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ISOTHERM STUDIES OF EQUILIBRIUM SORPTION OF Fe(III) ONTO UNMODIFIED HEN EGGSHELL ADSORBENT

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Abstract: ***The paper explores the study of equilibrium isotherms and potentiality of untreated hen egg shell as a bio waste sorbent for the removal of Fe (III) from aqueous solution. The adsorption data were fitted to different Isotherm models. Regression coefficient (R^2) for different models was calculated and observed to be in the order of Langmuir > Freundlich > Temkin > Dubinin–Radushkevich. Favourable adsorption was analysed by determining separation factor (R_L=0.136) in a Langmuir isotherm and cross verified by adsorption intensity (n=1.61) in a Freundlich isotherm. Moreover, physical adsorption was confirmed with the apparent energy of adsorption (1.0 kJ/mol) in a Dubinin-Radushkevich isotherm model and heat of adsorption (8.239 J/mol) from Tempkin isotherm model. Study shows that untreated hen egg shell can be utilised as a bio waste sorbent for the removal of Fe (III) from aqueous solution.***

Keywords: **Equilibrium adsorption modelling, Heavy metals, Hen egg shell, Isotherm, Sorption**

I. INTRODUCTION

Due to industrialization in last two decades, there has been growing concern over the diverse effects of heavy metals bearing waste water on humans and aquatic ecosystems [1]. Major source of heavy metal bearing waster water mainly includes steel industries, aeronautic, metal coating, etc and requires costlier treatment, e.g. ion exchange, biodegradation, oxidation, solvent extraction and adsorption [2, 3]. Recently, adsorption technique (with the use of waste solids) for the removal of heavy metals from the effluent is reported effective due to low cost, ease of handling and less chemical consumption. Moreover, resource recovery potential for the value added metal can be exploited [4, 5].

Food processing, egg breaking and hatching industries are the major source of egg shell waste (11 % of egg weight), which are available in huge quantities. About 2,50,000 tons of egg shell waste is produced annually worldwide by the food processing industry only. Most of the eggshell waste is commonly discarded of in landfills without any pretreatment because it is traditionally useless and ultimately creates serious environmental problems [6]. The chemical composition of egg shell (94% calcium

carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), as well as the porous nature of egg shell structure (7000-17000 pores) [7] leading to serve as attractive material as an adsorbent. Recovery and utilization of calcium in egg shell for the production of cellulose is reported [6]. Chicken egg shell membrane accounted to be effective low cost adsorbent for the removal of anion and cation dyes [8]. Many authors have developed costlier method for the removal of iron from waste water with the use of duck and crab egg shell [9, 10, 11].

The present work addresses the study for effect of adsorbent (eggshell) and adsorbate (stock solution) on the adsorption efficiency of Fe(III) from synthetic aqueous solution by hen eggshell. Besides, the present study is also aimed to evaluate the equilibrium of adsorption process using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D – R) Isotherms.

II. MATERIALS AND METHODS

A. *Preparation of Eggshell*

The hen eggshell used in this study was obtained from local food stall located in the city of Surat, India. The eggshell was washed with distilled water several times to remove surface impurities, sundried followed by oven dried at 105 °C for 2 hours. The dried eggshell was grounded using pestle and mortar and the particle size was adjusted in the range of 125-500 µm to increase the surface area for efficient adsorption. Physico-chemical properties of hen eggshell are shown in Table 1.

TABLE 1:- PHYSICO-CHEMICAL CHARACTERISTICS OF HEN EGGSHELL

Surface Area	7.0 m^2/g	Saers Method (Reference 12)
pH	8.1-8.9	IS 3025 (Part 11) (1983, Reaffirmed 2002)
Moisture	8 %	ASTM D5142- 02a
Particle Size	125-500 µm	Using Sieve Analysis
Bulk Density	1.346 g/cm^3	S. Toshiguki et al. (Reference 13)

B. *Preparation of Adsorbate*

The adsorbate was prepared by synthesizing standard stock solution of Fe(III) by dissolving in distilled water. All chemical used in the present study were of analytical grade from Fisher Scientific, India. Atomic Absorption Spectrophotometer (AAS Model A 303, Thermo Scientific) was used to measure the Fe(III) concentration.

C. *Experimental*

Series of solutions containing different initial concentrations of Fe(III) ions (in the range of 5-50 mg/L) was prepared and employed for the batch adsorption studies at 30°C to check the applicability of the Langmuir, Freundlich, Temkin and Dubinin– Radushkevich (D – R) adsorption isotherms under optimum conditions (120 minutes on the magnetic stirrer at constant revolution in the pH range between 6 to 6.5). The mixture was centrifuged and the iron concentration was determined using Atomic Absorption Spectrophotometer (AAS Model A 303, Thermo Scientific). As shown in Table 2 the amount of solute adsorbed and the removal efficiency was calculated with the use of reported mass balance equations [14].

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$$Q = \frac{V(C_i - C_e)}{M} \quad \text{................ (1)}$$

$$E = \frac{(C_i - C_e)}{C_i} \times 100 \quad \text{............ (2)}$$

Where, Q is the amount of solute adsorbed from the solution (mg/L). V is the volume of the adsorbate (L), C_i is the concentration before adsorption (mg/L), C_f is the concentration after adsorption (mg/L), M is the mass of eggshell used (g) and E is the percent removal efficiency.

III. RESULTS AND DISCUSSION

A. *LANGMUIR ADSORPTION MODEL*

Monolayer adsorption process is described quantitatively by Langmuir adsorption model. The model assumes uniform contact between the surface of adsorbate and adsorbent and that; there should be specific number of adsorption sites on the surface of the adsorbent onto which the solute molecules can be adsorbed [15]. Further, the energy of adsorption onto the surface should be uniform and there should be no transmigration of adsorbate in the plane of the surface [16]. Based upon these assumptions, the Langmuir adsorption model can be represented as under,

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \quad \text{................ (3)}$$

Adsorption parameters were evaluated following the linear form of equation 3,

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left[\frac{1}{q_{max} b}\right] \frac{1}{C_e} \quad \text{.............. (4)}$$

Where, q_{max} is the maximum monolayer capacity of adsorbent (mg/g), b is the Langmuir constant (L/mg), C_e is the concentration of adsorbate under equilibrium conditions (mg/L) and q_e is the amount of adsorbate per gram of adsorbent at equilibrium (mg/g).

The value of q_{max} and b was obtained from the slope and intercept of the plot of $1/q_e$ versus $1/C_e$ as shown in Fig 1. The results of Langmuir plot are shown in Table 3.

An important characteristic of the Langmuir isotherm may be expressed in terms of dimensionless equilibrium parameter constant R_L [17] expressed as,

$$R_L = \frac{1}{1 + (1 + bC_o)} \quad \text{............... (5)}$$

Where, C_o is the initial adsorbate concentration and b is the Langmuir isotherm constant. According to Hameed et al., 2007, Bayramoglu et al., 2009 and Ghanizdeh et al., 2010, the value of R_L gives a good approximation of adsorption characteristics, the nature of adsorption is unfavorable if $R_L>1$, linear if $R_L=1$, favorable if $0< R_L<1$ and irreversible if $R_L=0$. From the values computed in Table 3, it can be seen that the value of R_L lies between 0 and 1 indicating that the adsorption experiment considering the Langmuir isotherm model is favorable under the specified experimental conditions of this research work. Also, from the results it can be noted that the coefficient of regression value, R^2 is 0.926 which signifies that the isotherm model gives good and best fit with the experimental adsorption data under specified experimental conditions.

B. *FREUNDLICH ADSORPTION ISOTHERM*

The Freundlich adsorption model normally applies for the heterogeneous surface. The isotherm model was plotted to study the intensity of adsorption of adsorbent for the adsorbate [21]. The linear form of Freundlich isotherm equation is expressed as,

$$log\, q_e = log\, K_f + \frac{1}{n}\, log\, C_e \quad \text{............. (6)}$$

Where, K_f is the Freundlich isotherm constant signifies the capacity of adsorption process (mg/g), while n gives good approximation of the adsorption intensity. Equation 6 was plotted against $logq_e$ versus $logC_e$ as shown in Fig 2 to get the values of n and K_f from the slope and intercept respectively. The adsorption data shows a reasonable fit with Freundlich isotherm model with R^2 value of 0.884. A favorable adsorption process is estimated when the value of n lies between one and ten [22]. From the calculated results, it can be seen that the value of n is 1.61 indicating a favorable adsorption process. On the other hand, 1/n is anticipated as a function of the adsorption strength in the adsorption process [23]. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity [16]. If value of 1/n is below one it indicates a normal adsorption process, while 1/n being above one indicates cooperative adsorption [24]. From Table 3, the value of 1/n is 0.619 indicating a normal adsorption process. It can be seen from equation 6 that the amount of adsorption varies linearly with pressure until the specific saturation pressure is reached after that no further adsorption is possible and the system attains equilibrium.

C. *TEMPKIN ISOTHERM MODEL*

The Tempkin isotherm model represents a linear relationship between the amount of adsorbate per gram of adsorbent at equilibrium and lnC_e. Moreover, the adsorption model assumes that the heat of adsorption of each molecule decreases linearly with the coverage capacity by ignoring the extremities of concentration [25, 26]. The adsorption model is represented by following linear equation [25],

$$q_e = B\, ln\, A + B\, ln\, C_e \quad \text{............. (7)}$$

$$B = \frac{RT}{b_T} \quad \text{.................................... (8)}$$

Where, A represents the equilibrium Tempkin isotherm binding constant (L/g), R is the universal gas constant (8.314 J/mol/K), b_T is Tempkin constant, T is room temperature in K and B is the constant of heat of adsorption which usually express the type of adsorption (J/mol).

The linear equation 7 was plotted against q_e versus lnC_e to get the values of B and A as the slope and intercept respectively and the value of b_T was calculated from equation 8. Fig 3 shows scattered nature of the graph with R^2 value as 0.678 indicating less fit of Tempkin isotherm with the experimental adsorption data. From Table 3, the value of heat of adsorption is 8.239 J/mol indicating a physical adsorption process.

D. *DUBININ–RADUSHKEVICH ISOTHERM MODEL*

The adsorption mechanism considering the distribution of Gaussian energy onto heterogeneous surface is normally represented by Dubinin–Radushkevich isotherm model [27]. The model is represented by linear equation 9.

$$\ln q_e = \ln q_s - (K_{ad}\ \varepsilon^2) \text{ .... (9)}$$

Where, q_s is termed as the theoretical value of isotherm adsorption capacity (mg/g), K_{ad} is Dubinin–Radushkevich isotherm constant (mol^2/KJ^2) and ε is Dubinin–Radushkevich isotherm constant. The graph of lnq_e versus ε^2 considered as the DRK isotherm plot yields the value of logarithm of theoretical adsorption capacity lnq_s as the intercept and DRK constant K_{ad} as the slope of the characteristics curve. The apparent energy of adsorption (E) which is a measure of the characteristics of adsorption process is calculated from equation 10.

$$E = \frac{1}{\sqrt{2B_{DR}}} \text{ .... (10)}$$

Where B_{DR} is expressed as the isotherm constant, whereas, the parameter ε can be calculated by the equation 11,

$$\varepsilon = RT \times \ln\left[1 + \frac{1}{C_e}\right] \text{ .... (11)}$$

Where, R is gas constant (8.314 J/mol K), T is the absolute temperature (K) and C_e is the adsorbate equilibrium concentration (mg/L). The DRK isotherm parameters are tabulated as per Table 3. As can be seen from Fig 4 this isotherm model also does not provide a good fit with the adsorption data and the R^2 value is 0.545. P. Sivakumar et al. found that if the value of E lies between 8 and 16 kJ/mol then it indicates a chemisorptions process, whereas, if the value lies below 8 kJ/mol then it indicates a physical adsorption process. Here from the DRK plot the apparent energy of adsorption (E) value is obtained as 1 kJ/mol indicates physical adsorption process between unmodified eggshell and Fe(III) ions.

Table 2:- Parameters for plotting equilibrium Adsorption Isotherm Models of Fe(III) onto unmodified hen egg shell

Sr. No.	C_o	C_e	1/Ce	log C_e	ln C_e	Q_e (mg/g)	1/Q_e	log Q_e	ln Q_e	C_e/Q_e (g/l	ε^2
1	5	1.02	0.98039	0.0086	0.0198	3.98	0.25126	0.59988	1.38128	0.25628	2.86×10^6
2	10	2.82	0.35461	0.45025	1.03674	7.18	0.13928	0.85612	1.9713	0.39276	5.66×10^5
3	15	5.22	0.19157	0.71767	1.6525	9.78	0.10225	0.99034	2.28034	0.53374	1.88×10^5
4	20	10.5	0.09524	1.02119	2.35138	10.24	0.09766	1.0103	2.3263	1.02539	5.10×10^4
5	50	22.1	0.04525	1.34439	3.09558	33.7	0.02967	1.52763	3.5175	0.65579	1.20×10^4

Table 3:- Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherm constants for the adsorption of Fe(III) onto unmodified hen egg shell

Isotherm	Isotherm Constants			
Langmuir	q_{max} (mg/g)	b (L/mg)	R_L	R^2
	18.18	0.268	0.136	0.93
Freundlich	1/n	n	K_f (mg/g)	R^2
	0.619	1.61	3.61	0.88
Temkin	A (L/mg)	b_T	B (J/mol)	R^2
	0.945	300.86	8.239	0.68
Dubinin-Radushkevich	q_s (mg/g)	K_{ad} (mol^2/KJ^2)	E (KJ/mol)	R^2
	14.097	0.5×10^{-6}	1	0.55

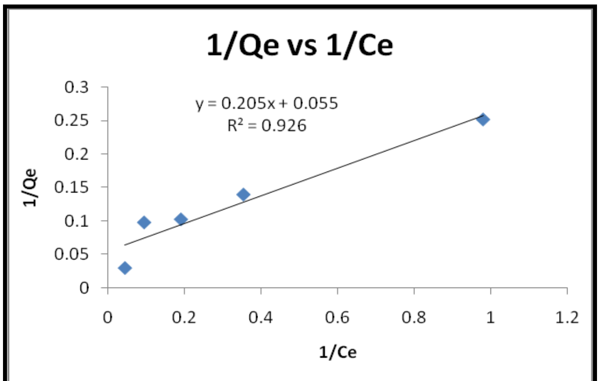

Fig 1: Langmuir Adsorption Isotherm

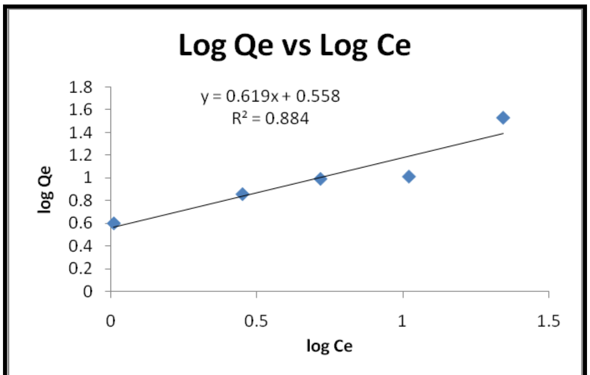

Fig 2: Freundlich Adsorption Isotherm

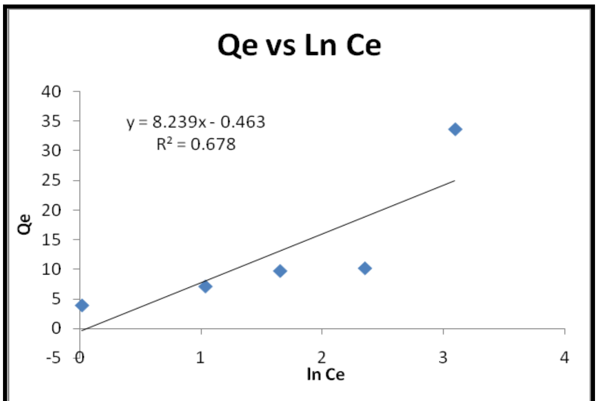

Fig 3: Tempkin Adsorption Isotherm

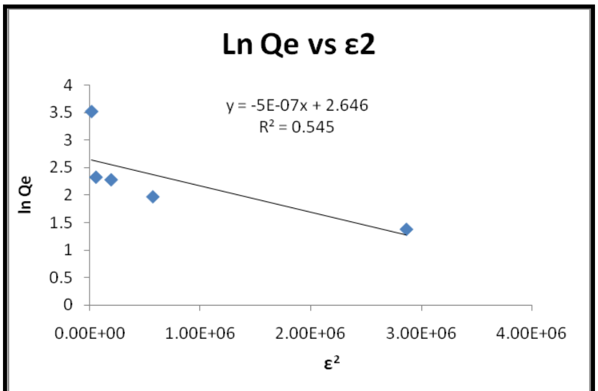

Fig 4: Dubinin Radushkevich Isotherm

IV. CONCLUSION

The experimental result showed the use of unmodified hen eggshell as a low cost adsorbent for Fe(III) bearing aqueous solution. The adsorption isotherm observed in the range of Langmuir > Freundlich > Temkin > Dubinin–Radushkevich. Physical adsorption was confirmed with the apparent energy of adsorption (1.0 kJ/mol) in a Dubinin-Radushkevich isotherm and heat of adsorption (8.239 J/mol) from Tempkin isotherm model. Favourable adsorption was analyzed from separation factor (R_L=0.136) in a Langmuir isotherm and cross verified by adsorption intensity (n=1.61) in a Freundlich isotherm. Hence, hen egg shell can be utilised as a low cost bio waste sorbent for the removal of Fe(III) from aqueous solution without chemical treatment as this will increase the cost of application.

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