INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE AND TECHNOLOGY
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www.vmsindia.org

STUDIES ON REMOVAL PERFORMANCE OF POROUS ADSORBENT FOR Mn^{2+} IONS FROM AQUEOUS SOLUTION

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ABSTRACT:
Water pollution due to harmful metals present in industrial wastewater stream is a major concern from environmental pollution point of view. In the present work, adsorption technique used for removal of Manganese ion from aqueous solution using Granular Activated Carbon F-300 and F-820 modified in conjunction with 3-Nitrophthalic were carried out at temperature 25 ± 0.1°C The adsorption isotherms of $Mn2^{+}$ on different GAC have been determined and the data fitted reasonably well to Langmuir and Freundlich isotherm for activated carbon. The adsorption parameter using Langmuir and Freundlich isotherm models were analysed for further study.

Keywords: *Adsorption, Manganese, Granular Activated Carbon (GAC), F-300, F-820, 3-Nitrophthalic Acid.*

INTRODUCTION:

Rapid industrialization leading to the severe problem in treatment and disposal of effluents. The effluent coming out of the different industries such as tannery industries, battery manufacturing unit, leather industries contain toxic pollutants and hence require proper treatment before it is discharged into any water bodies. The presence of highly toxic metals such as chromium, cobalt, arsenic, lead, manganese etc. in industrial waste water mainly contaminated the surface and ground water to large extent (Meena, et al., 2010). According to WHO, the maximum permissible limit of Mn^{2+} in drinking water is 0.5 mg/L.(WHO 2003). It therefore becomes necessary to remove toxic metals from wastewaters by an suitable treatment before discharging into the environment. Various methods had been used for the removal of heavy metals such as chemical precipitation (Matthew M. M, et al., 2002), ion exchange (Zbigniew, 2012), coagulation and membrane filter (Mohammad, et.al., 2015) and adsorption (Sud D, et al., 2008, Ghatbandhe, et al., 2009,Gawande, et al., 2012).

Adsorption is a well-established and extensively used method in which porous adsorbents such as Granular activated carbon used for the removal of toxic metal. Because of its low cost and high affinity towards the removal of metal ions it is widely used in industries. The capacity and rate of adsorption vary significantly for different potentially hazardous compound and different commercial carbon. The technique of complex formation between the metal ions and ligand was used in this study to enhance its efficacy for removal of Mn^{2+} metal ion (Nale, et al., 2012, Gunjate, et al., 2014, Datta, et al., 2015, Kinhikar, 2015).

A number of adsorbents have been used by several workers for scavenging toxic metals from their aqueous solution (Hete, et al., 2011, Hussain, et al., 2010, Joseph, et al., 2011). It is therefore proposed to carry out adsorption of Mn^{2+} from aqueous solution by using granular activated carbon in the presence of 3-Nitrophthalic Acid.

MATERIAL AND METHODS:

The reagents of analytical grade were used in present study. The standard solution of Mn^{2+} ion was prepared by dissolving requisite $MnSO_4$ (E-Merck) in 500 ml volumetric flask. Granular activated carbon of selected grades were first subjected to size fractionation by sieving them using a sieve shaker to obtain particle of mesh size 840 u to 1400 u (M/s Jayant Test Siever Mumbai). The sieved particles were washed several times with boiled distilled water until clear lechate was obtained and collected in a clean petridish. Then kept it in an oven for drying to remove moisture at a temperature of 100-110°C and then stored in $CaCl_2$ desiccators until use. 3-Nitrophthalic Acid was purified and recrystallized by standard method. The experimental melting point of 3-Nitrophthalic Acid was determined and compared with the literature value to check the purity. (Expt value: 218.5^{0}C, Lit. Value: 219 ^{0}C) (B.S. Furniss et al.2012). To construct adsorption isotherm of Mn^{2+} ion on GAC loaded with ligand, 0.5 gm of the 3-Nitrophthalic Acid dried Granular

Activated Carbon was shaken with 200 ml of 3-Nitrophthalic Acid solution of a specific concentration for about 5 hrs on a mechanical shaker (Remi Model No.R.S.24).The solution was then filtered off and the carbon particles were washed several time thoroughly with distilled water. These particles were transferred to shaking bottle and then 200 ml Mn^{2+} ion solution of p^H 5 was added to it. The mixture was then stirred for 5 hrs at constant temperature of 25 ±1°C. The initial and final concentration of the Mn^{2+} ion in mg/L was then determined from absorbances measured using spectrophotometer (CHEMITO). The mathematical equation obtained from Beer's law calibration curve constructed between absorbances and concentrations series of standard solutions was used to determine the concentration of Mn^{2+} and concentrations of. The experiments were repeated to ensure reproducible result.

RESULTS AND DISCUSSION:

Batch technique is used to determine adsorption of Mn^{2+} ion on ligand loaded GAC.The concentration of Mn^{2+} on the loaded GAC was determined from equat

$$q_e = (C_0 - C_e) \times \frac{V}{W}$$

Where

q_e = The amount of Mn^{2+}on the ligand loaded GAC in mg/milimole of ligand,

C_o = Initial Concentration of Mn^{2+} in solution in mg/L,

V = Volume of solution in Lit,

W = Weight of the carbon taken.

The adsorption isotherms of ligand loaded GAC obtained by plotting q_e and C_e are shown in and Fig-1and Fig-2.

Experimental data of equilibrium isotherm was tested for adherence to both Langmuir and Freundlich model. The linearised form of Langmuir isotherm can be represented by

$$\frac{1}{q_e} = \frac{1}{bQ^0} \times \frac{1}{Ce} + \frac{1}{Q^0}$$

Where,

Q^o = amount adsorbed per unit weight of the carbon forming a complex monolayer on the adsorbent surface,

b = Langmuir constant.

Freundlich equation on the other hand represented as

$$q_e = k_f\, C_e^{\frac{1}{n}}$$

Above equation may be linearised as

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

A plot of log q_e versus log C_e was fairly showing validity of Freundlich also over a range of concentration. Fig.3 to 6 illustrate the plot of Freundlich and Langmuir and isotherm for GAC (F-300) and GAC (F-820). The plot of $1/q_e$ versus $1/C_e$ found to be linear indicating applicability of Langmuir model. The adsorption parameter Q^o and b are Langmuir constant relating to the adsorption capacity and adsorption energy respectively.The plot of log Ce and logqe shown for Freundlich model. The intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$ and $1/q_e$ versus $1/C_e$ under given set of experimental condition provide values of k_f , 1/n ,Q^0 and b respectively. The corresponding Freundlich and Langmuir constant obtained are listed below inTable-1

The value of k_f and Q° for F-300 and F-820-3-Nitrophthalic acid _Mn^{2+} systems indicating the superiority of the later for this adsorption process

The saturation of monolayer q_e value were used for determination of surface area of the adsorbent For this purpose a plot of $1/q_e$ versus $1/C_e$ helped in determination of $1/Q^o$ and hence Q^o . The surface area of the carbon through Mn^{2+} adsorption can then be represented as

$$S = N\, Q^o A$$

Where,

S =Surface area of adsorbent m^2 /g

N =Avogadro number

A =Cross section area of the adsorbate molecule m^2

Thus it is possible to determine the surface area of the GAC using the technique of adsorbing Mn^{2+}on ligand loaded GAC at the saturation level when a monolayer of the Mn^{2+}would cover entire surface of adsorbent.

The determination of surface area occupied by a single Mn^{2+} ion, were calculated using the expression given by Bruanauer and Emmet.

$$A = 4 \times 0.866\, [M/\sqrt{4N_a} .d]^{2/3}$$

Where,

M=Atomic weight of Manganese (Vogel' 1989)

N = Avogadro number

d = Density of Manganese (7.3 gm/cm^3) (Aldrich Chemistry)

The values of A and the values of S obtained from Q^o and S′ obtained from q_{max} are reported in the Table-2.

CONCLUSION:

The granular activated carbon F-300 and F-820 shows a good potential for the removal of Mn^{2+} from wastewater.GACF-820 modified with 3-Nitrophthalic Acid showed high binding capacity for Mn^{2+} as compared to F-300 probably due to high surface area and more coordinating sites available for approaching metal ion during adsorption. Regression coefficient (R^2) clearly indicates that an experimental data fitted with the Langmuir and Freundlich isotherm. This studies quiet benefitted for the removal of other heavy metal ions from industrial effluents.

ACKNOWLEDGEMENT:

The author is thankful to the Principal of Shivaji Science College Congress Nagar, Nagpur for providing laboratory facilities to carry out the experimental work.

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Table 1: Isotherm Constant for the system F-300 and F-820-3-Nitrophthalic acid _Mn^{2+}

Sr.No	System	Langmuir Constant		Freundlich constant		q_{max}(mg/m mole)
		Q^0	b	1/n	K_f	
1	F-300_ 3-Nitrophthalic acid _Mn^{2+}	1.0493	0.2562	0.549	0.220	0.7750
2	F-820_ 3-Nitrophthalic acid _Mn^{2+}	1.3315	0.3427	0.365	0.5296	1.0500

Table 2: Surface area of Granular Activated Carbon

Sr.No	System	A (m^2)	S (cm^2/gm)	S'(cm^2/gm)
1	F-300_3-Nitrophthalic acid _Mn^{2+}	5.875×10^{-16}	2.7029×10^3	1.9964×10^3
2	F-820_3-Nitrophthalic acid _Mn^{2+}	5.875×10^{-16}	3.4299×10^3	2.7048×10^3

Table 3: Equations and Regression Analysis Data.

Sr. No	System	Langmuir Equation	Reg. Coefficient	Freundlich Equation	Reg. Coefficient
1	F-300_3-Nitrophthalic acid _Mn^{2+}	y = 3.7193x + 0.9531	R^2= 0.9159	y = 0.5494x - 0.6628	R^2 = 0.9013
2	F-820_3-Nitrophthalic acid _Mn^{2+}	y = 2.1914x + 0.7513	R^2 =0.9591	y = 0.2882x - 0.2767	R^2 = 0.9293

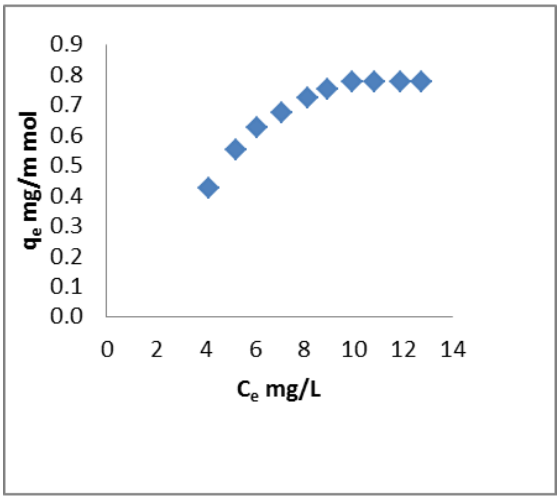

Fig-1 Adsorption Isotherm
System: F-300_ 3-Nitrophthalic acid

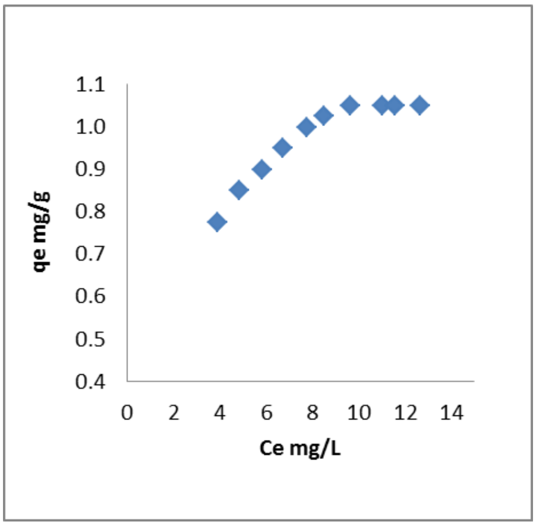

Fig-2 Adsorption Isotherm
System: F-820_ 3-Nitrophthalic acid

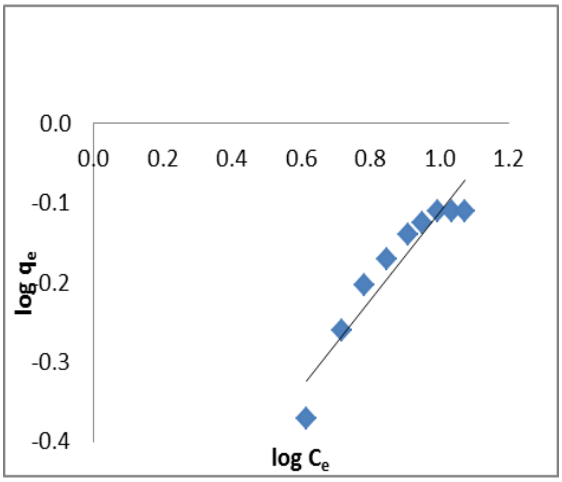

Fig 3- Freundlich Adsorption Isotherm
System: F-300_ 3-Nitrophthalic acid _Mn^{2+}

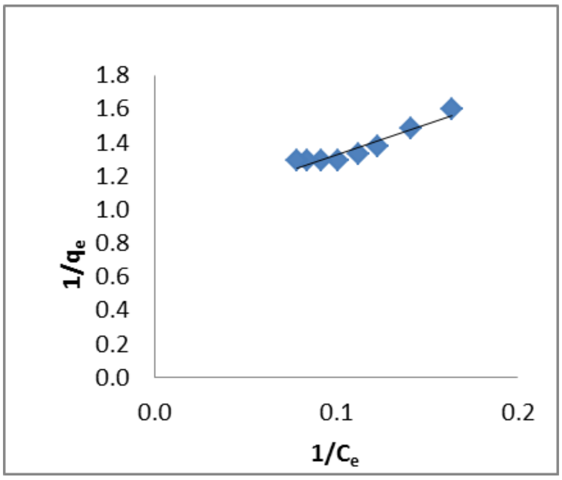

Fig 4- Langmuir Adsorption isotherm
System: F-300_ 3-Nitrophthalic acid _Mn^{2+}

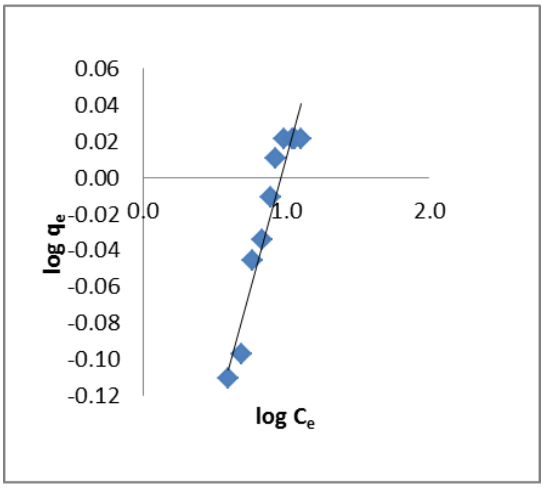

Fig 5- Freundlich Adsorption isotherm
System: F-820_ 3-Nitrophthalic acid _Mn^{2+}

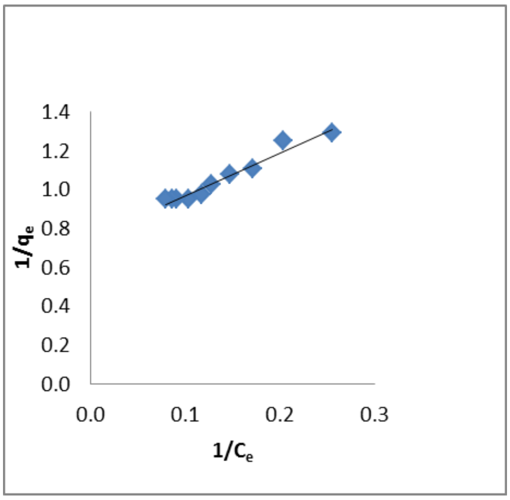

Fig 6- Langmuir Adsorption Isotherm
System: F-820_ 3-Nitrophthalic acid _Mn^{2+}