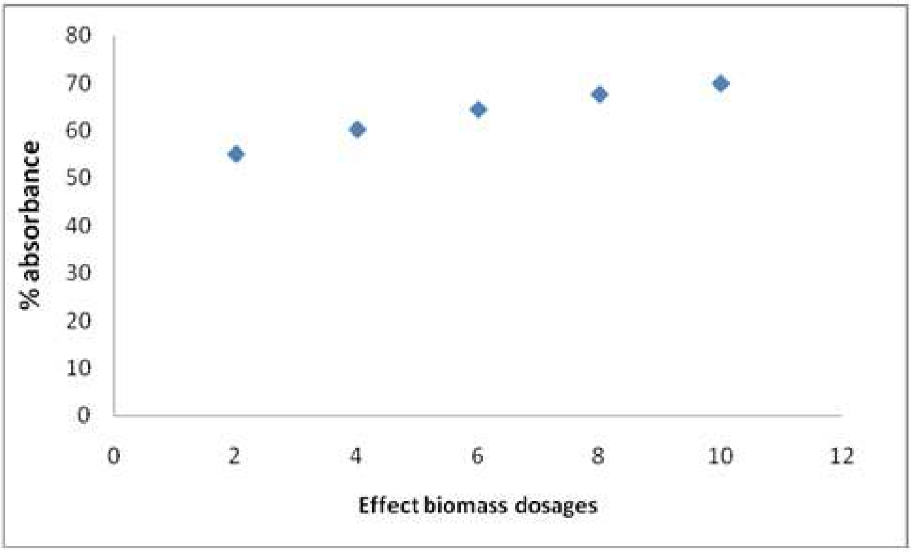

Fig: 4. Effect of biomass dosages

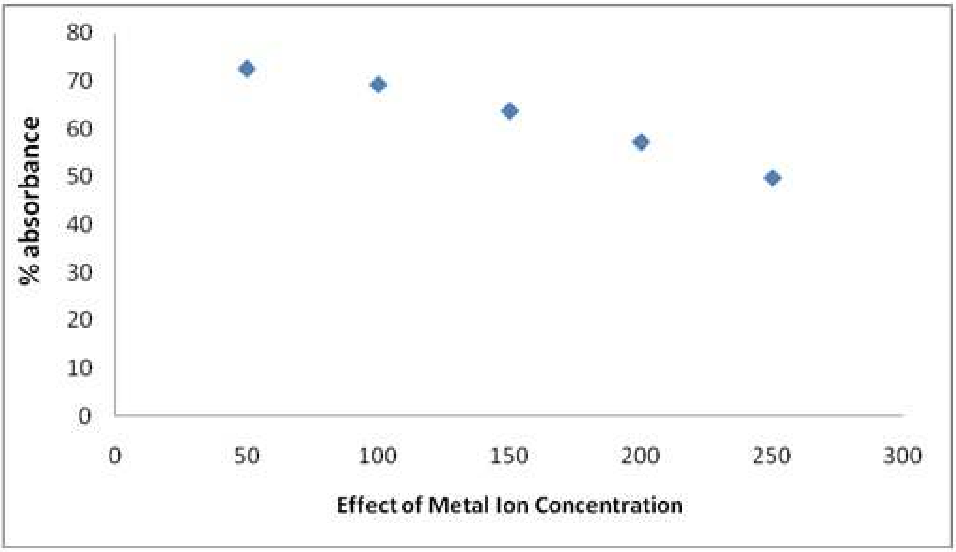

Fig: 5. Effect of Metal Ion Concentration

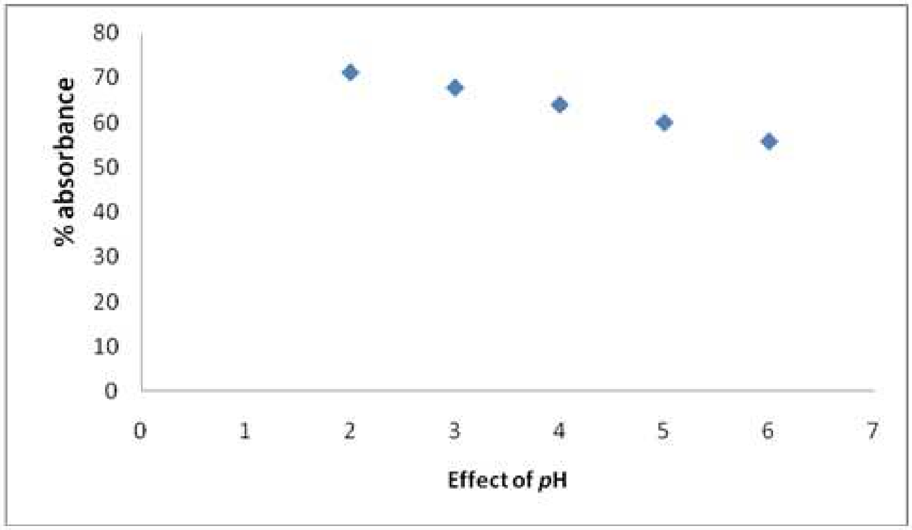

Fig: 6. Effect of *p*H

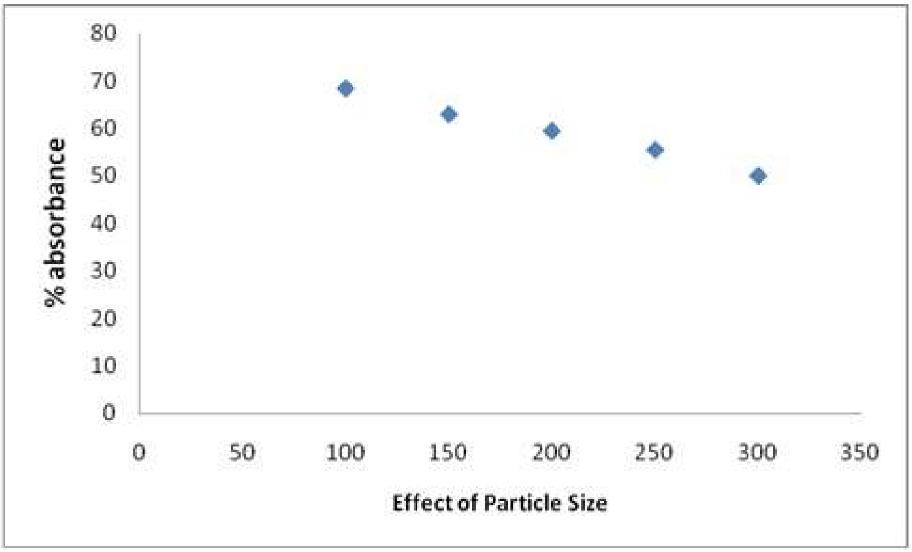

Fig: 7. Effect of Particle Size