The adsorptive potential of chicken egg shells for the removal of oxalic acid from wastewater

Muhammad Ikram1, 2, Afrasiab Ur Rehman1, Sharafat Ali1, Sher Ali1, Syed Ul Hasnain Bakhtiar1, Sultan Alam2

1. Key Laboratory of Functional Inorganic Materials Chemistry, Heilongjiang University, Harbin, China. 2. Department of Chemistry University of Malakand, KPK, Malakand, Pakistan.

Correspondence: Sultan Alam. Address: Department of Chemistry University of Malakand, KPK, Malakand, Pakistan. Email: drsultanalam@yahoo.com

Received: January 27, 2016 Accepted: March 6, 2016 Online Published: April 13, 2016

DOI: 10.5430/jbei.v2n2p118 URL: http://dx.doi.org/10.5430/jbei.v2n2p118

Abstract

Chicken egg shells were grinded and sieved to an exact particle size of 125 micron and treated with excess aqua regia and n-hexane to remove inorganic and organic impurities. Adsorption of oxalic acid from waste water was studied on treated powder egg shells by kinetics and batch adsorption techniques at different temperatures, 20ºC, 30ºC and 40ºC. The samples were characterized by BET surface area, scanning electron microscopy (SEM), and Fourier Transform Infra-red Spectroscopy (FTIR) and energy dispersive spectroscopy (EDS) techniques. The amount of acid adsorbed was determined with respect to initial acid concentration, equilibrium time and different acid concentration manually by titration method. Intra-particle diffusion, Elovich and Bhangam models were used for adsorption kinetics and thermodynamic parameters $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta E^\circ$ were calculated. The results obtained showed that adsorption process was spontaneous and entropy of adsorption had negative value. Freundlich, Langmuir, Tempkin and Harkins-Jura linear equations were used to investigate adsorption isotherms. This work will provide feasible routes for waste water treatment.

Key words

Egg shells, Titration, Oxalic acid, Adsorption kinetics, Adsorbent

1 Introduction

Urbanization and industrialization all around the world has affected the quality of ground and surface water as numerous untreated poisonous effluents are discharged continuously. Environmental pollution caused by the discharge of untreated poisonous effluents is a major concern of 21st century [1-4]. The industrial effluents cause serious environmental issues because of their adverse effects on the aquatic and terrestrial life as water eutrophication by these substances prevents the penetration of sunlight necessary for photosynthesis [5]. The effluents generated contain toxic substances including dyes, acids, carcinogenic metals, alkalis and aromatic amines which affect the quality, aesthetic merit, transparency and penetration of sun light required for aquatic bodies. The presence of these substances increases the risk of cancer in human being and is very difficult to remove under aerobic conditions.

Among these substances, dicarboxylic acids are the main concern as they are soluble in water [6]. Bacteria, fungi, algae, higher plants and some animals secrete organic acids. Important man made sources which participate in the release of
organic acids include different products of agriculture, food processing, organic waste, sewage sludge and land fill leachate. As a consequence, organic acids are unfit in ecosphere. Acidic water is dangerous for living organisms on land, aquatic-life and for other material like concrete pipe. The presence of acids also increases the solubility of heavy metals. Oxalic acid in waste water is important constituent responsible for unpleasant smell [7, 8].

Various wastewater treatment technologies are based on the process of coagulation, flocculation, biodegradation, adsorption, membrane separation, ion exchange, oxidation and selective bio-adsorbents for the elimination of these materials. Because of high cost and disposal problems, many of the conventional methods have not been applied at large scale in different industries.Adsorption has been found to be superior to other techniques in terms of low-cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [9]. In adsorption, different adsorbents used include activated carbon [10], zeolite [11], clays [12], silica beads [13], and polymeric acids [14] etc. However, due to high cost, these materials cannot be justified to cope with pollution and therefore, research has been directed towards methods of treatment using locally available low-cost natural materials such as biopolymers [10].

In the present work, powder egg shells have been used successfully for the removal of oxalic acid from wastewater. Egg shells are waste materials from hatcheries, households and fast food industries and can be readily collected in plenty. It is about 11% of the total egg weight and consists of about 95% calcium carbonate and 5% of others materials such as Al₂O₃, SiO₂, S, Cl, Cr₂O₃ and MnO₂. Egg shells are waste product as about 28% of the total eggs are used commercially in egg products and their disposal contributes to environmental pollution because these cannot be used traditionally [15-17]. These wastes are directly disposed without any pretreatment; challenges associated with disposal include cost, availability of disposal sites, odor, flies and abrasiveness. However, these egg shells can be used as an excellent adsorbent because of their porous nature; about 700 to 1,700 pores are present on the surface an egg shell [18, 19]. The egg shells are also attractive as adsorbent due to their good mechanical properties and thermal stability [20] and already used as adsorbent for the removal of heavy metals [21], phenolic compounds [22], dyes [23], and pesticides [24].

2 Materials and methods

2.1 Sample preparation (Adsorbent)

Chicken egg shells collected from bakery shops (Mardan, Pakistan) were washed with distilled water several times and dried in the oven. The dried samples were grinded into powder form and sieved to an exact particle size of 125 micron by Glenammer Sieves, Ayrshire. Scotland. Half of the powder sample was treated with excess of 0.2 M solution of HCl and HNO₃ solution for 24 hours to remove inorganic materials from the sample and again washed thoroughly with distilled water until its pH reached 7. Then the sample was treated with n-hexane for 24 hours to remove organic impurities and dried in oven at 105°C. The sample was referred as modified egg shell and used as such.

2.2 Oxalic acid (Adsorbate)

All solutions were prepared in distilled water. Oxalic acid was used as adsorbate. First stock solution of acid was prepared, and then from this solution, different other working solutions were prepared by dilution method.

3 Characterizations

The surface area of powder egg shells was determined by Bruner-Emmet-Teller, BET N₂-adsorption. The experiment was performed manometrically at -196°C using surface area and pore size analyzer (Model: Quanachrome NOVA 2200).

FTIR spectra of the samples were found by 8201PC Shimadzu and FTCOM-1 computer control disc unit using dried KBr pellet technique. Different ratios of KBr were used to obtain an acceptable resolution spectrum.
Scanning electron micrographs (SEM) of the samples was carried out with the help of SEM-Model-JSM-5910, Japan JEOL, by mounting the sample on aluminum (1 cm × 0.25 cm) while energy dispersive spectrum (EDS) was taken with the help of EDS-INCA 200 Oxford for metal detection.

For the calculation of moisture contents in egg shell, one gram of powder sample was taken in a china dish, covered it with a watch glass and then heated in a vacuum oven at 105ºC ± 2ºC for 2 hours. The china dish was cooled in desiccators and weighed to calculate the percent weight loss (see Table 1).

| Table 1. Characteristics of treated egg shells sample |
|-----------------|-----------------|
| Parameters      | Results         |
| Particle size   | 125 µm          |
| % Ash content   | 4.3%            |
| % Moisture content | 1%            |

In order to determine the ash contents in egg shells, one gram of powder sample was taken in a porcelain crucible and ignited at 600ºC in a Muffle furnace with partially opened door. After ignition the crucible was allowed to cool to room temperature naturally and percent weight loss was calculated (see Table 1).

**4 Adsorption study**

**4.1 Time equilibration**

The raw (0.2 g) and treated powder egg shells (0.2 g) were taken in each of different reagent bottles and 20 cm³ of oxalic acid solution was added to each of them. Two different initial concentration of oxalic acid was taken for each sample and the reagent bottles were shaken in a thermostat water bath shaker for different time periods of 0.5, 1, 2, 4, 6 and 8 hours at 250ºC. The slurry obtained after specified time was filtered, pH was noted before and after experiment. The filtrate was titrated against standard NaOH solution to determine change in acid concentration. The amount of acid adsorbed (\( C_\emptyset \) mol·g⁻¹) was calculated by Eq (1):

\[
C_\emptyset = \frac{(C_0 - C_\sigma)}{S} V
\]

where \( C_\emptyset \) is the amount of acid adsorbed, \( C_0 \) is the initial concentration and \( C_\sigma \) is equilibrium concentration of the acid, \( V \) is volume of acid taken and \( S \) is the adsorbent weight.

**4.2 Adsorption kinetics study**

The adsorbent (0.2 g) and 20 cm³ of adsorbate solution were mixed in reagent bottle. The reaction mixture was shaken in thermostat water bath shaker at 20ºC, 30ºC and 40ºC from 5 to 30 minutes. The solution was filtered and the filtrate was analyzed against standard NaOH solution to determine the change in acid concentration. pH was noted before and after filtration. The amount of acid adsorbed was calculated by Eq (1).

**4.3 Adsorption isotherm study**

The adsorbent (0.2 g) was mixed with 20 cm³ of adsorbate solution in a reagent bottle. The mixture was shaken in the shaker at 20ºC, 30ºC and 40ºC for 2 hours. The mixture was filtered and the clear filtrate was analyzed against standard NaOH solution.
5 Results and discussion

5.1 BET surface area

To determine the BET surface area of treated egg shells the Bruner-Emmet-Teller procedure\cite{21} was used. It is based on multilayer adsorption of nitrogen gas on adsorbent surface and investigates the micro porous surface of adsorbent. The linear form of BET equation is as follows:

\[
\frac{1}{V[(P_0/P - 1)]} = \frac{C-1}{V_m V} \left( \frac{P}{P_0} \right) + \frac{1}{V_m V}
\]

(2)

where \(P\) and \(P_0\) are diffusion pressure of adsorbate, \(V\) is the quantity of adsorbed gas on the surface of adsorbent, \(V_m\) is the monolayer adsorbed N\(_2\) and \(C\) is constant defined by Eq (3):

\[
C = \frac{E_1 - E_L}{RT}
\]

(3)

where \(E_1\) is the heat of adsorption for the first adsorbed layer while \(E_L\) for the onward layers.

Eq (2) is used for adsorption isotherm by plotting \(1/V[(P_0/P - 1)]\) vs. \(P/P_0\) of the adsorption of N\(_2\) and the changes in surface area of treated sample were determined Table 2.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Egg shells sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated</td>
<td>273</td>
</tr>
</tbody>
</table>

The result obtained shows that the surface area of adsorbent increases when treated with chemicals. During the chemical treatment the surface of the sample clean and the other impurities were removed and the surface becomes exposed for attachment of oxalic acid molecule. At high temperature the surface of the sample with non-polarity is another reason for high surface area is due to the fact that these groups present on the surface and leaving the surface for homogeneous \cite{23}.
5.2 SEM/EDS analysis
To identify the characteristic morphology of samples, SEM of egg shells was determined. The SEM images clearly show that pores of different shapes and size are present on the surface of the samples (see Figure 1). EDS spectra shows that modified egg shells composed of calcium, oxygen and carbon elements (see Figure 2 and Table 3).
Table 3. Elemental composition of treated Egg shells sample by EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>13.82</td>
<td>21.59</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>53.83</td>
<td>63.18</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>32.34</td>
<td>15.20</td>
</tr>
</tbody>
</table>

5.3 FTIR analysis

FTIR spectra of treated egg shell are given in Figure 3. The region 1,427.32 cm\(^{-1}\) to 1,336.67 cm\(^{-1}\) in the spectra shows the presence of carbonyl group, CH and NO stretching group\(^{[26]}\). The treated samples of egg shells show bands at 1,413.82 cm\(^{-1}\), 1,336.67 cm\(^{-1}\), 873.75 cm\(^{-1}\) and 711.73 cm\(^{-1}\). The peak at 873.75 cm\(^{-1}\) is due to the presence of NO stretching group. The band at 2,370.51 cm\(^{-1}\) is due to C-H stretching mode.

![Figure 4](image1.png)

**Figure 4.** Equilibration time for the adsorption of oxalic acid on treated egg shells sample

![Figure 5](image2.png)

**Figure 5.** Adsorption kinetics for the adsorption of oxalic acid on treated egg shells sample

5.4 Adsorption study

5.4.1 Equilibrium time and adsorption kinetics

Equilibrium time for the adsorption of oxalic acid on samples was studied at room temperature (25ºC) for the period of 0.5, 1, 2, 4, 6 and 8 hours. Figure 4 shows that the equilibrium was reached after 2 hours which indicates that 2 hours is the
optimum time for complete surface coverage. From equilibrium time study, adsorption kinetics of acid at 20°C, 30°C and at 40°C temperature was determined as shown in Figure 5. It is observed that in the initial 15 minutes, adsorption was fast due to the availability of more sorption sites and decreases gradually as more and more surface is occupied by the adsorbed molecules. It is also observed that the sorption of acids increases on the surface of adsorbent with an increase in temperature. This shows that the process is an endothermic process.

5.4.2 Adsorption kinetic linear equations

From the sorption of oxalic acid on powder egg shell samples, the rate constant was calculated by using the first order rate equation [27]:

\[ \ln C_\phi = \ln C_0 - k_{ad} t \]  

(8)

\( C_0 \) is initial and \( C_\phi \) is the equilibrium concentration of acids (mol·dm \(^{-3}\)) and \( k_{ad} \) is rate constant. A plot of \( C_\phi \) versus \( t \) at different temperatures as shown in Figure 5 gives the rate constant. It is clear from Table 4 that the values of rate constant increases with an increase in temperature. From the first order rate equation the value of regression coefficient (R\(^2\)) is in between (0.91-0.99) which is closer to 1 and shows best agreement with literature.

Table 4. Comparison of the parameters of rate equations for the oxalic acid onto treated egg shells sample

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Parameter</th>
<th>Adsorption temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Elovich</td>
<td>( A_k ) (g/mg)</td>
<td>5.549</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9724</td>
</tr>
<tr>
<td></td>
<td>C (mg/g)</td>
<td>2.2823</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9793</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>( K_{ad} ) (mg/gmin(^{1/2}))</td>
<td>0.1014</td>
</tr>
<tr>
<td></td>
<td>( K_{ad} ) (mg/gmin(^{1/2}))</td>
<td>0.1014</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9793</td>
</tr>
<tr>
<td>Bangham</td>
<td>A</td>
<td>-0.6188</td>
</tr>
<tr>
<td></td>
<td>( K_0 )</td>
<td>10.179</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.8601</td>
</tr>
</tbody>
</table>

Energy of activation was calculated from Arrhenius straight line equation [27] which is as follows:

\[ \ln \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \]  

(9)

\( K_2 \) and \( K_1 \) are rate constants, \( E_a \) is the activation energy, \( R \) is gas constant and \( T \) is absolute temperature. The activation energies calculated for acid adsorbed on raw and treated powder egg shells are given in Table 4. The activation energies (5.997 kJ·mol\(^{-1}\)) of treated egg shells are comparatively low indicating that the process of adsorption is governed by weak physical forces as reported by earlier research workers [28]. Similarly other thermodynamic parameters like enthalpy of activation (\( \Delta H^\neq \)) and entropy of activation (\( \Delta S^\neq \)) were calculated from activation energy and are given in Table 4. The positive value of \( \Delta H^\neq \) shows that adsorption of oxalic acid on egg shell is endothermic in nature. Similarly the negative value of \( \Delta S^\neq \) shows the affinity of adsorbate towards powder egg shells.

5.4.3 Elovich model

Elovich model equation is expressed in linear form as follows [29, 30]:

\[ C_\phi = \frac{1}{A} \ln(AB) + \frac{1}{A} t \]  

(10)

When \( C_\phi \) was plotted against Int, a straight line was obtained with slope equal to \( 1/A \), and intercept \( 1/A \ln(AB) \) as shown in Figure 6. It is clear that the value of “A” decreases with increasing temperature from 20°C in to 40°C. The results show that
adsorption of acid increases on the surface of adsorbent at high temperature. The $R^2$ value is about equal to 1 reveals that the model is best fitted for the adsorption of acid on the surface of bio-sorbent powder sample.

![Figure 6](http://jbei.sciedupress.com)  
*Figure 6.* Elovich plots for the adsorption of oxalic acid on treated egg shells

### 5.4.4 Bangham equation

Linear form of Bangham equation is follows:

$$\log \left( \log \frac{C_0}{C_0 - C_\sigma} \right) = \log \frac{KW}{2.303V} + \alpha \log t \quad (11)$$

Where $C_0$ is the initial concentration of acid in solution, $V$ is volume of solution, $W$ is the weight of adsorbate and $C_\sigma$ is the amount adsorbed and $t$ is time. By using the slope and intercept of linear plots (see Figure 7), to calculate the value of $K_0$ and $A$ (see Table 5). The results show that the value of $A$ gradually decreases with the increasing of shaking temperature, while the value of $K_0$ increases with the increasing of temperature. It also shows that the adsorption of acid into the pores of the adsorbent is well controlled, suitable and important process $^{[31,32]}$.

![Figure 7](http://jbei.sciedupress.com)  
*Figure 7.* Bhangum plots for adsorption of oxalic acid on treated egg shells
5.4.5 Parabolic diffusion model (Intraparticle diffusion)

Our results show that plot of $C_0$ versus $t^{1/2}$ indicates multi linearity, which describes the distinctive nature of different steps in the adsorption process [33]. According to Morris and Weber intra-particle diffusion:

$$C_0 = k_{id} t^{1/2} + B$$  \hspace{1cm} (12)

The value of $k_{id}$ was calculated by plotting $C_0$ against $t^{1/2}$ as shown in Figure 8. The value of $R^2$ of intra-particle diffusion adsorption is closer to 1. The results are given in Table 5 and show the best coincidence to fit for the adsorption of oxalic acid [33, 34].

Table 5. Thermodynamic constants for adsorption of oxalic acid onto egg shells sample

<table>
<thead>
<tr>
<th>Acids</th>
<th>Sample</th>
<th>$k$ (min$^{-1}$)</th>
<th>$\Delta E^0$ (kJ·mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S^0$ (J·mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>Treated</td>
<td>0.0456</td>
<td>0.0532</td>
<td>0.0537</td>
<td>5.997</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.560</td>
<td>3.477</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.394</td>
<td>-292.328</td>
</tr>
</tbody>
</table>

![Figure 8. Intraparticle diffusion plots for adsorption of oxalic acid on treated egg shells](image)

**Figure 8.** Intraparticle diffusion plots for adsorption of oxalic acid on treated egg shells

![Figure 9. Adsorption isotherm for the adsorption of oxalic acid on treated egg shells sample](image)

**Figure 9.** Adsorption isotherm for the adsorption of oxalic acid on treated egg shells sample
6 Adsorption isotherm studies

Adsorption isotherms of oxalic acid on powder egg shell samples are shown in Figure 9. After equilibrium the graph becomes straight showing maximum adsorption and the adsorption of acid increases with increasing temperature. This high adsorption is mainly attributed to high surface area and large opening size in treated egg shell powder causing more interaction of acid molecules with the samples.

![Figure 10. Freundlich isotherm plots for adsorption of oxalic acid on treated egg shells sample](image)

6.1 Freundlich isotherm

The Freundlich isotherm plots for adsorption of oxalic acid on treated egg shells sample are shown in Figure 10. According to the linear form of Freundlich equation \(^{[35]}\) as given below:

\[
\ln C_r = \ln k + \frac{1}{n} \ln C_a
\]  

(13)

The values of \(n\) and \(k\) were obtained as given in Table 6. The constant value of \(n\) gives information about the surface morphology and the ability of adsorbed solute particles \(^{[36,37]}\). The efficiency of adsorption increases with increasing \(1/n\) ratio. The value of \(k\) (mol·g\(^{-1}\)) indicates the adsorption capacity of powder egg shells. It is clear from the given data in Table 6 that adsorption capacity of egg shell powder increases with increasing temperature.

<p>| Table 6. Comparison of adsorption isotherm constants of oxalic acid adsorption onto treated egg shells samples |
|---------------------------------|-----------------|-----------------|-----------------|
| Isotherm            | Parameter     | Shaking Temperature |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th>20°C</th>
<th>30°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>(1/n)</td>
<td>0.3116</td>
<td>0.3149</td>
<td>0.3681</td>
</tr>
<tr>
<td></td>
<td>(K_f) (mg/g)</td>
<td>18.344</td>
<td>20.438</td>
<td>35.666</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.7056</td>
<td>0.7195</td>
<td>0.7335</td>
</tr>
<tr>
<td>Langmuir</td>
<td>(b) (mg/g)</td>
<td>0.585</td>
<td>0.621</td>
<td>0.763</td>
</tr>
<tr>
<td></td>
<td>(K_L) (L/mg)</td>
<td>6.944</td>
<td>9.009</td>
<td>7.194</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9975</td>
<td>0.9959</td>
<td>0.9962</td>
</tr>
<tr>
<td>Tempkin</td>
<td>(\alpha) (dm(^3)/g)</td>
<td>139.491</td>
<td>155.866</td>
<td>111.944</td>
</tr>
<tr>
<td></td>
<td>(\beta) (mg/dm(^3))</td>
<td>0.9752</td>
<td>1.0339</td>
<td>1.3908</td>
</tr>
<tr>
<td></td>
<td>(B)</td>
<td>2498.463</td>
<td>2436.543</td>
<td>1871.068</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.8295</td>
<td>0.8538</td>
<td>0.9085</td>
</tr>
<tr>
<td>Harkins-jura</td>
<td>A</td>
<td>45.258</td>
<td>43.290</td>
<td>34.843</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.154</td>
<td>0.427</td>
<td>1.125</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.8781</td>
<td>0.9011</td>
<td>0.8634</td>
</tr>
</tbody>
</table>
6.2 Langmuir isotherm

The linear form of this isotherm\textsuperscript{[38, 39]} is given by:

\[ \frac{C_\sigma}{C_\emptyset} = \frac{1}{bk} + \frac{C_\sigma}{b} \]  

(14)

Where \( b \) (mol/g) is the amount of adsorbed oxalic acid in complete monolayer coverage and \( k_l \) (L/g) is the binding energy constants. By plotting \( \frac{C_\sigma}{C_\emptyset} \) (g·dm\(^{-3}\)) against \( C_\sigma \), a straight line was obtained as shown in the Figure 11. From the plot the values of \( b \) and \( k \) were calculated as shown in Table 7. It is evident from the graph that adsorption capacity (b) of the adsorbent increases with increasing temperature. The regression coefficient \( R^2 \) is close to 1 which shows that the Langmuir isotherm model is best fit for the adsorption of acids on egg shells adsorbent.

![Figure 11. Langmuir isotherm plots for the adsorption of oxalic on treated egg shells](image)

\( \Delta G^0 \) was calculated by the following equations (15):

\[ \Delta G^0 = -RT \ln K_t \]  

(15)

where \( b \) (mol·g\(^{-1}\)) is the capacity of Langmuir monolayer adsorption and \( K_t = bM_d \), where \( M_d \) is the molecular mass of acid. The obtained data is show in Table 7. The negative values of \( \Delta G^0 \) show that adsorption on the surface of egg shell powder is spontaneous. It is clear that the values of Gibbs free energy decrease with increasing temperature indicating that the extent of adsorption increases with increasing temperature.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Sample</th>
<th>( \Delta G^0 \times 10^2 ) (kJ·mol(^{-1}))</th>
</tr>
</thead>
</table>
| Oxalic acid | Treated   | -96.56  
|             |           | -101.37  
|             |           | -110.07  |

6.3 Tempkin isotherm

The linear form of Tempkin isotherm model is given as\textsuperscript{[40]}:

\[ C_\emptyset = \beta \ln \alpha + \beta \ln C_\sigma \]  

(16)
By plotting $C_\sigma$ vs. $\ln C_\sigma$, a straight line was obtained with slope equal to $\beta$ and intercept equal to $\beta \ln \alpha$ as shown in Figure 12. The obtained values of $b$ are given in Table 6. It is evident that the value of $b$ increases with increasing temperature.

![Figure 12](image1.png)

**Figure 12.** Tempkin isotherm plot for the adsorption of oxalic acid on treated egg shells sample

### 6.4 Harkins–jura adsorption isotherm

The equation of Harkins-jura adsorption isotherm$^[41]$ is as follows:

$$\frac{1}{(C_\sigma)^2} = \frac{B}{A} - \frac{1}{A} \log C_\sigma$$

(17)

By plotting $1/(C_\sigma)^2$ against $C_\sigma$, a straight line curve was obtained as shown in the Figure 13. The value of constant $A$ and $B$ were calculated from the intercept and slope of the curve and are shown in Table 6. It is clear that by increasing temperature, the values of $B$ also increase indicating the adsorption of oxalic acid on the surface of egg shell powder.

![Figure 13](image2.png)

**Figure 13.** Harkins–jura isotherm plots for adsorption of oxalic acid on treated egg shells sample

### 7 Conclusions

We have successfully adsorbed oxalic acid on the surface of powder egg shell with pores of different size and shapes and surface area nearly equal to 273 m$^2$·g$^{-1}$. Intra-particle diffusion, Elovich and Bhagam models were used for adsorption
kinetics and thermodynamic parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta E^\ddagger$ were calculated. Equilibrium time required for complete coverage of surface was about 2 hours. The experimental data shows that adsorption of acid on powder egg shell samples is best fitted to the linear equation and it was concluded that the process was diffusion control process and was spontaneous. Entropy of adsorption has negative value which shows that the acid molecules on the surface of adsorbent take an oriented position. Freundlich, Langmuir, Tempkin and Harkins-Jura linear equations were used to investigate adsorption isotherms. The results demonstrate that this work is suitable for waste water purification.

**Acknowledgments**

We are grateful for financial support from Malakand University KPK, Malakand, Pakistan.

**Conflicts of Interest**

The authors declared no conflict of interest.

**References**


[40] Vickerstaff Y. The physical Chemistry of Dyeing, Inc, 100. 1954.