

Formulation of Mathematical Model for the Investigation of Removal Capacity of Modified Adsorbents

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Abstract: In present study data based mathematical simulations was developed to established empirical relation between input and output variables. Simulation is the process of using a model to study the behavior and performance of an actual and theoretical system. In a simulation, a model can be used to study the existing characteristic of a system. Simulation allows for the evaluation of a model to optimize the performance of adsorption system or to make predication about a real system.

Adsorption studies were carried out at constant temperature of $25 \pm 1^{\circ}\text{C}$ to scavenge the manganese ions from synthetic wastewater using chemically modified adsorbents. In present work Filtrasorb-400 (F-400) and Filtrasorb-300 (F-300) Granular Activated Carbon in conjunction with Resorcinol at pH 5 were used as adsorbents. To predict the optimum performance of the system experimental data were used to established mathematical model using Buckingham theorem and contemporary mathematical tools.

Keywords: Adsorption, Buckingham theorem, Manganese, Resorcinol.

INTRODUCTION

Adsorption is one of the efficient methods used for decontamination of organic and inorganic impurities present in small traces from wastewater. In present study Granular activated carbon (GAC) was used as an adsorbent as it possessed large surface area, porosity and nonhazardous nature with respect to temperature, pressure and pH [1-5]. Mathematical modeling is simple method, readily used to predict the parameters to optimized the removal efficiency of GAC. Currently, a variety of mathematical models have been used to describe and predict the adsorption isotherm of GAC with different toxic metals [6-11]. The experimental data were used to established the relationship between the amount of adsorbate adsorb on selected adsorbent at constant temperature $25 \pm 1^{\circ}\text{C}$

C and pH 5. In present study Buckingham Π theorem was adopted to develop dimensionless Π terms for reduction of input parameters. Adsorption isotherm model was used to calculate the design parameters such as adsorption capacity and isotherm constants.

Adsorption Isotherm:

Adsorption isotherm is the mathematical relationship between the quantity of adsorbate accumulated on the surface of adsorbent at constant temperature and pH. Glueckauf developed the first equilibrium theory of multicomponents [12]. This theory mainly used to study the multicomponent interference effects in the adsorption process of metal content on GAC [13-14]. Variety of applications of adsorption isotherm model has been reported by many researchers [15-26].

In this laboratory work was initiated to remove manganese metal from synthetic wastewater using coal-based GAC in presence of organic ligand such as resorcinol. Resorcinol is derivative of benzene containing two OH groups highly affect the removal process because of the formation of coordinate bond with metal ion during adsorption.

MATERIALS AND METHODS

Bituminous coal based Granular Activated Carbons namely Filtrasorb 400 (F- 400) and Filtrasorb 300 (F-300) supplied by Calgon Carbon Corporation Limited, Pittsburgh, USA were used as adsorbents. The partials of approximately equal sized were obtained by using sieve (M/s Jayant Test Sieves, Mumbai) and particles retained between 1400 micron and 1600 micron were used in the present study. The GACs particles were considered fit for use when the distilled water obtained after washing was visibly clear and then dried in an oven at a temperature of $100-110^{\circ}\text{C}$ for one hour and stored in CaCl_2 desiccator until use. All chemicals used were of AR

grade. A stock solution of Mn^{2+} ions was prepared by dissolving required quantity of Manganese Sulphate (E. Merck) in freshly prepared distilled water. The series of solutions of known concentration of Mn^{2+} ions were prepared from the stock solution in 50 ml volumetric flask. Spectrophotometrically, standard calibration curve was established for Mn^{2+} , from these standard solutions [27].

A sample of resorcinol was recrystallised by the routine method. The purity of sample was tested from the measurement of melting point of resorcinol. The observed melting point $109.5^{\circ}C$ was compared with the literature value ($110^{\circ}C$) [28]. All experimental systems were carried out in batches of five units at a time. For surface modification of GAC, 0.5 g of the carbon and 200 ml of 0.001M resorcinol solution were taken in each clean reagent bottle. The solution was stirred for about five hours using Remi stirrers (Type L-157 M/s Remi Udyog, Mumbai, India) in a constant temperature bath at around 500 rpm. The solution was then filtered off and the carbon was washed thoroughly with distilled water.

The dried carbon particles were then transferred to a clean shaking bottle of wide mouth and 200 ml of manganese solution of pH = 5 was added carefully. The pH of all experimental solution was adjusted to 5

using nitric acid, sodium hydroxide and buffer solutions. All the systems were then stirred for five hours completely with the same speed at constant temperature $25 \pm 0.5^{\circ}C$. The initial and final concentrations of the Mn^{2+} were then determined spectrophotometrically (Type 166 Systronics India Ltd.) at a wavelength of 525 nm.

RESULTS AND DISCUSSION

The mathematical interpretation of the adsorption isotherms for different grades of GAC was studied using mathematical model. These isotherms for different grades of granular activated carbon are shown in Fig.1. The amount of manganese on the GAC, chemically modified by ligand (resorcinol) was determined using the equation

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

where,

q_e = Concentration of Mn^{2+} on the ligand loaded GAC in mg/mill moles of ligand

C_o = Initial concentration of Mn^{2+} in solution in mg/L.

C_e = Final concentration of the Mn^{2+} in solution in mg/L.

V = Volume of solution in liters

W = Millimoles of the ligand actually present on GAC.

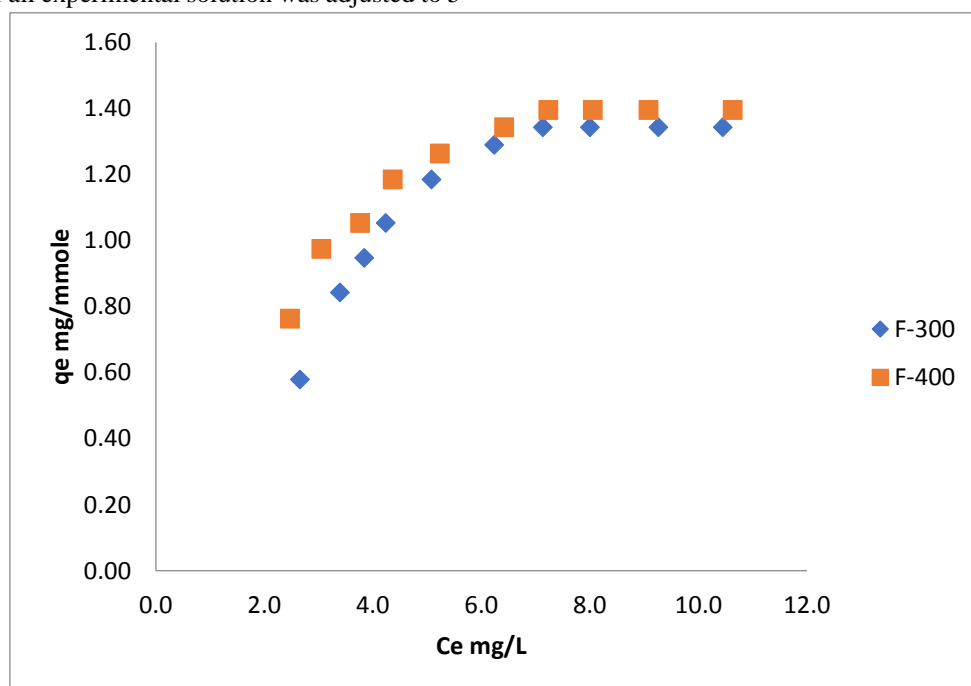


Fig. 1: Adsorption Isotherm
System: GAC- Resorcinol- Mn^{2+}

Formulation of Mathematical Model

Data based mathematical simulations was developed to established empirical relationship between inputs

and outputs. Simulation is the process of using a model to study the behavior and performance of an actual and theoretical system. In a simulation, models

can be used to study the existing characteristics of a system. Simulations allow for the evaluation of a model to optimize the system performance or to make predictions about a real system. The mathematical model is developed using experimental data and contemporary mathematical tools.

The Buckingham theorem is suitable for developing the model because it states that if the inputs and

outputs can be represented as dimensionless Π terms by dimensional analysis, then they can be represented by their product and the indices can be obtained by multiple regressions. Any Physical quantity that undergoes a change is called variable. If particular variable is changed without affecting other variables, it is called independent variable. Similarly if a particular variable changes in response to variation of one or more variable it is called dependent variable.

The variables are listed in below.

Sr. No.	Variables	Unit	Type
1	C_o = Initial Concentration of solution	mg/L	Independent Variable
2	R = Rotation per minute	sec^{-1}	Independent Variable
3	C_e = Final Concentration of solution	mg/L	Independent Variable
4	V_s = Volume of solution	ml	Independent Variable
5	A_{pc} = Average particle size of carbon	cm^2	Independent Variable
6	V_B = Volume of shaking bottle	ml	Independent Variable
7	W_c = weight of Carbon	Gm	Independent Variable
9	T = Time	Sec	Independent Variable
10	S_{ac} = Surface area of Carbon	cm^2/gm	Independent Variable
11	M = Molecular weight	gm/mole	Independent Variable
12	q_e = Manganese ion adsorbed on GAC	mg/m. mole	Dependent Variable

Buckingham's Π theorem was adopted to develop dimensionless Π terms for reduction of process parameters. Dimension analysis to reduce number of independent variables

$$DV2 = f(IV1, IV2, IV3, IV4, IV5, \dots) \quad (a)$$

Where

IV = Independent Variable

DV = Dependent Variable

$$\Pi_4 = k \times \Pi_1^a \times \Pi_2^b \times \Pi_3^c$$

(b)

Where

Π_4 = Function of dependent variable

Π_1, Π_2, Π_3 = Functions of independent variables

a, b, c = Constants

K = Proportionality Constant

$$\begin{aligned} \Pi_1 &= \frac{C_o}{C_e} \\ \Pi_2 &= \frac{W_c S_{ac}}{A_{pa}} \\ \Pi_3 &= \frac{R \times T \times V_c}{pH \times V_s} \\ \Pi_4 &= \frac{q_e}{M} \end{aligned}$$

To solve equation (b) Taking Log on both side

$$\text{Log } \Pi_4 = n \text{ Log } K + a \text{ Log } \Pi_1 + b \text{ Log } \Pi_2 + c \text{ Log } \Pi_3 \quad (c)$$

Where,

$$\Pi_1' = \text{Log } \Pi_1,$$

$$\Pi_2' = \text{Log } \Pi_2$$

$$K' = \text{Log } K$$

$$\Pi_3' = \text{Log } \Pi_3$$

$$\Pi_4' = \text{Log } \Pi_4$$

$$\Pi_4' = nK' + a \Pi_1' + b \Pi_2' + c \Pi_3'$$

$$\Sigma \Pi_4' = nK' + a \Sigma \Pi_1' + b \Sigma \Pi_2' + c \Sigma \Pi_3' \quad (d)$$

$$\Sigma \Pi_4' \times \Pi_1' = nK' \times \Sigma \Pi_1' + a \Sigma \Pi_1' \times \Pi_1' + b \Sigma \Pi_2' \times \Pi_1' + c \Sigma \Pi_3' \times \Pi_1' \quad (e)$$

$$\Sigma \Pi_4' \times \Pi_2' = nK' \times \Sigma \Pi_2' + a \Sigma \Pi_1' \times \Pi_2' + b \Sigma \Pi_2' \times \Pi_2' + c \Sigma \Pi_3' \times \Pi_2' \quad (f)$$

$$\Sigma \Pi_4' \times \Pi_3' = nK' \times \Sigma \Pi_3' + a \Sigma \Pi_1' \times \Pi_3' + b \Sigma \Pi_2' \times \Pi_3' + c \Sigma \Pi_3' \times \Pi_3' \quad (g)$$

TABLE

Table: I
Adsorption Isotherm
System: F-300_ Resorcinol _Mn²⁺

Sr. No.	C ₀ IV1	C _e IV2	pH IV3	A _{pc} IV4	R IV5	V _s IV6	V _B IV7	W _c IV8	T IV9	S _{ac} IV10	M IV11	q _e DVI
1	3.2368	2.6579	5	1500	500	200	300	0.5	300	1100	184.106	0.5789
2	4.2368	3.3947	5	1500	500	200	300	0.5	300	1100	184.106	0.8421
3	4.7895	3.8421	5	1500	500	200	300	0.5	300	1100	184.106	0.9474
4	5.2895	4.2368	5	1500	500	200	300	0.5	300	1100	184.106	1.0526
5	6.2632	5.0789	5	1500	500	200	300	0.5	300	1100	184.106	1.1842
6	7.5263	6.2368	5	1500	500	200	300	0.5	300	1100	184.106	1.2895
7	8.4737	7.1316	5	1500	500	200	300	0.5	300	1100	184.106	1.3421
8	9.3421	8.0000	5	1500	500	200	300	0.5	300	1100	184.106	1.3421
9	10.6053	9.2632	5	1500	500	200	300	0.5	300	1100	184.106	1.3421
10	11.7895	10.4474	5	1500	500	200	300	0.5	300	1100	184.106	1.3421

Table: II
Adsorption Isotherm
System: F-400_ Resorcinol _Mn²⁺

Sr. No.	C ₀ IV1	C _e IV2	pH IV3	A _{pc} IV4	R IV5	V _s IV6	V _B IV7	W _c IV8	T IV9	S _{ac} IV10	M IV11	q _e DVI
1	3.2368	2.4737	5	1500	500	200	300	0.5	300	1100	184.106	0.7632
2	4.0263	3.0526	5	1500	500	200	300	0.5	300	1100	184.106	0.9737
3	4.8158	3.7632	5	1500	500	200	300	0.5	300	1100	184.106	1.0526
4	5.5526	4.3684	5	1500	500	200	300	0.5	300	1100	184.106	1.1842
5	6.5000	5.2368	5	1500	500	200	300	0.5	300	1100	184.106	1.2632
6	7.7632	6.4211	5	1500	500	200	300	0.5	300	1100	184.106	1.3421
7	8.6316	7.2368	5	1500	500	200	300	0.5	300	1100	184.106	1.3947
8	9.4474	8.0526	5	1500	500	200	300	0.5	300	1100	184.106	1.3947
9	10.4737	9.0789	5	1500	500	200	300	0.5	300	1100	184.106	1.3947
10	12.0263	10.6316	5	1500	500	200	300	0.5	300	1100	184.106	1.3947

Table: III
Adsorption Isotherm Data Converted to Dimensionless Analysis
System: F-300_ Resorcinol _Mn²⁺

Sr. No.	Π ₁	Π ₂	Π ₃	Π ₄	Log (Π ₁) Π' ₁	Log (Π ₂) Π' ₂	Log (Π ₃) Π' ₃	Log (Π ₄) Π' ₄
1	1.2178	0.3667	20000	0.0031	0.0856	-0.4357	4.3010	-2.5024
2	1.2481	0.3667	20000	0.0046	0.0962	-0.4357	4.3010	-2.3397
3	1.2466	0.3667	20000	0.0051	0.0957	-0.4357	4.3010	-2.2885
4	1.2484	0.3667	20000	0.0057	0.0964	-0.4357	4.3010	-2.2428
5	1.2332	0.3667	20000	0.0064	0.0910	-0.4357	4.3010	-2.1916
6	1.2068	0.3667	20000	0.0070	0.0816	-0.4357	4.3010	-2.1547
7	1.1882	0.3667	20000	0.0073	0.0749	-0.4357	4.3010	-2.1373
8	1.1678	0.3667	20000	0.0073	0.0674	-0.4357	4.3010	-2.1373
9	1.1449	0.3667	20000	0.0073	0.0588	-0.4357	4.3010	-2.1373
10	1.1285	0.3667	20000	0.0073	0.7475	-3.9216	38.7093	-2.1373
Σ	12.0301	3.6667	200000	0.0612	1.4951	-7.8431	77.4185	-22.2689

Table: IV
Adsorption Isotherm Data Converted to Dimensionless Analysis
System: F-400_ Resorcinol _Mn²⁺

Sr. No.	Π_1	Π_2	Π_3	Π_4	$\text{Log}(\Pi_1)$ Π'_1	$\text{Log}(\Pi_2)$ Π'_2	$\text{Log}(\Pi_3)$ Π'_3	$\text{Log}(\Pi_4)$ Π'_4
1	1.3085	0.3667	20000	0.0041	0.1168	-0.4357	4.3010	-2.3825
2	1.3190	0.3667	20000	0.0053	0.1202	-0.4357	4.3010	-2.2766
3	1.2797	0.3667	20000	0.0057	0.1071	-0.4357	4.3010	-2.2428
4	1.2711	0.3667	20000	0.0064	0.1042	-0.4357	4.3010	-2.1916
5	1.2412	0.3667	20000	0.0069	0.0938	-0.4357	4.3010	-2.1636
6	1.2090	0.3667	20000	0.0073	0.0824	-0.4357	4.3010	-2.1373
7	1.1927	0.3667	20000	0.0076	0.0765	-0.4357	4.3010	-2.1206
8	1.1732	0.3667	20000	0.0076	0.0694	-0.4357	4.3010	-2.1206
9	1.1536	0.3667	20000	0.0076	0.0621	-0.4357	4.3010	-2.1206
10	1.1312	0.3667	20000	0.0076	0.0535	-0.4357	4.3010	-2.1206
Σ	12.2792	3.6667	200000.0000	0.0660	0.8861	-4.3573	43.0103	-21.8767

Table: V
Logarithmic Value
System: F-300_ Resorcinol _Mn²⁺

$\Pi_1' \times \Pi_1'$	$\Pi_1' \times \Pi_2'$	$\Pi_1' \times \Pi_3'$	$\Pi_1' \times \Pi_4'$	$\Pi_2' \times \Pi_2'$	$\Pi_2' \times \Pi_3'$	$\Pi_2' \times \Pi_4'$	$\Pi_3' \times \Pi_3'$	$\Pi_3' \times \Pi_4'$	$\Pi_4' \times \Pi_4'$
0.0073	-0.0373	0.3681	-0.2142	0.1899	-1.8741	1.0904	18.4989	-10.7630	6.2622
0.0093	-0.0419	0.4139	-0.2252	0.1899	-1.8741	1.0195	18.4989	-10.0631	5.4742
0.0092	-0.0417	0.4117	-0.2191	0.1899	-1.8741	0.9972	18.4989	-9.8431	5.2375
0.0093	-0.0420	0.4145	-0.2161	0.1899	-1.8741	0.9772	18.4989	-9.6463	5.0301
0.0083	-0.0397	0.3915	-0.1995	0.1899	-1.8741	0.9550	18.4989	-9.4263	4.8033
0.0067	-0.0356	0.3510	-0.1759	0.1899	-1.8741	0.9388	18.4989	-9.2672	4.6425
0.0056	-0.0326	0.3221	-0.1601	0.1899	-1.8741	0.9313	18.4989	-9.1925	4.5680
0.0045	-0.0293	0.2897	-0.1440	0.1899	-1.8741	0.9313	18.4989	-9.1925	4.5680
0.0035	-0.0256	0.2527	-0.1256	0.1899	-1.8741	0.9313	18.4989	-9.1925	4.5680
0.5588	-2.9316	3.2152	-1.6795	1.7087	-16.8667	8.7719	166.4897	-86.5867	4.5680
$\Sigma 0.6224$	$\Sigma -3.2573$	$\Sigma 6.4305$	$\Sigma -3.3589$	$\Sigma 3.4175$	$\Sigma -33.7335$	$\Sigma 17.5438$	$\Sigma 332.9795$	$\Sigma -173.1733$	$\Sigma 49.7216$

Table: VI
Logarithmic Value
System: F-400_ Resorcinol _Mn²⁺

$\Pi_1' \times \Pi_1'$	$\Pi_1' \times \Pi_2'$	$\Pi_1' \times \Pi_3'$	$\Pi_1' \times \Pi_4'$	$\Pi_2' \times \Pi_2'$	$\Pi_2' \times \Pi_3'$	$\Pi_2' \times \Pi_4'$	$\Pi_3' \times \Pi_3'$	$\Pi_3' \times \Pi_4'$	$\Pi_4' \times \Pi_4'$
0.0136	-0.0509	0.5023	-0.2782	0.1899	-1.8741	1.0381	18.4989	-10.2470	5.6761
0.0145	-0.0524	0.5171	-0.2737	0.1899	-1.8741	0.9920	18.4989	-9.7919	5.1831
0.0115	-0.0467	0.4607	-0.2402	0.1899	-1.8741	0.9772	18.4989	-9.6463	5.0301
0.0109	-0.0454	0.4481	-0.2283	0.1899	-1.8741	0.9550	18.4989	-9.4263	4.8033
0.0088	-0.0409	0.4036	-0.2030	0.1899	-1.8741	0.9427	18.4989	-9.3058	4.6812
0.0068	-0.0359	0.3545	-0.1762	0.1899	-1.8741	0.9313	18.4989	-9.1925	4.5680
0.0059	-0.0334	0.3292	-0.1623	0.1899	-1.8741	0.9240	18.4989	-9.1207	4.4968
0.0048	-0.0302	0.2984	-0.1471	0.1899	-1.8741	0.9240	18.4989	-9.1207	4.4968
0.0039	-0.0270	0.2669	-0.1316	0.1899	-1.8741	0.9240	18.4989	-9.1207	4.4968
0.0029	-0.0233	0.2303	-0.1135	0.1899	-1.8741	0.9240	18.4989	-9.1207	4.4968
$\Sigma 0.0834$	$\Sigma -0.3861$	$\Sigma 3.8111$	$\Sigma -1.9543$	$\Sigma 1.8986$	$\Sigma -18.7408$	$\Sigma 9.5323$	$\Sigma 184.9886$	$\Sigma -94.0925$	$\Sigma 47.9292$

System: F-300_ Resorcinol _Mn²⁺

From Table III and V, putting values in equations d, e, f, g we get,

$$(-22.2689) = 10 K' + (1.4951) a + (-7.8431) b + (77.4185) c \quad (h)$$

$$(-3.3589) = 14.951 K' + (0.6224) a + (-3.2573) b + (6.4305) c \quad (i)$$

$$(17.5438) = (-78.431) K' + (-3.2573) a + (3.4175) b + (-33.7335) c \quad (j)$$

$$(173.1733) = (774.185) K' + (6.4305) a + (-33.7335) b + (332.9795) c \quad (k)$$

By solving equations h, i, j, k we get

$$K' = 0.3678$$

$$a = -13.4650$$

$$b = -0.0020$$

$$c = -0.0753$$

System: F-400_ Resorcinol _Mn²⁺

From Table IV and VI, putting values in equations d, e, f, g we get,

$$(-21.8767) = 10 K' + (0.8861) a + (-4.3573) b + (43.0103) c \quad (l)$$

$$(-1.9543) = 8.861 K' + (0.0834) a + (-0.3861) b + (3.8111) c \quad (m)$$

$$(9.5323) = (-43.573) K' + (0.3861) a + (1.8986) b + (-18.7408) c \quad (n)$$

$$(-94.0925) = (430.103) K' + (3.8111) a + (-18.7408) b + (184.9886) c \quad (o)$$

By solving equations l, m, n, o we get

$$K' = 0.0000$$

$$a = -3.2457$$

$$b = -6.3998$$

$$c = -1.0901$$

The mathematical model is developed using experimental data for kinetic adsorption system

CONCLUSION

Mathematical modelling quite helpful to relate the number of variables that define the problem of interest with number of base dimension involve in the adsorption phenomenon. The obtained simplified model reduces the parameter to realize the actual behaviour of designated system and helped to avoid time consuming experimentation.

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