ADSORPTION OF ACETIC ACID ON ORANGE PEELS BIO-ADSORBENT AND VERIFICATION OF FREUNDLICH AND LANGMUIR ADSORPTION ISOTHERMS

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This paper reports an investigation on the adsorption of acetic acid onto activated carbons prepared from orange peels. The activated carbons were prepared by chemical activation method. The adsorption data were well described by the Langmuir and Freundlich adsorption methods. A variety of adsorbents are available naturally-bagasse, rice husk, neem bark, clays etc. that can be used to remove acids from the discharged waste. In this review, we look at the various adsorbents available particularly orange peels and see how effectively they can be utilized to meet our requirements. The acid removal process followed Freundlich isotherm in most of the cases and in few investigations, it followed Langmuir.

KEYWORDS : Adsorptions, Acetic Acid, Orange peels, bio-adsorbent, Freundlich, Langmuir isotherm.

INTRODUCTION

It is necessary that the water reserves be treated carefully and wastewater treatment be done [1]. Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies [2]. Adsorption appears to be good for the treatment of effluents [3]. The first thing for an efficient adsorption process is the search for a low cost adsorbent with high adsorption capacity and second it should be biodegradable [4]. The activated carbon has been till now the most used adsorbent but is expensive to use on a large scale [5] and the idea of using natural.

Dicarboxylic acids include maleic and oxalic acids which results due to partial oxidation of phenol and its derivatives [6]. It has been reported that high levels of maleic and oxalic acids in potable water cause health problems to humans like kidney stones, uraemia, erosion of enamel and mouth, vomiting and hematemesis [7]. In that case elimination or lowering the levels of these acids in wastewaters is not optional. Adsorption method in the removal of lower aliphatic carboxylic acids from wastewater is, however, overwhelmingly recommended by the literature [8]. Unfortunately the choice of a cost-effective adsorbent is big challenge. A good adsorbent is supposed to be cheap, abundant, with high carbon content. Activated carbon widely reported as a suitable adsorbent for the acids. Unfortunately it is expensive. In an effort to reduce the cost, an attention is now directed towards the use of agro wastes as sources of the activated carbons [9].

They are used in water treatment and in industrial applications such as in the extraction of metal ions, air handling, and purification [10], the discoloration of food in the food industry and in the pharmaceutical industry [11].

Milind R. Gidde, Julie Datta, Snehal Jadhav *et al.* Activated Rice Husk (ARH) and Rice Husk Ash (RHA) were used as adsorbents for decolourisation. ARH was prepared from rice husk treated with nitric acid and RHA was collected directly from mill [11]. There adsorption capacity was evaluated for the decolourisation of wastewater containing methylene blue. The effect of system variables such as pH, contact time, initial concentration and adsorbent dose were investigated [12]. The result shows that efficient varies with the variation in adsorbate concentrations and adsorbent [13]. Color removal efficiency was found to be 88% to 94% at the dose of 20 g/l for ARH and 80% to 95% at the adsorbent dose of 2.5 g/l for RHA. The studies were carried out at methylene blue concentration of 50 mg/l, 30 mg/l and 10 mg/l. On the basis of adsorption isotherm graphs, R-square values were determined and found to fit the adsorption data. The Linear, Langmuir and Freindlich adsorption isotherms are good fitted for the experimental data [14].

Freindlich adsorption isotherm :

A/c to Freindlich adsorption isotherm, change ($\Delta S°$) showed increased randomness at the solid/solution interface**.** At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto P^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$\frac{x}{m} \propto P^0$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power $1/n$. Here n is a variable whose value is greater than one.

$$\therefore \qquad \frac{x}{m} \propto P^{\frac{1}{n}}$$

Using constant of proportionality, k, also known as adsorption constant we get

$$\frac{x}{m} \propto kP^{\frac{1}{n}}$$

The above equation is known as Freindlich adsorption equation.

1. Plotting of Freindlich Adsorption Isotherm:

As per Freindlich adsorption equation

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Taking log both sides of equation, we get,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}p$$

The equation above equation is comparable with comparable with equation of straight line, $y = m\,x + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between log (x/m) and log p, we will get a straight line with value of slope equal to $1/n$ and log k as y-axis intercept.
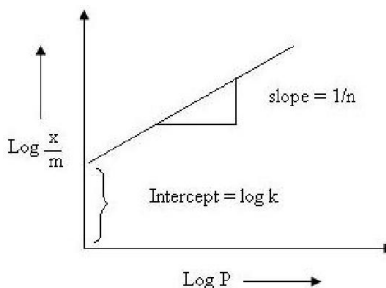
Log (x/m) vs. log p graph

2. Derivations of the Langmuir Adsorption Equation:

Derivation: Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (*i.e.* extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter 'θ' is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be $(1 - θ)$.

Now, Rate of forward direction depends upon two factors: Number of sited available on the surface of adsorbent, $(1 - θ)$ and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors.

Rate of forward reaction $\propto P(1-θ)$

Rate of adsorption $\propto P(1-θ)$

or,   Rate of adsorption $= K_a P(1-θ)$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\propto θ$

or,   Rate of desorption $= K_d θ$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - θ) = K_d θ$$

We can solve the above equation to write it in terms of θ.

$$K_a P - K_a P θ = K_d θ$$

$$K_a P = K_a P θ - K_d θ$$

$$K_a P = (K_a + K_a P)\,θ$$

$$θ = \frac{K_a P}{K_d + K_a P}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \frac{\dfrac{K_a}{K_d}P}{\dfrac{K_d}{K_d} - \dfrac{K_a}{K_d}}$$

Now put
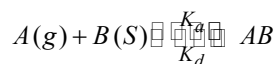
$$K = \frac{K_a}{K_d}$$

in above equation we get

$$\theta = \frac{KP}{1 + KP}$$

Langmuir Adsorption Equation

This is known as **Langmuir Adsorption Equation**.

Calculation of Equilibrium Constant:

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

$$A(g) + B(S) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AB$$

where K_a represents equilibrium constant for forward reaction and K_d represents equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction = $K_a[A][B]$

Rate of backward reaction = $K_d[AB]$

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a[A][B] = K_d[AB]$$

or,

$$\frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

MATERIALS AND METHODS

A. Preparation of Adsorbent :

A weighed amount of orange peels charged into the furnace at a temperature of 300, 400, 500 and 600°C for 0.5, 1.0, 1.5 and 2 h. The resulting charred material was collected and cooled at room temperature. The domain of variation of these factors is defined according to

Bornemann *et al.,* [18]. A known amount of rice husk charcoal (10 g) was transferred in a beaker (250 mL) and added 100 mL distilled water to it and continued adding water to it up to 200 mL to completely soak the charring rice straw in beaker. When the charring rice husk completely settled down then decanted the distilled water and repeated this process for several times until the decanted water become cleared. Rice husk charcoal was then filtered through ordinary filter paper and washed again with distilled water. Cleaned rice husk charcoal was dried in an oven to get a constant weight and stored as Orange peels bio adsorbent.

Orange peels bio adsorbent

B. Methods:

   I. Prepare 0.1 N oxalic acid solution by dissolving 0.63g oxalic acid in 100 ml distilled water.
  II. Standardize the given NaOH solution using phenolphthalein indicator.
 III. Take 6 clean reagent bottles and number them from 1 to 5.
  IV. Weigh out accurately about 1 g finely ground activated charcoal in each of them.
   V. Shake these bottles vigorously and keep for one hour.
  VI. Filter each solution through filter paper and titrate 10 ml of each of them with 0.1N NaOH solution.

C. Observations and Calculations

Table 1. Observation table for Acetic acid.

Bottle No.	Vol. of acetic acid sol. V (ml)	Vol. of water (ml)	Amt of charcoal (mg)	Initial conc. of acetic acid Co	Vol. of filtrate taken V_1 (ml)	Vol. of NaOH sol required V_2 (ml)	Eqn conc. of acetic acid Ce	Acetic acid adsorbed X (g)	X/M	Log (x/m)	Log Ce
1	50	0	1	10	10	36.6	0.3843	8.8471	8.8471	0.9468	− 0.4153
2	40	10	1	8	10	32.2	0.3381	6.9857	6.9857	0.8442	− 0.4709
3	30	20	1	6	10	24.6	0.2583	5.2491	5.2491	0.7200	− 0.5878
4	20	30	1	4	10	15.4	0.1617	3.5144	3.5144	0.5459	− 0.7912
5	10	40	1	2	10	8.3	0.08715	1.7385	1.7385	0.2401	− 1.0597

Table 2. Percentage adsorption for Acetic acid on orange peels.

| Concentration	Co	Ce	Co-Ce	Co-Ce/Co	% adsorption
0.5	10	0.3843	9.6157	0.96157	96.15
0.4	8	0.3381	7.6619	0.957738	95.77
0.3	6	0.2583	5.7417	0.95695	95.69
0.2	4	0.1617	3.8183	0.954575	95.45
0.1	2	0.08715	1.90785	0.953925	95.39

Graph 1: Verification of Freindlich adsorption isotherm of Acetic acid on Orange peel adsorbent.
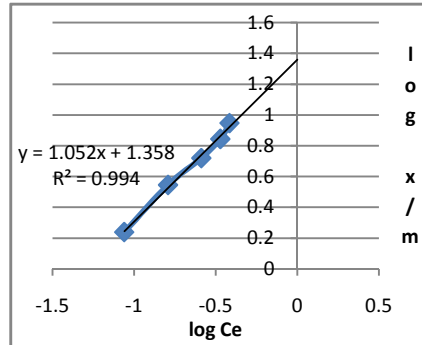
Graph 2: Verification of Langmuir adsorption isotherm of Acetic acid on Orange peel adsorbent.
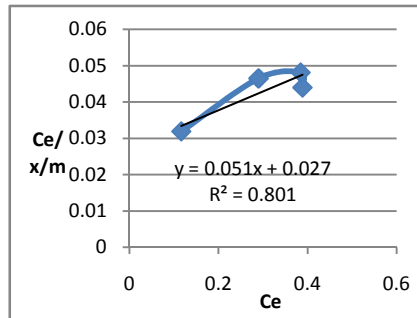
Graph 3: % adsorption vs. concentration of Acetic acid on Orange peel adsorbent.
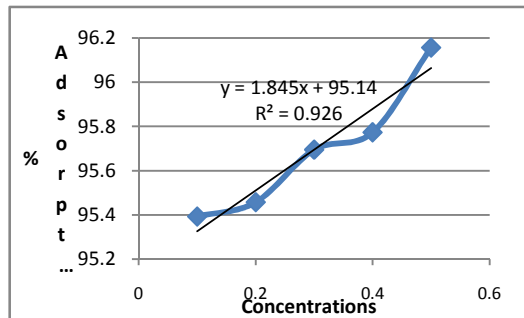
Table 3. Calculation of Freindlich and Langmuir constant.

	Acetic acid		**Acetic acid**
N	0.950	A	0.4822
K	22.80	B	37.03
R^2	0.99	R^2	0.80

RESULTS AND DISCUSSION

In our work we have try to determine adsorption of acetic acid on activated orange peels as a bio adsorbent. Different concentration of acetic acid solution we are prepared and determine the adsorption for 1 hr. contact time. From the table 1 we have determine the values of log x/m and log Ce the graph 1 of freindlich adsorption isotherm of Acetic acid on orange peels the straight line is obtained. From the graph R^2, n, k values were determined. From the values it was observed that Freindlich adsorption is verified.

Similarly, from graph 2 $Ce/x/m$ vs. Ce of Acetic acid on activated orange peels, straight line is obtained. From the graph a, b, $R2$ were determined. This value shows the Langmuir adsorption is verified.

Also, from table 3 the values of % adsorption vs. concentration graph 3 were plotted. From the graph it was observed that as the concentration of acid solution decreases % adsorption decreases.

From graph 1 and 4 the Freindlich adsorption isotherm can be said to be good fit for the given experimental adsorption data, since the linear regression of log x/m is log Ce gave R^2 value in the range of 0.99 for the different concentration of Acetic acid with orange peels adsorbents. Application of adsorbents for different effluents amplest understand the actual application of this adsorption method on the results obtained the experiments were conducted on different waste water samples collected from different industries. The activated orange peel and orange peel ash can be used as good adsorbent for selected effluent having specific concentration adsorbate (color/organic matter).

Similarly, from graph 2of the Langmuir adsorption isotherm can be said to be good fit for the given experimental adsorption data, since the linear regression of $Ce/x/m$ is Ce gave R^2 values in the range of 0.80 for the different concentration of Acetic acid with orange peels adsorbents. Application of adsorbents for different effluent samples. To understand the actual application of this adsorption method on the results obtained the experiments were conducted on different waste water samples collected from different industries. The activated orange peel and orange peels can be used as good adsorbent for selected effluent having specific concentration adsorbate (color/organic matter).

From the table 3 Freindlich constant for acetic acid 'n' having value 0.950 and 'K' having value 22.80 and Langmuir constant 'a' having value 0.4822 and 'b' having value 37.03 indicate that both Freindlich and Langmuir adsorption isotherm is verified.

From graph 3, it is concluded that the adsorption of acids decreases with decrease in concentration of acid. As the concentration of acid decreases from system 1 to 5 the adsorption of acid on orange peels adsorbent also get decreases.

From the above all graphs we can conclude that having R^2 value greater than 0.70 indicate the adsorbent gives better adsorption of acids.

CONCLUSION

The result of present study clearly shows that acid treated orange peels are effective in adsorption of acids. It is evident that experimental adsorption data for the adsorption of color in this research can be explained by more than one adsorption isotherms. The result shows that

the R^2 values are closer to 1 for all adsorption isotherm plots. Thus, Linear, Langmuir and Freindlich isotherm models are good fitted to the experimental data.

Thus full utilization of agro-waste and treatment of wastewater is one of the good prospective for good environment. The orange peels can be proved as good, effective and eco-friendly adsorbent.

Orange peels are cheap, less expensive in market. As it is a waste material of orange after threshing of orange, generally it is available in free of cost. It gives better adsorption of acids so instead of activated carbon it is more beneficial for adsorption as an adsorbent.

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