



ADSORPTION CAPACITY OF Mn (II) FROM WATER AND WASTEWATER USING FLY ASH AS AN ADSORBENT

*Dr. P. P. Vishwakarma

Associate Professor Chemistry Sahu Jain College Najibabad, Distt-Bijnor 246763(UP).

*Corresponding Author: Dr. P. P. Vishwakarma

Associate Professor Chemistry Sahu Jain College Najibabad, Distt-Bijnor 246763(UP).

Article Received on 21/05/2021

Article Revised on 11/06/2021

Article Accepted on 01/07/2021

ABSTRACT

Fly ash was found to have good adsorption capacity for Mn (II) ion. Studies indicated that adsorption of Mn (II) ion increases with increase in pH and a contact time of 60 minutes was found to be optimum. The effect of contact time, adsorbent dosage, pH of system and initial concentration on the kinetics of adsorption was studied. The rate constants for the removal of Mn(II) with adsorbent for varying metal ion concentration showed it to be a first order kinetics. Adsorption data was fitted well into Freundlich adsorption isotherm.

KEYWORDS: Fly ash, Adsorption, pH, Manganese, Batch adsorption technique.

INTRODUCTION

The removal of metal ions like Mn (II) ion 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 water use. These include training laundry and ceramic fixtures such as toilets where concentrations are greater than 0.05 mg/l.^[5] Federal relations therefore control discharge limits. In drinking water sources, the secondary maximum contaminant level (SMCL) for Mn(II) ion must not exceed 0.05mg/L.^[6]

Many studies have been conducted on Mn(II) ion removal in the past, including those designed to evaluate chemical dynamics, experiment with packed columns of limestone, and evaluate passive treatment systems.^[7-9] Microbial remediation efforts include designed wetlands, microbial bioreactors, and pellets of mixed microbial cultures etc.^[10-13] Prasenjit Mondal^[14] reported that Mn can be removed by 41% by using GAC. Dinesh Mohan^[15] reported that Mn is removed by using lignite upto 25.84%. M.M.Nassar^[16] reported that removal of manganese ion by adsorption on palm fruit bunch and maize cobs was in the range of 79-50%. M. Saad^[17] reported that manganese is removed from wastewater by using sulphureted activated carbon obtained from burnt date stones. In the present water management study the author prepared some adsorbent materials from agricultural wastes and an attempt was given to remove water soluble Mn (II) ions by adsorption with Fly ash.

EXPERIMENTAL

All the reagents used in the experiment were of analytical grade. A initial stock solution of Mn(II) ion was prepared by dissolving requisite manganese sulphates. A standard solution of Mn(II) ion were prepared by taking different aliquot from stock solution with subsequent dilution with distilled water.

Preparation of Adsorbent

1: Adsorbents and their Characterization

The physico-chemical nature of the adsorbates significantly affects the rate and extent of adsorption of pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents is quite essential in order to have a better insight into the mechanism of the adsorption process. Fly ash was obtained from Obera Thermal Power Plant, Mirzapur, UP (INDIA). They were used as such without any pretreatment just after sieving through 53µm pore size sieve (Table:1).

Constituents	Percentage by weight
SiO ₂	56.04
Al ₂ O ₃	25.90
CaO	2.22
Fe ₂ O ₃	1.26
MgO	0.94
Loss of ignition	13.64
Particle size	53µm
Mean Particle size diameter	48x10 ⁻⁴ cm
Surface Area	5.77 m ² g ⁻¹
Porosity	0.360
Density	3.420 gcm ⁻³

2: Batch adsorption studies

Standard manganese solution preparation: A stock solution of manganese solution used in this study was prepared by dissolving an accurate quantity of 1.000 g of manganese metal in 50 ml of 6N HNO₃ and dilute to 1000 ml. Other concentrations were prepared from this stock solution by dilution. Fresh dilutions were used for each experiment. The entire chemicals used were in analytical grade.

Apparatus

The apparatus used are

1. Atomic absorption spectrophotometer(ECIL AAS4103/AAS4127)
2. Elico-pH Meter
3. Remi shaker(2L)

Analytical method: Mn(II) 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 hollow cathode lamp. Deuterium back ground correction was used and the spectral slit width was 0.2 nm. The working current and wave length were 5.0 mA and 279.5 nm,

respectively. The instrument response was periodically checked by using standard metal solutions.

Sensitivity: for the standard conditions described above, 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 up to concentration of approximately 60 mg/L in aqueous solution.

RESULTS AND DISCUSSION

1: Effect of pH

The effect of pH on adsorption of Mn(II) ion on Fly ash is studied in the range 5.0 to 9.0 pH and the results are summarized in Table 1 and Figure1. The percentage removal of Mn(II) ion increases with increase in the pH from 5.0 to 7.0 and it is almost constant up to pH 9.0. From this study, it is observed that the change in pH is significant up to pH 7.0 and there is no considerable change after the pH 7.0.

Table-1: Effect of pH.

pH of solution	Ce (mg/l)	Qe (mg g ⁻¹)	% Removal
5.00	1.765	1.6470	82.35
6.00	1.234	1.7532	87.66
7.00	0.774	1.8452	92.26
8.00	0.474	1.9052	95.26
9.00	0.324	1.9560	97.80

Table-2: Effect of adsorbate Concentration.

Concentration	Ce (mg/l)	Qe (mg g ⁻¹)	% Removal
5.00	0.235	0.9530	95.30
7.00	0.462	1.3076	93.40
10.00	1.000	1.8000	90.00
12.00	1.536	2.0928	87.20
15.00	2.580	2.4840	82.80
20.00	4.180	3.1640	79.10
25.00	6.000	3.8000	76.00

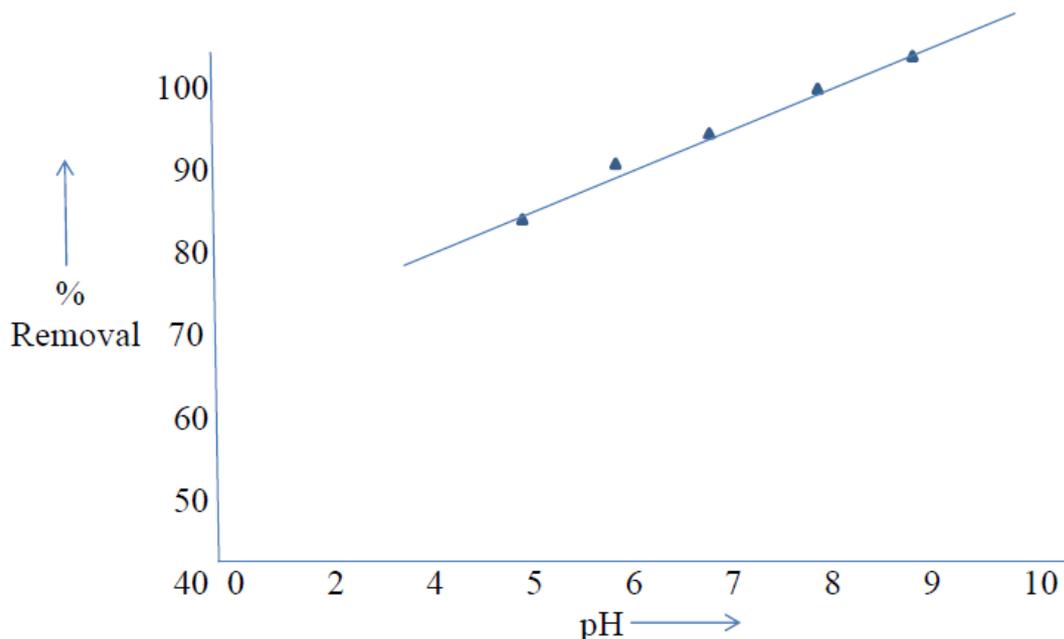


Figure-1: Effect of Adsorbate initial pH.

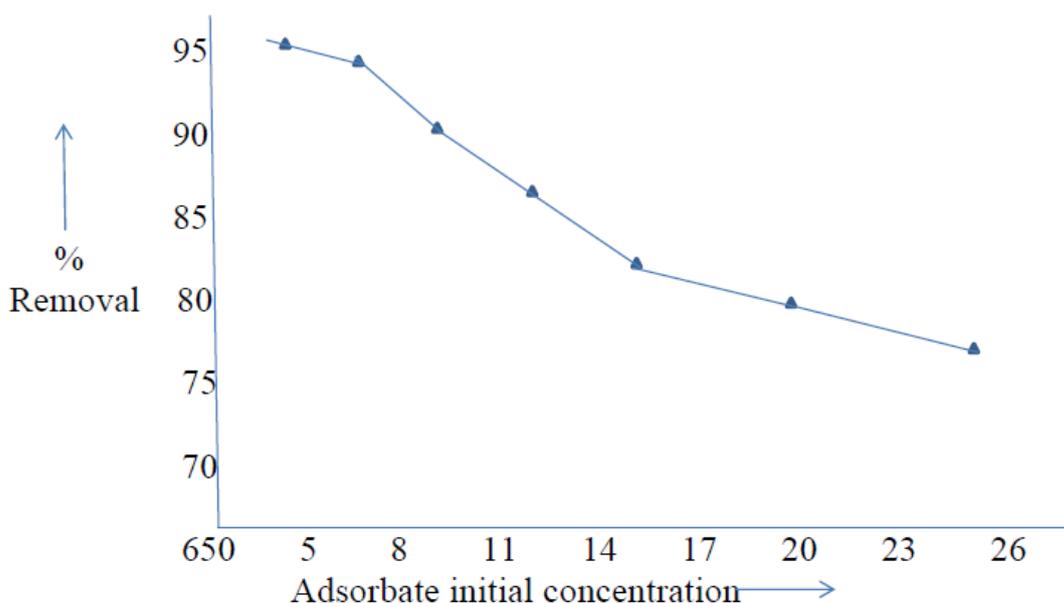


Figure-2: Effect of Adsorbate initial concentration.

2: Effect of adsorbate ion concentration

The effect of adsorbate ion concentration is studied by taking 5,7,10,12,15,20,25 mg/L with an optimum pH value. The rate of Mn(II) ion adsorption on Fly ash is achieved as presented in the Table 2 and Figure 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.

3: Effect of adsorbent dose

The study of effect of dose of adsorbent is necessary and very useful to find out the optimum amount of adsorbent required for the removal of Mn(II) ion. The effect of adsorbent dose studies is observed from 1.00mg/L to

20.00 mg/L and is shown in Table 3 and in Figure 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 5g/L in the case of Fly ash which is fixed as the optimum dose of adsorbent.

Table-3: Effect of adsorbent dose.

Adsorbent Dose	Ce (mg/l)	Qe (mg g ⁻¹)	% Removal
1.00	3.000	7.0000	70.00
2.00	1.800	4.1000	82.00
3.00	0.900	3.0233	90.70
4.00	0.700	2.3825	95.30
5.00	0.210	1.9580	97.90
6.00	0.130	1.6450	98.70
8.00	0.060	1.2425	99.40
10.00	0.040	0.9960	99.60
15.00	0.010	0.6660	99.90
20.00	0.000	0.5000	100.00

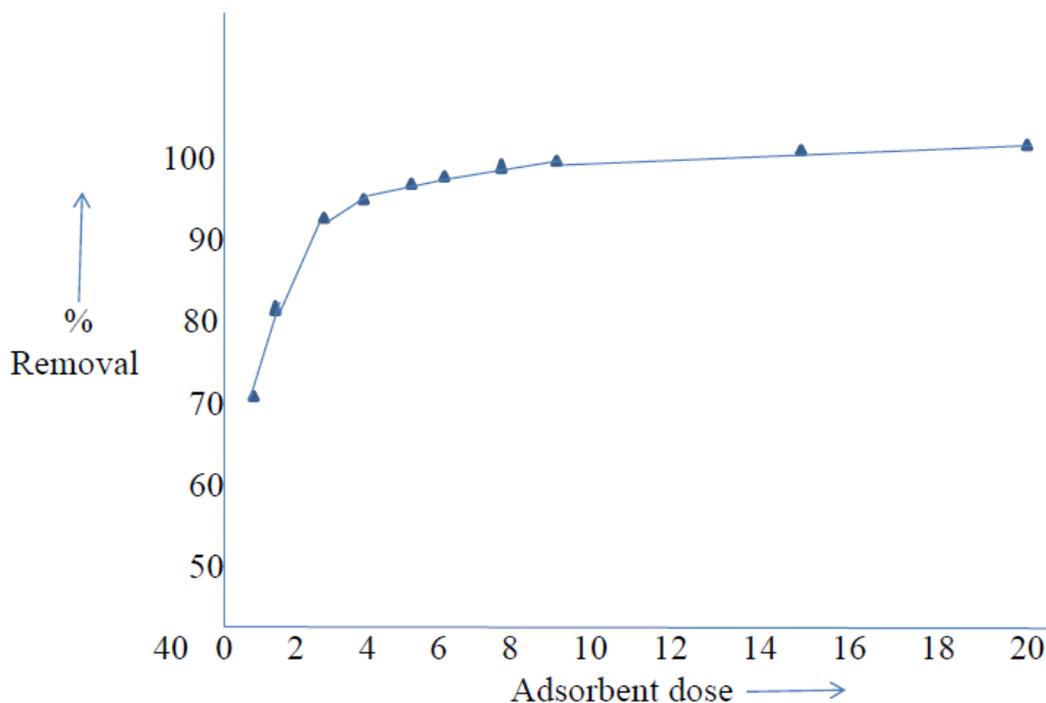


Figure: 3 Effect of Adsorbent Dose.

4: Effect of contact time

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

increase in contact time to some extent. The removal of metal ion (in terms of metal adsorbed i.e. Q_e) by the adsorbent 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 60 minutes of contact time is constant and hence it is the optimum contact time.

Table-4: Effect of Contact time.

Time (minutes)	Ce (mg/l)	Qe (mg g ⁻¹)	% Removal
10	2.464	1.5072	75.36
20	1.960	1.6080	80.40
30	1.560	1.6880	84.40
40	1.200	1.7600	88.00
50	1.080	1.7840	89.20
60	1.050	1.7900	89.50
70	1.050	1.7900	89.50
80	1.050	1.7900	89.50
90	1.050	1.7900	89.50

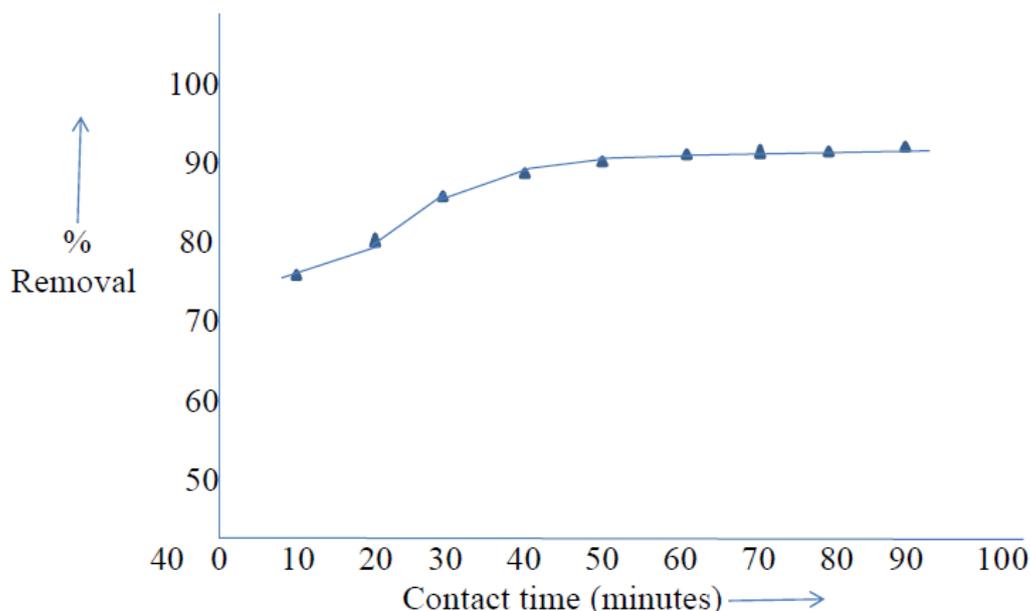


Figure: 4 Effect of Contact time.

Adsorption isotherms

Adsorption isotherms are essential for the description of how metal ion concentration will interact with surface of adsorbent and are useful to optimize the use of adsorbents for the removal of Mn(II). The equilibrium adsorption isotherms are one of the most important data to understand adsorption mechanism. Freundlich and Langmuir models were used for the evaluation of experimental results.

1-Freundlich Isotherm model:

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

Freundlich adsorption isotherm in its usual logarithmic form as follows:

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

Where, K_f and $1/n$ are the Freundlich constants, q_e is the amount of Mn(II) adsorbed per unit weight of the

adsorbent (in mg/g), C_e is the equilibrium concentration of Mn(II) (in mg/L).^[18]

Linear plots of $\log(C_e)$ vs $\log(q_e)$ at different manganese ion concentrations are applied to confirm the applicability of Freundlich isotherm model (Figure 5) and the results were given in Table 6. The linear plot confirm about the monolayer coverage of manganese ions on adsorbent at various concentrations of (temperature:30⁰C) of Mn(II) ions at the surface of adsorbent materials.^[19] The Freundlich constants, i.e. K_f and $1/n$ for the systems were obtained by intercept and slope of the straight line. The numerical value of K_f and $1/n$ are 0.19, and 0.38. The fractional value of $(1/n)$ indicates that the surface of adsorbent is of the heterogeneous type with an exponential distribution of energy sites.^[20] The higher numerical values of K_f confirm the significant affinity of metal ions.

Isotherm Modals	Parameters	Values
Langmuir Isotherm	a	0.4156
	b	0.1638
	r	0.9792
	R ²	0.9587
	RL	0.3791
Freundlich Isotherm	KF	0.1984
	1/n	0.3818
	r	0.9985
	R ²	0.9969

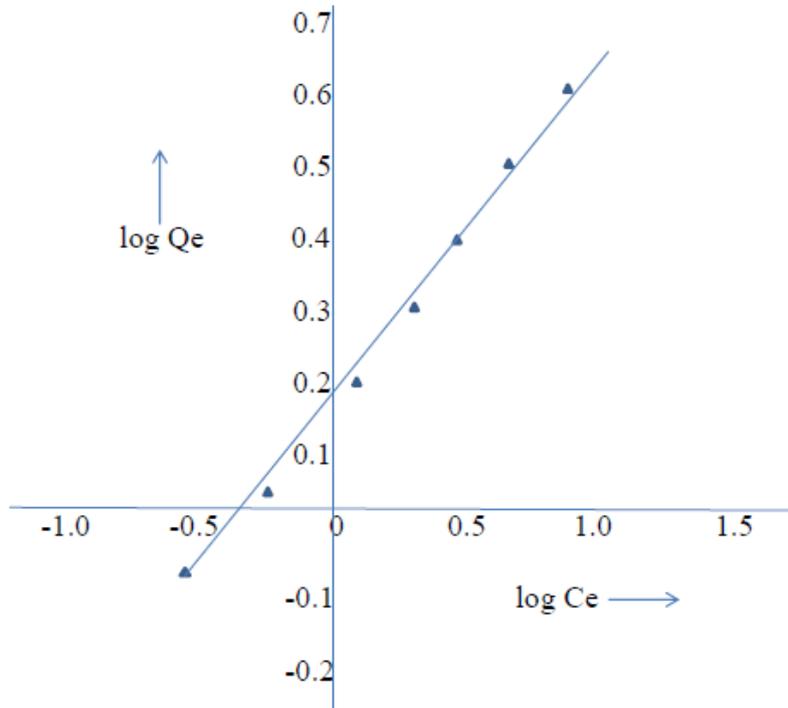


Figure 5: log Qe vs log Ce [Freundlich Isotherm]

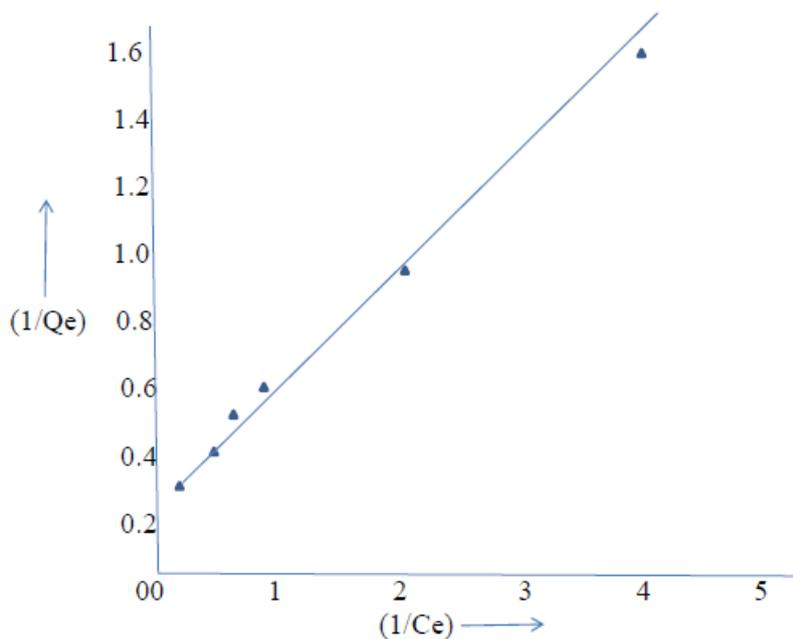


Figure 6: (1/Qe) vs (1/Ce) [Langmuir isotherm].

2-Langmuir isotherms: modal

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 in thickness. 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 Langmuir equation is written as $q_e = ab Ce / (1 + b Ce)$ (3)

where q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/l), a and b are the Langmuir constants related to adsorption capacity

and energy of adsorption, respectively. The linear form of the Langmuir isotherm can be expressed as,

$$1/q_e = (1/a) + (1/ba C_e) \quad \dots\dots(4)$$

When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/ba$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 6. The Langmuir constants 'b' and 'a' are calculated from the slope and intercept with Y-axis.

The isotherm parameters along with the correlation coefficients (r- values) for adsorbents are presented in Table 6. The observed linear relationships as evidenced by r-values close to unity (0.9) confirm that these two adsorption isotherms are applicable.

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;

$$R_L = 1 / (1 + b C_i) \quad \dots\dots(5)$$

Where, C_i is the initial concentration of Mn(II) (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 unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study the value of $R_L = 0.37$ (Table 6) indicating that the adsorption process is favorable for low-cost adsorbent. Where b and C_i are terms appearing in Langmuir isotherm. From Figure 5 and 6 it is found that the R^2 value for Langmuir model is near to unity (0.9 ± 0.1) and hence it follows the Langmuir isotherm model. Table gives the calculations of Langmuir model for the removal of Mn(II) ions and the various constants of this model. The Langmuir and Freundlich parameters for the adsorption of Mn(II) ion onto Fly ash are listed in Table 6. In other words, all of the isotherm models fit very well when the R^2 values are compared in Table 6.

CONCLUSION

The Fly ash 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 raw materials employed are widely available and inexpensive. Its metal ion binding capacity is appreciably high. Thus, it can be concluded that it seems to offer a very cheap and useful products for effective removal and recovery of toxic heavy metal ions from industrial ion can be recovered there by solving the problems of toxic effect of waste water on living organism, this also helps to solve waste water pollution problems.

REFERENCES

1. C.F.Jordan and T.D.Phillips, The removal of iron and manganese from mine water effluents: Symposium on Surface Mining Hydrology, Sedimentology and Reclamation, University of Kentucky, Lexington, KY, 1981; 247-249.
2. R.P.Richards and S.N.Foellmi, Utility battles iron and manganese: Public Works, 1985; 116(6): 91-95.
3. G.R.Watzlaf, Chemical stability of manganese and other metals in acid mine drainage sludge: Bureau of Mines Information Circular 9183, Proceedings of the Mine Drainage and Surface Mining Restoration Conference, Pittsburgh, PA, USA, April 1988; 17-22: 83-90.
4. R.S.Grippio and W.A.Dunson, *Environmental Toxicology and Chemistry*, 1996; 15: 1955-1963.
5. M.D.Kozar and D.P.Brown, Location and site characteristics of the ambient ground water quality monitoring network in West Virginia:
6. U.S. Geological Survey Open-file Report 95-0130, 48 p. (1995).
7. U.S. Environmental Protection Agency, EPA drinking water regulations and health advisories: Office of Water 4301, EPA 822-R- 94-003, 11 p. (1994).
8. V.P.Evangelou, U.M. Sainju and Huang Xiao, Evaluation and quantification of armoring mechanisms of calcite, dolomite, and rock phosphate by manganese, in Younos, Tamim, Diplas, P., and Mostaghimi, S., eds., Land Reclamation; Advances in Research and Technology: St. Joseph, MI, American Society of Agricultural Engineers, Publication 14-92, p. 304-316. (1992).
9. J.A.Gordon and J.L.Burr, Manganese treatment by two methods at abandoned coal sites in North Alabama, in Proceedings, National Symposium on Mining, Hydrology, Sedimentology, and Reclamation: Lexington, KY, University of Kentucky College of Engineering, 1987; 383-393.
10. R.S.Hedin, R.W.Nairn and R.L.P.Kleinmann, Passive treatment of coal mine drainage: Bureau of Mines Information Circular 9389, 35 p.(1994).
11. Jo.Davison, Bio-carb and wetlands - Passive affordable acid mine drainage treatment: Proceedings, 12th Ann. West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, 11 p. (1991).
12. J.A.Gordon and N.S.Chuang, Biological treatment of manganese from mining seepage: Pilot plant studies, in Proceedings of the 44th Purdue Industrial Waste Conference: Boca Raton, FL, CRC Press, 1990; 299-305.
13. W.J.Vail and R.K.Riley, U.S. Patent 5,441,641, Process for removing manganese from solutions including aqueous industrial waste: U.S. Patent Office, 1995; 2.
14. W.J.Vail, S.Wilson and R.K.Riley, Mine water and mine waste; Isolation and culture of manganese-oxidizing bacterium from a man- made cattail wetland: Bureau Mines IC 9183, Proceedings of the Mine Drainage and Surface Mining Restoration Conference, Pittsburgh, PA, USA, April 17-22, p. 399. (1988).
15. Prasenjit Mondal, Chandrajit Balomajumder and Bikash Mohanty, *Journal of Hazardous Materials*,

- 2007; 144(1-2): 420-426.
16. Dinesh Mohan and Subhash Chander, *Journal of Colloid and Interface Science*, 2006; 299(1): 76-87.
 17. M. M. Nassar, K. T. Ewida, E. E. Ebrahiem, Y. H. Magdy, M. H.Mheaedi, *Journal of Environmental Science and Health*, 2005; 39(2): 421 – 434.
 18. <http://www.eea.gov/eng/lish/main/Env2003/Day2/Water/saad.nwri.pdf>
 19. W.J. Weber, Jr., *Physico chemical processes for water quality control*, Chap. 5, Wiley Interscience, New York (1972).
 20. W.J.Weber, J.C. Morris In:Eckenfelder WW, editor. *Advances in water pollution research*. Oxford: Pergamon press, (1964).
 21. J.Hu, G.H.Chen, M.C. Lo, Selective removal and recovery of various heavy metals by maghemite nanopar-ticles. In: *International Symposium on Nanotechnology in Environmental Protection and Pollution*. Asia PacificNanotechnology Forum (APNF), Bangkok, Thailand (2005).
 22. V.K.Gupta., *J. Ind. Inst. Chem. Engg*, 1998; 37: 192-202.