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Mn(II) Removal From Ground Water by Using *Ipomea batatas* Carbon

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The aim of this study is to investigate the preparation of low-cost activated carbon from *Ipomoea batatas* (IBC) and to explore their potential application for the removal of heavy metals from aqueous solutions. Conventional physical (water vapour) activation was used for synthesizing the adsorbent. The obtained carbon was employed for the removal of Mn(II) from aqueous solutions at different initial concentrations and pH values. Adsorption of Mn(II) ion follows Langmuir isotherm, the maximum loading capacity for Mn(II) ion is 23.4 mg g^{-1}. According to the experimental data it can be inferred that the basic character of the surface, *i.e.*, the high content of basic groups, favours adsorption of ion. Regarding manganese adsorption herein obtained carbon presented higher uptake adsorption than that of activated carbons reported in the literature.

Key Words: *Ipomoea batatas*, Adsorption, pH, Mn(II) removal.

INTRODUCTION

The elimination of Mn(II) from aqueous solution is serious problem in many countries. Manganese is one of the most difficult elements to remove from surface waters[1-3]. Although dissolved Mn(II) ion is not known to be toxic and even blocks the toxic effect of H^+ ion[4]. It has undesirable effects on domestic water. These include training laundry and ceramic fixtures such as toilets where concentrations are greater[5] than 0.05 mg/L. Federal relations therefore control discharge limits. In drinking water sources, the secondary maximum contaminant level[6] for Mn(II) ion must not exceed 0.05 mg/L.

Many studies have been carried out on the removal of Mn(II) ion, including those designed to evaluate chemical dynamics, experiment with packed columns of limestone and evaluate passive treatment systems[7,8]. Microbial remediation efforts include designed wetlands, microbial bioreactors and pellets of mixed microbial cultures *etc*.[9,10]. Mondal[11] reported that Mn can be removed by 41 % by using GAC. Mohan[12] reported that Mn is removed by using lignite upto 25.84 %. Nassar[13] reported that removal of manganese ion by adsorption on palm fruit bunch and maize cobs was in the range of 79-50 %. Saad[14] reported that manganese is removed from wastewater by using sulphurized activated carbon obtained from burnt date stones.

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In the present water management study, the authors prepared the adsorbent from plant material and an attempt was made to remove water soluble Mn(II) ions by adsorption.

EXPERIMENTAL

All the reagents used in the experiment were of analytical grade.

Preparation of adsorbent: Dried fruit of *Ipomoea batatas* were carbonized in the electrical conventional heating reactor by two stages carbonization process in the range of 250-600 ºC and 600-800 ºC, respectively. The materials were placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out at 40 ºC for 0.5 h followed by next stage to develop the pore size structure so that an accessible internal surface could be created.

The carbonized product was treated with acid (0.5 M HNO_3) for the removal of undesired materials. The acid washed product was thoroughly washed with hot distilled water to remove acidity and chlorides. Indigenously prepared carbon thus produced was thermally activated at 120 ºC for 1 h in an air oven. The product was finally dried and sieved to get particular particle size *i.e.*, 45 µ.

Preparation of standard manganese solution: A stock solution of manganese used in this study was prepared by dissolving an accurate quantity of 1 g of manganese metal in 50 mL of 6 N HNO_3 and dilute to 1000 mL. Other concentrations were prepared from this stock solution by dilution. Fresh dilutions were used for each experiment.

Analytical method: Manganese ion concentration of the solutions were determined by using an atomic absorption spectrophotometer (ECIL AAS4103/AAS4127) with an air-acetylene flame oxidizing (lean, blue) and with light source of hallow cathode lamp. Deuterium back ground correction was used and the spectral slit width was 0.2 nm. The working current and wavelength were 5 mA and 279.5 nm, respectively. The instrument response was periodically checked by using standard metal solutions.

Sensitivity: For the standard conditions, the sensitivity about 0.04 mg/mL Mn(II) ion for 1 % absorption. A standard containing 1 mg/mL Mn(II) ion will typically give an absorbance reading of about 0.11 absorbance units (about 40 % absorption).

Linear working range: For the standard conditions described above the working range for Mn(II) ion is linear upto concentration of approximately 60 mg/L in aqueous solution.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on the adsorption of Mn(II) ion on *Ipomoea batatas* is studied in the range 5-9 pH and the results are summarized in Table-1. The percentage removal of Mn(II) ion increases with increase in the pH from 5-7 and it is almost constant up to pH 9. From this study, it is observed that the change in pH is significant up to pH 7 and there is no considerable change after the pH 7.

TABLE-1
EFFECT OF pH ON ADSORPTION OF Mn(II)

pH	*Ipomea batatas*		Removal (%)
	C_e (mg/L)	Q_e (mg/g)	
5	2.431	1.5138	75.69
6	1.995	1.6010	80.05
7	1.535	1.6930	84.65
8	1.323	1.7354	86.77
9	1.129	1.7742	88.71

Effect of adsorbate ion concentration: The effect of adsorbate ion concentration is studied by taking 5, 7, 10, 12, 15, 20 and 25 mg/L with an optimum pH value. The rate of Mn(II) ion adsorption on *Ipomoea batatas* is achieved as presented in the Table-2. The percentage removal decreased with increase of initial concentration of the Mn(II) ion. This may be due to the lack of available active sites for the adsorption of high initial concentration of Mn(II) ion.

TABLE-2
EFFECT OF ADSORBATE CONCENTRATION ON ADSORPTION OF Mn(II)

Concentration (M)	*Ipomea batatas*		Removal (%)
	C_e (mg/L)	Q_e (mg/g)	
5	0.489	0.9022	90.22
7	1.120	1.1760	84.00
10	2.400	1.5200	76.00
12	3.360	1.7280	72.00
15	4.800	2.0400	68.00
20	7.200	2.5600	64.00
25	10.000	3.0000	60.00

Effect of adsorbent dose: It is important to study the effect of dose of adsorbent to find out the optimum amount of carbon required to remove Mn(II) ion. The effect of adsorbent dose studies is observed from 1-20 mg/L and is shown in Table-3. The equilibrium value of amount adsorbed (Q_e) decreases with increase in dose. The percentage removal of metal ion was found to increase exponentially with the increase in dose of adsorbent. 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 relative increase in the extent of removal of Mn(II) ion is found to be insignificant after a dose 5 g/L in the case of *Ipomoea batatas* which is fixed as the optimum dose of adsorbent.

Effect of contact time: In the adsorption system contact time place a vital role, irrespective of the other experimental parameters that affects the adsorption kinetics. The effect of contact time on the per cent removal of Mn(II) ion was investigated at the optimum initial concentration of Mn(II) ion and the data are represented in Table-4. It was found that the removal of metal ion increases with

TABLE-3
EFFECT OF ADSORBENT DOSE ON ADSORPTION OF Mn(II)

Dose	*Ipomea batatas*		Removal (%)
	C_e (mg/L)	Q_e (mg/g)	
1	4.000	6.0000	60.00
2	3.100	3.4500	69.00
3	2.284	2.5720	77.16
4	1.700	2.0750	83.00
5	1.260	1.7480	87.40
6	1.000	1.5000	90.00
8	0.730	1.1588	92.70
10	0.570	0.9430	94.30
15	0.410	0.6393	95.90
20	0.330	0.4835	96.70

TABLE-4
EFFECT OF CONTACT TIME ON ADSORPTION OF Mn(II)

Time (min)	*Ipomea batatas*		Removal (%)
	C_e (mg/L)	Q_e (mg/g)	
10	3.400	1.3200	66.00
20	2.710	1.4580	72.90
30	2.400	1.5200	76.00
40	2.190	1.5620	78.10
50	2.100	1.5800	79.00
60	1.960	1.6080	80.40
70	1.950	1.6100	80.50
80	1.900	1.6200	81.00
90	1.820	1.6360	81.80

increase in contact time to some extent. The removal of metal ion (in terms of metal adsorbed *i.e.*, Q_e) by the adsorbent (*Ipomoea batatas*) increases, reaches maximum value and then decreases with the increase in contact time (may be due to desorption process). The relative increase in the extent of removal of metal ion (Q_e) after 50 min of contact time is negligible and hence it is fixed as the optimum contact time.

Effect of common ions: The presence of the common ions along with manganese invariably implies that there is a competition for available adsorption sites. Several experiments are carried out to investigate whether the Mn(II) ions are really adsorbed on different sites. It is evident that some adsorption sites can adsorb only certain solutes and not all solutes. The presence of other solutes will reduce the adsorption of any given solute to some extent. Moreover, the adsorption of the other ions affects the recovery of Mn(II) ion directly. In potable water and in some industrial effluents, the main cation is Fe^{2+} ion and the anion is F^-. 100 mL of 10 mg/L solution as Mn(II) ion containing each of the above ions (50 or 100 mg/L) was shaken with 5 g *Ipomoea batatas* at a pH 7.20. It was shown in Table-5 that the influence of Fe^{2+} on the adsorption of Mn(II) ion were rather significant since they compete for the

TABLE-5
EFFECT OF FLUORIDE ION AND Fe(II) ION CONCENTRATION

Mn(II) ion concentration (M)	F^- ion concentration			Fe^{2+} ion concentration		
	Ipomea batatas		Removal (%)	*Ipomea batatas*		Removal (%)
	C_i	C_e		C_i	C_e	
10	0.5	1.05	89.50	0.5	1.19	88.10
10	1.0	1.41	85.90	0.7	1.56	84.40
10	1.5	1.81	81.90	0.9	1.94	80.60
10	2.0	2.27	77.30	1.1	2.43	75.70
10	2.5	2.73	72.70	1.3	2.89	71.10
10	3.0	3.20	68.00	1.5	3.40	66.00
10	3.5	3.77	62.30	1.7	4.06	59.40
10	4.0	4.38	56.20	1.9	4.56	54.40

active surface with manganese ions at this pH. In present study, the results indicate that the concentrations of added elements decreases the adsorption efficiency of *Ipomoea batatas* in the removal of manganese and also it reveals that the efficiency slightly decreases when Fe^{2+} ion concentration increases. This also supports that there is a more competition between Mn^{2+} and Fe^{2+} ions into outer surface of the *Ipomoea batatas*.

Adsorption isotherms: Adsorption isotherms are essential for the description of how metal ion concentration will interact with activated carbon surface and are useful to optimize the use of activated carbon as adsorbents for the removal of manganese ion. The equilibrium adsorption isotherms are one of the most important data to understand the sorption mechanism. Several isotherm equations are available and three important isotherms are selected in this study, *i.e.*, Langmuir, Freundlich and Dubinin-Radushkevich isotherms. Both Freundlich and Langmuir models were used for the evaluation of experimental results.

The Freundlich model is as follows:

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

Freundlich adsorption isotherm in its usual logarithmic form as follows:

$$\log (q_e) = 1/n \log (C_e) + \log (K_f) \quad (2)$$

where, K_f and 1/n are the Freundlich constants, q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (in mg/g), C_e is the equilibrium concentration of fluoride (in mg/L)[15].

Linear plots of log (C_e) *versus* log (q_e) at different manganese ion concentrations are applied to confirm the applicability of Freundlich isotherm model for the removal of Mn(II) ion are shown in Fig. 1 (Table-6). The linear plot confirm about the monolayer coverage of manganese ions on various adsorbent carbons at various concentrations of sorptive (temperature: 30 ± 1 ºC) of Mn(II) ions at the surface of sorbent materials[16]. The Freundlich constants, *i.e.*, K_f and 1/n for the systems were obtained by intercept and slope of the line. The numerical value of K_f and 1/n for *Ipomoea batatas* are 0.19 and 0.38. The fractional value of (1/n) indicates that the

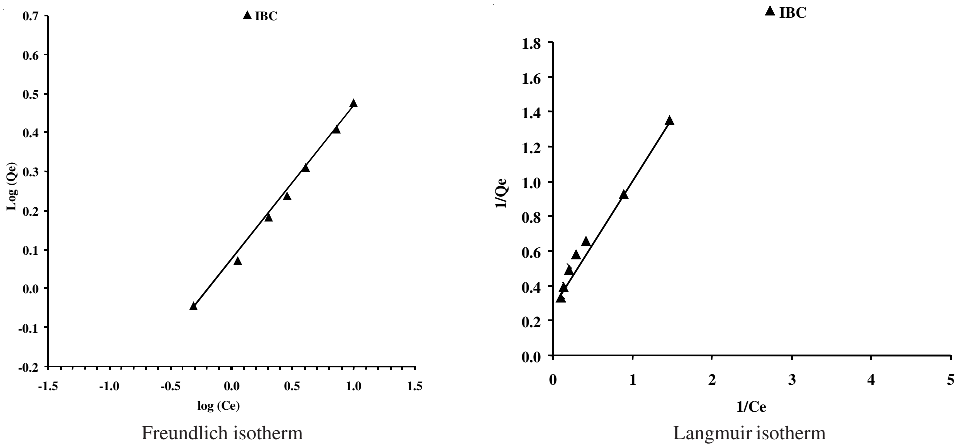

Fig. 1. Isotherm of *Ipomea batatas* carbon

TABLE-6
ADSORPTION ISOTHERM PARAMETERS

Isotherm	Parameter	IBC
Langmuir isotherm	a	0.3627
	b	0.3330
	r	0.9475
	R^2	0.8978
	R_L	0.2309
Freundlich isotherm	K_f	0.1376
	1/n	0.3410
	r	0.9928
	R^2	0.9857

surface of sorbent is of the heterogeneous type with an exponential distribution of energy sites[17]. The higher numerical values of K_f confirm the significant affinity of metal ions for activated carbon.

Langmuir isotherms: The most important model of monolayer adsorption came from the work of Langmuir[21]. The Langmuir adsorption isotherm assumes that the adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule (monolayer) and the sites are homogeneous. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

The observed linear relationships as evidenced by r-values close to unity (0.9) confirmed that these two adsorption isotherms are applicable (Table-6).

The applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate on outer surface of the adsorbent. Further, the essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor and describe the type of isotherm defined by;

$$R_L = 1/(1 + bC_i)$$

where, C_i is the initial concentration of Mn(II) ion (in mg/L) and b is the Langmuir constant (in g/L). The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study the value of R_L (Table-6) for *Ipomoea batatas* 0.37, indicating that the sorption process is favourable for all these low-cost adsorbents. From Fig. 1, it is found that the R^2 value for Langmuir model is near to unity (0.9 ± 0.1) and hence the process of removal of Mn(II) using treated biosorbents follows the Langmuir isotherm well. The Langmuir and Freundlich parameters for the biosorption of Mn(II) ion onto activated carbon are given in Table-6.

Conclusion

The *Ipomoea batatas* substrate seems to have very efficient and economical for removing toxic heavy metal ion such as Mn(II) from industrial waste water. For the preparation of the substrate raw materials employed are widely available and inexpensive. Its metal ion binding capacity is appreciably high. Thus, it can be concluded that *Ipomoea batatas* seems to offer a cheap and useful products for effective removal and recovery of toxic heavy metal ions from industrial effluents. The ion can be recovered thereby solving the problems of toxic effect of waste water on living organism, this also helps to solve wastewater pollution.

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