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Adsorption Studies of Acetic Acid on the Surface of *Solanum nigrum*

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The object of the present investigation is to study the adsorption of acetic acid on *Solarium nigrum.* The effect of certain parameters on adsorption has been studied. Applicability of Fruendlich adsorption isotherm and Langmuir adsorption isotherm has been tested. Various thermodynamic parameters such as ΔG, ΔH and ΔS are reported . The adsorption power of *Solanum nigrum* is calculated. The experiments are carried out using batch adsorption process.

Key Words : Adsorption, Acetic acid, *Solanum nigrum*.

INTRODUCTION

The removal of foreign substances from the waste water is of prime environmental importance. The presence of excess amount of undesirable constituents causes water pollution; it is an established fact that polluted water is harmful to human and aquatic life. There are various adsorbents available for the removal of inorganic and organic substances from polluted water. Various researchers have reported low cost adsorbents for pollution control. Acetic acid is used in the manufacturing of vinegar, cellulose acetate, perfumes, dyes, plastic and pharmaceutical companies. It is the chief constituent of vinegar. It is a corrosive liquid; the vapours are suffocative and causing damage to lungs.

Various researchers used plant-materials as adsorbents. Plant materials are used as cheap and low cost materials for adsorption, for example, modified corn starch[1], modified onion skins[2], saw dust[3], phosphate treated saw dust[4], water lettuce[5], etc. Adsorption of different metal ions and organic compounds on to solid surfaces has emerged as a promising field of great application value and has been extensively studied in the recent past.

EXPERIMENTAL

Acetic acid, sodium hydroxide, phenolphthalein, formaldehyde, concentrated sulphuric acid were supplied by S.D. Fine Chemicals Ltd. and were used without any purification.

The plant material was collected from local fields. It was dried and powdered and treated with formaldehyde and concentrated sulphuric acid and used for the adsorption study. Batch experiments were carried out in which solution of acetic acid was treated with 1 g of plant powder and kept shaking at room temperature for a contact time of 1 h. Finally the solution was filtered through Whatmann filter paper No. 42.

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The amount of acetic acid was determined volumetrically using phenolphthalein as a reagent[6]. Effect of contact time, temperature and effect of initial concentration were also determined.

RESULTS AND DISCUSSION

On the surface of a substance there are free valencies. When the adsorbate comes in contact with the surface, each valency is satisfied by a weak bond formation. The adsorption of solute from solution takes place due to decrease in interfacial tension or due to the solid surface acquiring electrostatic charge in solvent. This charged surface of the adsorbent then attains oppositely charged ions from the solution. During the formation of solids such as zeolites, gases are evolved and the solid becomes porous; such solids can be used as selective adsorbents for ion exchange.

In the present paper we present the adsorption behaviour of acetic acid on the charcoal obtained from the plant *Solanum nigrum.* It is important to know the adsorption capacity of various adsorbents, because adsorption can be used effectively in the prevention of environmental pollution. It is used for catalytic processes. Langmuir suggested that the forces operating between adsorbate and adsorbent are mostly short-range forces; these may be dispersion forces, the orientation forces and induction forces. Dispersion forces arise from attraction between temporary or instantaneous dipoles. The orientation forces appear upon adsorption of polar molecules carrying constant electrical charges. Polar molecules tend to orient themselves with their positive poles towards the negatively charged surface or negative poles toward the positively charged surface. The induction forces also play an important role in the adsorption process. The electric charge present on the surface of an adsorbent may induce dipoles in the adsorbate molecule thereby attracting them. In addition to these forces, hydrogen bonds may also form which cause interaction between adsorbate and adsorbent.

Effect of contact time : It was observed that *Solanum nigrum* can be used as a low cost adsorbent effectively. The maximum time required for adsorption is 40 min for 60% adsorption; after that the amount adsorbed remains constant.

The removal curve was found to be smooth and continuous indicating the formation of monolayer coverage of adsorbent on the other surface of adsorbate.

Adsorption isotherm: To study the validity of Freundlich adsorption isotherm the following equation was used:

$$\frac{x}{m} = K_c^{1/n}$$

The linear plot of log x/m *vs.* log C indicates the applicability of Freundlich adsorption isotherm. This shows a system which causes a monolayer coverage of the adsorbent on the other surface of the adsorbate. To verify Langmuir adsorption isotherm $1/C_e$ is plotted against 1/q; the value of 'b' is calculated graphically which is used to calculate the equilibrium parameter R_L

$$R_L = \frac{1}{1 + bC_0}$$

The range $0 < R_L < 1$ reflects favourable adsorption.

In the present study the value of R_L was found to be less than 1. The Langmuir adsorption parameters are very useful for predicting adsorption capacities and also for incorporating into mass transfer relationship. The isotherm can be written as

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{q_L}{K_L} C_e$$

where C_e is the concentration of the adsorbate at equilibrium, Q_e is the amount of metal ions adsorbed per unit weight of the adsorbent, a_L and K_L are Langmuir constants, q_L indicates the intensity of adsorption and $K_L = q_L b_L$ where b_L is the adsorption capacity. For the present study we obtained $a_L = 7.105$ L/mg, $b_L = 1.021$ mg/g.

The rate of acid adsorption (removal) falls off to give a smooth curve; this part of the plot is due to intra-particle diffusion. The initial portion of the plot can be interpreted by supposing a three step model as follows:

1. Mass transfer of acid from the bulk solution to the particle surface,
2. Intra-particle diffusion,
3. Adsorption at an interior side.

It is assumed that step 3 is much rapid with respect to the first two steps[8].

The mathematical theory of diffusion is based on Fick's first law, *e.g.*, molecular adsorption processes involve diffusive mass transport and the interpretation of the overall behaviour in terms of two diffusivity and intrinsic equilibrium sorption properties is difficult.

Intra-particle diffusion is an important rate controlling step during the adsorption process.

The following equations were used to find out the adsorption capacity of the plant *Solanum nigrum*:

$$y = \frac{(C_0 - C)V}{M}$$

$$F_r = \frac{(C_0 - C)}{C_0}$$

TABLE-1

ADSORPTION CAPACITIES (INITIAL CONCENTRATION Co= 23.1 gm/Ltr.)

Mass of adsorbent (g)	Equilibrium concentration C_e (g/L)	log C_e	$X = (C_0 - C_e)$	$Y = \frac{(C_0 - C_e)v}{M}$	$F_r = \frac{(C_0 - C)v}{C_0}$	X/M	log X/M	C/X/M
0.250	21.3	1.3283	1.8	360	0.077	7.2	0.8573	0.25
0.300	21.0	1.3222	2.1	350	0.090	7.0	0.8450	0.30
0.400	19.5	1.2900	3.6	450	0.155	9.0	0.9542	0.40
0.500	18.0	1.2552	5.1	510	0.220	10.2	1.008	0.50
0.600	17.4	1.2405	5.7	475	0.246	9.5	0.9772	0.60

Thermodynamic study: Experiments were carried out at different temperatures to study the effect of temperature on adsorption. Thermodynamic parameters such as ΔG, ΔH and ΔS were determined using the following equations:

$$K_c = \frac{C_{ad}}{C_e} \quad (1)$$

$$\Delta G = -RT \ln K_c \quad (2)$$

$$\log K_c = \frac{\Delta S}{2.303R} \frac{\Delta H}{2.303RT} \quad (3)$$

where K_c = equilibrium constant, C_{ad} = amount of metal ion adsorbed per litre of the solution at equilibrium, C_e = Equilibrium concentration (mg/L) of the metal in the solution.

TABLE-2
THERMODYNAMIC PARAMETERS

Temp. (K)	$1/T \times 10^3$	K_c	ΔG (J/mol)	log K_c
303	3.30	0.0845	–6225.88	–1.073
308	3.24	0.1323	–5180.40	–0.8484
313	3.19	0.2222	–3914.97	–0.6532
318	23.14	0.2833	–3335.13	–0.5477
323	3.09	0.2522	–3595.45	–0.5813

TABLE-3
EFFECT OF CONTACT TIME

Time (min)	$\sqrt{t}$	C_e	$q = C_0 - C_e$	$q_e - q$	$\log q_e - q$
5	2323	22.5	0.6	4.5	0.6532
10	3.16	20.4	2.7	2.4	0.3802
15	3.87	21.0	2.1	3.0	0.4771
20	4.47	19.5	3.6	1.5	0.1760
30	–	18.0	5.1	–	–0.000

Kinetics: Kinetic study of the adsorption process of acetic acid has been studied and it was observed that it obeys the Lagergren equation

$$\log (Q_e - Q_t) = \log Q_e - (K_d/2.303) \cdot t$$

where Q_e and Q_t are the metal ions adsorbed (mg/g) at equilibrium and at time t.

Intraparticle diffusion was also studied by plotting mass of solute adsorbed *vs.* square root of contact time. The plot was linear. From the slope, intraparticle diffusion constant was determined.

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