Biosorption of Formic Acid

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Abstract: *Present study deals with the biosorption of formic acid from aqueous solutions by using different biosorbents. The biosorbents are saw dust, potato peel & rice husk. These are essentially waste material and are easily available in abundance and having low cost. The study is carried out using batch reactor at room temperature. The sorption capacity of these biosorbents is compared at constant concentration using Rotary flask shaker type reactor. The data obtained in reactor is fitted in equilibrium isotherm namely Langmuir and frendlich. It is found that the selected biosorbents shows effective sorption capacity for formic acid and can be used as an alternative method for its recovery.*

Keywords: *Biosorption, Formic acid, potato peel, rice husk, saw dust, Equilibrium*

1. INTRODUCTION

Formic acid (FA, HCOOH) also called methanoic acid, it is simplest carboxylic acids, used in processing textiles and leather. It was first isolated from certain ants and was named after the Latin *formica,* meaning "ant." FA is made by the action of sulfuric acid upon sodium formate, which is produced from carbon monoxide and sodium hydroxide. It is a colorless liquid having a highly pungent, penetrating odor at room temperature and miscible with water. FA is polar organic solvents, and is somewhat soluble in hydrocarbons. It is also prepared in the form of its esters by treatment of carbon monoxide with an alcohol such as methanol in the presence of a catalyst. FA is mainly used as a preservative and antibacterial agent in livestock feed. In Europe, it is applied on silage (including fresh hay) to promote the fermentation of lactic acid and to suppress the formation of butyric acid. It also allows fermentation to occur quickly, and at a lower temperature, reducing the loss of nutritional value. FA arrests certain decay processes and causes the feed to retain its nutritive value longer, and so it is widely used to preserve winter feed for cattle. In the poultry industry, it is sometimes added to feed to kill E. coli bacteria. Use as preservative for silage and (other) animal feed constituted 30% of the global consumption in 2009. FA is also significantly used in the production of leather, including tanning (23% of the global consumption in 2009, and in dyeing and finishing of textile (9% of the global consumption in 2009) because of its acidic nature.

For recovery of FA is essential from its various sources of production. There are many technologies for the recovery of FA such as adsorption, extraction, electro dialysis, reverse osmosis etc. Among all these, adsorption is widely used technology employed in waste water treatment process for recovery of certain useful products. Adsorbents are classified into three different types i) oxygen containing compounds e.g. silica gel and zeolite; ii) carbon based compounds e.g. activated carbon and iii) polymer based compounds e.g. porous polymer matrix. Although synthetic polymeric and silica based adsorbents are used for waste water adsorption but since they are costly, cheap adsorbents such as activated charcoal, potato peel, rice husk, sawdust, bagasse fly ash, tea waste etc. are generally used in advanced wastewater treatment.

Hasan uslu et al. (2009) [1], weakly basic adsorbent (Amberlite IRA-670 is used to adsorb formic acid at three different temperatures (298 K, 318 K, and 328 K). Petter Perssona et al. (2000) [2] Adsorption of formic acid (HCOOH) on ZnO surfaces investigated by means of quantum-chemical ab initio periodi Hartree–Fock calculations. Graeme J. Millar et al. (1991) [3] Adsorption of formic acid on silica- supported copper, oxidized copper. L Kieu et al. (2001) [4] Adsorption over rutile titanium dioxide (TiO2) surface have been studied.

Separation of formic acid by azeotropic distillation using chloroform or paraffinic hydrocarbons as entrainers as in US. Patent specification No. 3,024,170 [5] and in British patent specification No. 727,078 also involves great expense which is not warranted by the value of the formic acid recovered.

Biosorption has advantages compared with conventional techniques as reported by Volesky (1999) [6]. Some of these are listed below:

- The cost of the biosorbent is low since they often are made from abundant or waste material.

- As is the case with many other techniques, for example, precipitation, no secondary problems with sludge occur with biosorption.

- Biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

- Abundant in nature.

In view of the applications of adsorbent, it has been decided to study the adsorption characteristics of potato peel, rice husk & saw dust for the removal of FA from dilute solutions. Effect of adsorbent doses, initial acid concentration, and contact time were studied.

2. MATERIALS & METHODS

Potato peel was obtained from college mess ggv, Rice husk and Saw dust from rice & saw mill, CG, India. The adsorbents were washed, dried, activated in a furnace at 300° C for 3 hrs washed with tab water then grind in grinder. The average particle size of biosorbent is kept 125 μm or 120 mesh. Formic acid (HCOOH; molecular weight 46.01; density 1.22 g/mL) was obtained from fisher scientific.

Concentrations of FA were prepared from (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 mol/L). 50ml each of these solutions were taken in 100ml conical flasks and known amount of adsorbents are added. The conical flask in which the aqueous solution of formic acid and adsorbent are added kept in the Rotary flask shaker with a speed of 80 rpm. The samples are left for 4hrs. The mixtures were finally filtered to separate the adsorbents. They are allowed 2hrs to settle to attain equilibrium. The solution is filtered and titrated with NaOH 0.1N using phenolphthalein as indicator. The same experiment is carried out using all the adsorbents.

3. RESULT AND DISCUSSION

3.1. Equilibrium Studies: Effect of Process Variables

The amount of acid adsorbed (Qe) g/mg and the adsorption efficiency (%) can be calculated according to the expressions:

$$Q_e = \frac{[HA]_o - [HA]^*}{w_s} \times V$$

$$\text{(1)}$$

$$\text{Adsorption efficiency } AE(\%) = \frac{[HA]_o - [HA]^*}{[HA]_o} \times 100$$

$$\text{(2)}$$

where, Qe = amount of acid adsorbed g/mg, [HA]o and [HA]* are the initial and equilibrium concentrations (mol/l), V the volume of solution (l), ws the weight of adsorbents (g).

3.2. Effect of Adsorbent Concentration

Effect of adsorption solute was investigated by varying its doses (ws) from 0.1 to 10gm for different adsorbent using 0.4 mol/l of formic acid at 303 K. The adsorption (maximum) was obtained from Eq. (2) to be 46.75 %, 41.62 %, 40.09 %, for potato peel, saw dust and for rice husk respectively as shown in Figure (1).

3.3. Effect of Initial Acid Concentration

To study the effect of initial acid concentration on adsorption for formic acid, for a fixed adsorbent (1gm) its concentration was varied from 0.2 mol/l to 1.2 mol/l. It can be observed that increasing the initial acid concentration from 0.2 mol/l to 1.2mol/l. Percentage of acid removed decreases from 49.2-25.60%, 45.0%-24.6%, 43.52-20% for potato peel, saw dust and for rice husk shown in Figure (2).

Decrease may be caused with the rate uptake of adsorbate is found to increase non-linearly with increasing concentration of solute (weber et al. 1963).

3.4. Effect of Contact Time

Time for the attainment of equilibrium (t) was determined when the formic acid and adsorbent was contacted with each other in a mechanically agitated contactor (2000 rpm). Time was varied from 0-90 min for the initial acid concentration of 0.4 mol/l and 1 gm adsorbent dosage at 303K. Within 85 minutes of shaking a quasi stationary state were obtained and is independent of adsorbent dose shown in Figure (3).
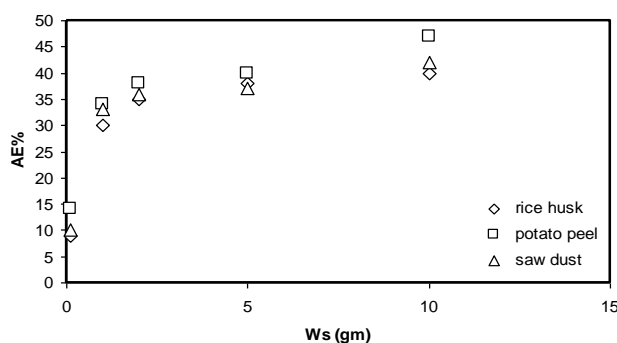

Fig1. *Graph of adsorbents dosage (0.1-10gm) on the adsorption of FA using different adsorbents*

4. EQUILIBRIUM ISOTHERMS

4.1. Langmuir Isotherm

Langmuir isotherm (1916) derived a simple adsorption isotherm based on theoretical consideration. The isotherm is based on the following assumptions (Hall et al. 1996) [7]:

The Langmuir equation is defined as:

$$Q_e = \frac{K_A.Q_{max}.C_e}{1 + K_A.C_e} \qquad (3)$$

where Qmax denotes the maximum adsorbent, Qe denotes the experimental adsorbent uptake at equilibrium (g/mg). Ce is the equilibrium concentration of solute in the solutions (g/l). KA is a Langmuir model coefficient and it is related to the affinity between the adsorbent & adsorbate. The value of KA & Qmax could be determined by equation (3) as

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}.K_A} + \frac{C_e}{Q_{max}} \qquad (4)$$

The values of KA & Qmax could be determined from the intercept & slope of the straight line in equation. (4). Langmuir isotherm was fitted to the experimental data for different acid concentration (0.2-1.2 mol/l) and 1 gm of different adsorbents at temperatures (303 K). The calculated model parameters determined by least square fit of the experimental sorption data and their corresponding regression coefficients (R^2) are given in Table 1. The graphical comparison of the isotherm and the experimental data is given in Figure 4 and Table 1.

The important characteristics of Langmuir isotherm can be expressed in terms of dimensionless constants separation factor or equilibrium parameter (R_L).
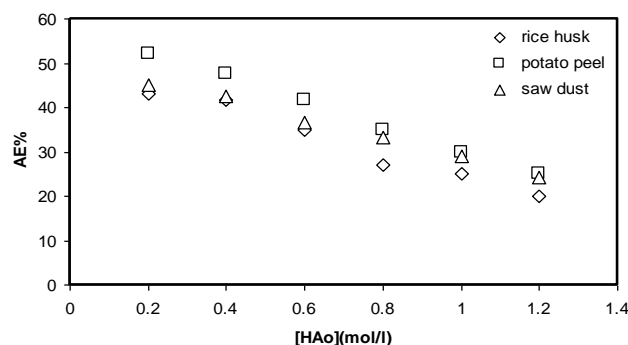
$$R_L = 1/1 + K_L [HA]_o \qquad (5)$$

Fig2. *Graph of initial acid concentration on the adsorption of FA using different adsorbents*
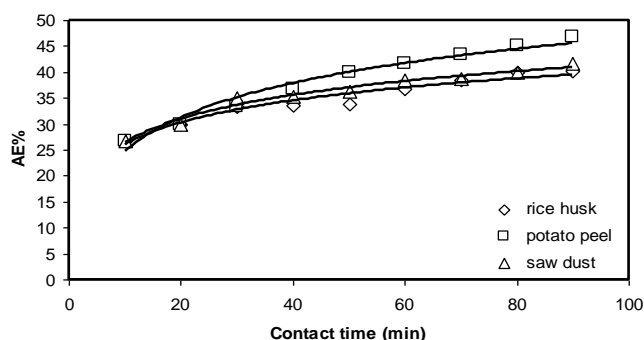

Fig3. *Graph of contact time on the adsorption of FA using different adsorbents*

Table1. *Langmuir isotherm parameters for adsorption of formic acid*

Adsorbents	Langmuir Isotherm
	Q_{max} K_A R^2
Rice husk	0.00366 5.176 0.9823
Saw dust	0.004107 5.479 0.9797
Potato peel	0.00454 5.77 0.9927

Where $[HA]_o$, the initial formic acid concentration (mg/L) and K_L is the Langmuir constant. R_L indicates the type of isotherm favourable: $R_L > 1$ means unfavourable; $R_L = 1$ means linear; $0 < R_L < 1$ means favourable, $R_L = 0$ means irreversible. Adsorption system is favourable or unfavourable were predicted according to the effect of isotherm shape.

Table2. *Freundlich isotherm parameters for adsorption of formic acid*

Adsorbents	Freundlich Isotherm
	K_f n R^2
Rice husk	0.00376 0.43 0.9987
Saw dust	0.00684 0.48 0.9954
Potato peel	0.01140 0.52 0.9914

Regression coefficient R^2 magnitude has been asses for the fit of the isotherm. Langmuir isotherm fitted to the experimental results for formic acid, provides R^2 values of 0.9823, 0.9797, 0.9927 for rice husk, saw dust & potato peel respectively.

4.2. Freundlich Isotherm

Freundlich (1912) was the second isotherm method employed for studying the equilibrium characteristics:

$$Q_e = K_f . C_e^{1/n} \tag{6}$$

Q_e and C_e were same as describe in Langmuir's isotherm. A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined,

$$\log Q_e = \log K_f + (1/n) \log C_e \tag{7}$$

K_f is the freundlich capacity factor, (mg absorbate/g adsorbent)(L water/mg adsorbate)$^{1/n}$ and $1/n$ is the Freundlich intensity parameter. The value of K_f and $1/n$ at different concentrations were determined from the slope and intercept of the linear plots of log Q_e and log C_e. Figure 5, shows the plots of Freundlich equilibrium isotherms for formic acid adsorption using different adsorbent. Results of Freundlich equation were presented in Table 2. This is equation for a straight line. Thus a plot of log Q_e and log C_e should be a straight line with slope $1/n$ and intercept log k_f. Presents the Freundlich capacity factor and Freundlich intensity parameter determined by least square fit and their corresponding regression coefficients (R^2). The graphical comparison of the isotherm and the experimental data is given in Figure 4 and 5, Table 1 and 2. However, it is actually found that the plots were straight lines at low pressures, while at higher pressures they showed a slight curvature, especially at low temperatures. This indicates that Freundlich equation is approximate and does not apply to adsorption of gases by solids at higher pressures. Regression coefficient of freundlich isotherm R^2 is shown in fig 5 and Table 2.
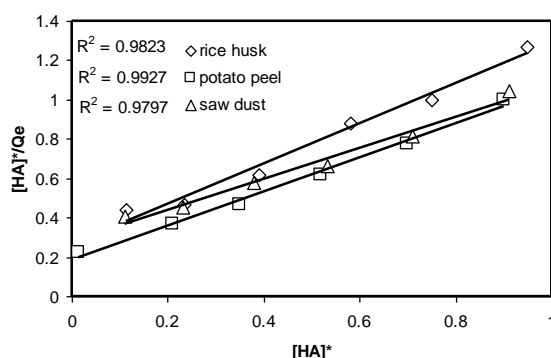

Fig4. *Graph of Langmuir isotherm for the adsorption of FA using different adsorbents*

5. CONCLUSION

FA equilibrium adsorptions recovery from dilute solution was studied. When acid concentration was varied from 0.2 mol/L to 1.2 mol/L, it was found that adsorption percentage decreases with increase in acid concentration. Langmuir and freundlich isotherms provides R^2 values of 0.9823, 0.9927, 0.9797 and 0.9575, 0.9435, 0.9457 for rice husk, potato peel and saw dust respectively at room temperature (300 K). Langmuir found to be more fitting as compared to Freundlich for all the adsorbents. The chosen biosorbents have shown to be a good alternative for formic acid recovery as the conventional adsorbents are costlier and the procedure of its preparation are hectic compared to biosorbents which are technically treated as waste and are easy to prepare for use as adsorbent.
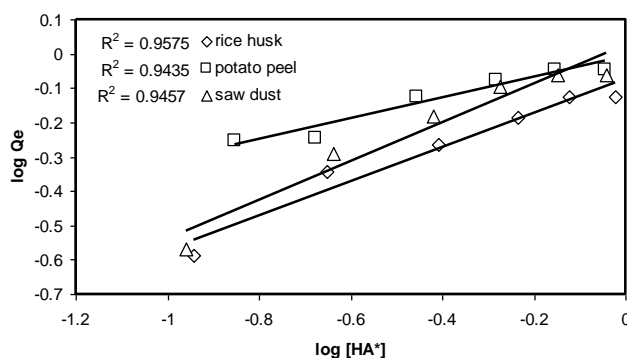

Fig5. *Fit of freundlich isotherm for the adsorption of FA at room temperature using different adsorbents*

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