

Removal of Glycolic Acid From Aqueous Solution using Bagasse Flyash

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ABSTRACT: Present study deals with the adsorption of glycolic acid (GA) from aqueous solutions by using bagasse fly ash (BFA). BFA is a solid waste generated from bagasse fired boilers and can be used as an adsorbent. Batch adsorption studies were carried out to evaluate the effect of various parameters like adsorbent dose, contact time, initial concentration and temperature on the removal of GA from aqueous solutions. For the selected dosage, it was found that the adsorption increases with increase in BFA doses and decreases with increase in acid concentration. The effect of contact time on removal shows that the adsorption of glycolic acid on BFA is very fast. The kinetics of the sorption of GA was well represented by Elovich model, first order, pseudo-second order and Weber and Morris intra-particle diffusion model. The adsorption isotherm analyses were also carried out by using Langmuir and Freundlich isotherm equations. Freundlich equation was found satisfactory to represent the equilibrium data. Thermodynamic studies revealed that the adsorption of GA on BFA is exothermic in nature.

Key words: Glycolic acid, Adsorption, Bagasse fly ash, Equilibrium, Kinetics

INTRODUCTION

Glycolic acid (Alpha hydroxy acid, GA) also known as hydroxyacetate acid, is the most frequently used alpha-hydroxy acid in facial treatments or chemical peels. GA is a key ingredient in an increasing number of skin care products that are available in the market today, including peels, creams, exfoliants, cleansers and toners. It may reduce wrinkles, acne scarring, hyperpigmentation. It is also a useful intermediate for organic synthesis in a range of reactions including: oxidation-reductions, esterification, long chain polymerization, and is used as a monomer in the preparation of polyglycolic acid. Among other uses this compound finds employment in the textile industry as a dyeing and tanning agent, in food processing as a flavoring agent and as a preservative. GA is often included into emulsion polymers, solvents, and additives for ink and paint in order to improve flow properties and impart gloss. Natural sources of GA include sugar cane, sugar beets, pine apple, canteloupe, and unripe grapes. By synthetic means it can also be prepared, example by reaction of carbon monoxide with formaldehyde, preferably in the presence of water (Leupold *et al.*, 1978).

Recovery of GA is essential from its various sources of production. There are many technologies for the recovery of acids from dilute solution such as adsorption, extraction, electrodialysis, reverse osmosis etc. Among all these, adsorption is widely used technology employed in waste water treatment process for recovery of certain useful products for further processing. 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 graphite 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, bagasse fly ash (BFA), tea waste etc. are gaining attractiveness in advanced wastewater treatment.

Glycolic acid could also be obtained from sea water. Shah and Wright (1994) studied the adsorption of glycolic acid by alumina from sea water (Ipswich Bay (Gulf of Maine, USA)), followed by extraction with sulphuric acid and then colorimetry. The overall efficiency of recovery of this method, which is standardized internally, is approximately 67%, and about 20-fold concentration of glycolic acid is

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achieved. Method for improved quantification of glycolic acid dissolved in seawater has been described by Leboulanger et al. (1994). The extraction of glycolic acid was performed by an organic solvent and its quantification by HPLC. With this method, the glycolic acid dissolved in seawater is extracted in a reproducible manner with a constant yield, and dosed with a precision $\geq \pm 7.5\%$. Removal of glycolic acid by the weakly basic adsorbent Amberlite IRA-67 has been studied at three different temperatures by Uslu et al. (2010). The maximum adsorption efficiency has been found to be 86.29 % for glycolic acid. The Langmuir isotherm fitted the experimental data better than the Freundlich isotherm for both acids. Thermodynamic parameters ΔG , ΔH , and ΔS were also evaluated.

Another successful method for recovery of glycolic acid has been using reactive extraction. Many successful works have been presented in the literature. Datta and Kumar (2011) presented the removal of glycolic acid from aqueous solution by two different extractants (tri-*n*-butyl phosphate (TBP) and tri-*n*-octylamine (TOA)) at constant concentration of 0.573 kmol/m³ dissolving in a wide range of diluents (*n*-hexane, decane-1-ol, *n*-hexane + decane-1-ol (1:1 v/v), 4-methylpentan-2-one (MIBK), benzene, and dichloromethane (DCM)). Effects of various parameters such as acid concentration (0.10-0.57 kmol/m³), extractant type, and type of diluents have been presented. Extraction of glycolic acid was investigated from aqueous solutions by different organic solutions containing Amberlite LA-2, a secondary amine mixture. 1-octanol, cyclohexane, isooctane, toluene, 2-octanone, and methyl isobutyl ketone (MIBK) were used as diluents (Selim and Inci, 2009). The effect of solvent type, amine concentration, and initial acid concentration has been investigated. The maximum removal of glycolic acid was 79.43 % with MIBK and 0.93 mol/L initial concentration of Amberlite LA-2. Partitioning of glycolic acid from aqueous solutions by TOMAC in mixtures of three individual diluting solvents (propanol, cyclohexane, isooctane, butanol, toluene, methyl isobutyl ketone, and ethyl acetate) was presented by Inci and Uslu (2005). The distribution coefficients, loading factors and extraction efficiencies were derived. The maximum removal of glycolic acid was 49% with propanol with a 1.76 mol/L initial concentration of trioctyl methylammonium chloride. Inci (2002) presented novel distribution data of glycolic acid between water and different organic solutions of trioctylamine and Alamine 336. Diluting solvents used in this study were heptane, cyclohexane, toluene and methyl isobutyl ketone (MIBK). The distribution coefficients and loading factors are calculated and interpreted from experimental results.

In the present study, BFA has been employed for the recovery of GA from dilute aqueous solutions. BFA, a waste produced in sugar industries, could be an inexpensive and effective adsorbent for the removal of carboxylic acid from dilute solutions. Only a limited number of studies, however, have so far been focused on the use of BFA and that for the removal of ions from wastewater.

Gupta et al. (2000) studied the utilization of BFA for the removal of copper and zinc from wastewater. Nassar et al. (2004) studied the kinetic and thermodynamic parameters during thermal decomposition of dye when BFA was used as adsorbent. Equilibrium, kinetics and thermodynamics of adsorption of phenol on BFA and activated carbon-commercial grade (ACC) and laboratory grade (ACL) were investigated by Srivastava et al. (2005). Karnitz et al. (2006) studied adsorption of heavy metal ion from aqueous single metal solution by chemically modified BFA. The obtained materials were characterized by elemental analysis and infrared spectroscopy (IR). The second part of this report features the comparative evaluation of the adsorption capacity of the modified BFA for Cu²⁺, Cd²⁺, and Pb²⁺ ions.

In view of the applications of BFA as adsorbent, it has been decided to study the adsorption characteristics of BFA for the removal of GA from dilute solutions. Effect of BFA doses, initial acid concentration, contact time, thermodynamic were investigated. Also the kinetics of adsorption was presented and various models were fitted to the kinetic data such as Elovich model, first order, second order model, Weber & Morris intra-particle diffusion model.

MATERIALS & METHODS

BFA was obtained from Deoband sugar mill, UP, India which was collected from the particulate collection device that is attached to the flue gas line of a bagasse fired boiler stack and it was used without any pre-treatment other than sieving. Glycolic acid (C₂H₄O₃; molecular weight 76.05; density 1.27 g/cm³) was obtained from the Luba Chemical India. The average particle size of BFA used for the sorption of BA is in the range of 180 to 1400 μ m. The BET surface area of BFA was estimated by the standard adsorption of N₂ at 77.15 K (Brunauer *et al.*, 1938). The Bulk density of BFA was determined using MAC bulk density meter. SEM analysis of BFA was carried out before and after the adsorption of BA by using LEO 435 VP Scanning electron microscope.

Different concentrations of GA were prepared (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 weight of BFA was added and the contents were shaken

for 4 hrs and made to settle for 2 h. The mixtures were finally filtered to separate BFA. The left out solution was titrated with standard NaOH solution using phenolphthalein as an indicator.

Kinetics

Kinetics was studied in CSTR operating at 2000 rpm. The stirring duration was from 0-90 min. 10ml of solution was pipetted out every 10 minutes and settled for 2 h and filtered with filter paper. 3 ml of this solution was taken and titrated against NaOH using phenolphthalein as an indicator.

Thermodynamics

Effect of temperature on the adsorption was studied for various concentrations of acid (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 mol/L) using BFA as adsorbent. Temperature was varied from 303 – 323 K. Experiments involved shaking equal volumes of aqueous phase at different temperatures in water bath shaker. Settling was done at the same temperature and samples were titrated using NaOH for determination of acid concentration in the aqueous phase after the experiment.

RESULTS & DISCUSSION

It is observed that BFA has bulk density (121.04 kg/m^3). The amount of carbon content is high in BFA when compared to other adsorbents like rice husk ash. The average particle size is $375.34 \mu\text{m}$ and BET surface area of pores is $230.07 \text{ m}^2/\text{g}$. Physical characteristics of BFA are follows: Moisture (14.39%), Volatile matter (9.80%), Ash (53.22%), Fixed carbon (23.59%). The morphologies of blank and GA-loaded BFA, was examined by scanning electron microscopy (SEM). SEM micrograph of BFA is at 1000X magnification. Fig (1) shows the fibrous structure and strands of the fiber.

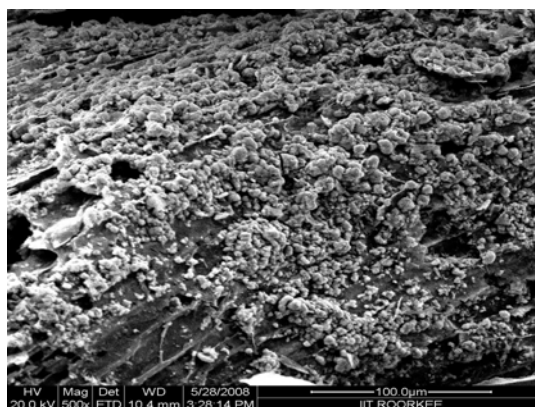
It can be inferred from these fig.s that the surface texture of the blank adsorbents changes after the adsorption of GA. The chemical structure of the adsorbents is very important in understanding the sorption process by using FTIR spectroscopy analysis. The sorption capacity of BFA is strongly influenced by the chemical structure of their surface. The carbon-oxygen functional groups are by far the most important structures in influencing the surface characteristics and surface behavior of BFA.

BFA spectra is shown in (Fig. 2a). A broad band between 3100 and 3800 cm^{-1} in the BFA is indicative of the presence of both free and hydrogen bonded OH groups on the surface of BFA. This stretching is due to both the silanol groups (SiOH) and adsorbed water (peak at 3800 cm^{-1}) on the surface. C-O group stretching from aldehydes and ketones can also be inferred from peaks at $\sim 1500 \text{ cm}^{-1}$. The band around $\sim 1400 \text{ cm}^{-1}$ in all both the adsorbents may be attributed to the carboxyl-carbonate structures. The functional groups suggested most often are: (i) carboxyl groups, (ii) phenolic hydroxyl groups, (iii) carbonyl groups (e.g. quinone-type), and (iv) lactone groups (e.g. fluorescein-type). (Fig. 2b) shows the FTIR spectra of the blank and BFA loaded GA. Two clear peaks around 1300 to 1800 cm^{-1} can be identified which seemed to be affected due to GA-adsorption onto BFA. These peaks are normally attributed to adsorbed bound water onto the sorbent surface. The peak around 1300 cm^{-1} corresponds to bound water coordinated to cations. This may also be attributed to single C-N bond (not to hydrogen).

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

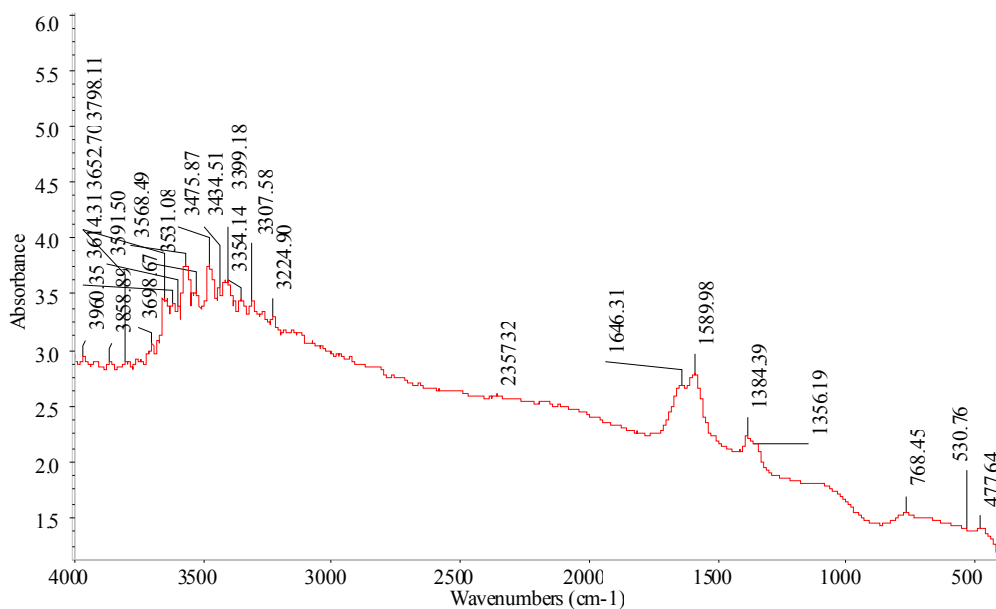


Blank-BFA

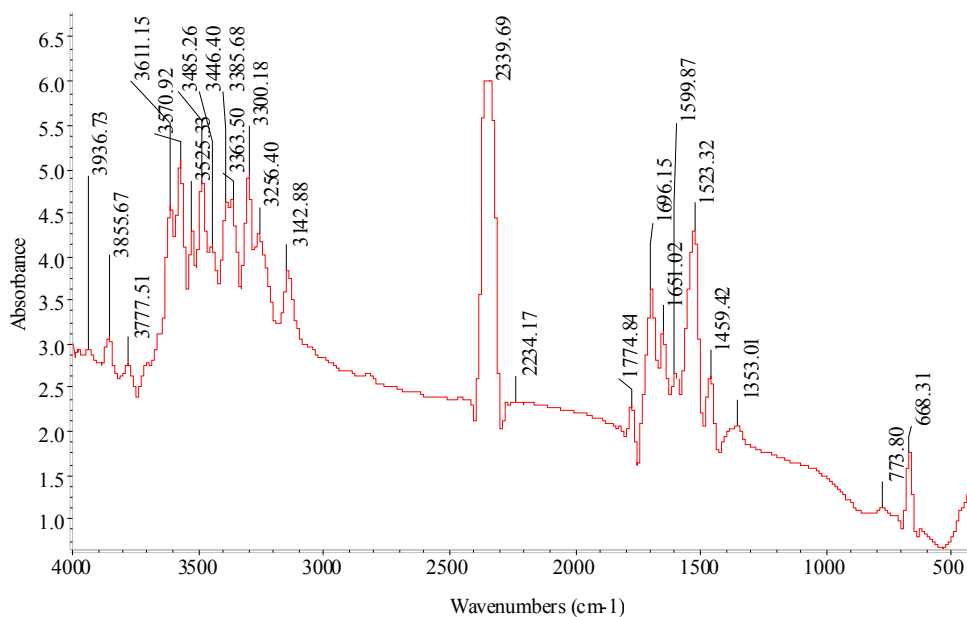


GA-BFA

Fig. 1. SEM of blank-BFA and GA-loaded BFA at 500X and 1000X



(a). Blank-BFA



(b). GA-loaded BFA

Fig. 2. FTIR spectra of blank-BFA and GA-loaded BFA. (a). Blank-BFA. (b). GA-loaded BFA

$$Q_e = \frac{[HA]_0 - [HA]^*}{w_s} \times V \quad (1)$$

$$\text{Adsorption efficiency AE (\%)} = \frac{[HA]_0 - [HA]^*}{[HA]_0} \times 100 \quad (2)$$

Where, Q_e = amount of acid adsorbed g/mg, $[HA]_0$ and $[HA]^*$ are the initial and equilibrium concentrations (mol/L) of acid, V the volume of solution (l), w_s the weight of adsorbents (g).

The effect of solute adsorption was investigated by varying BFA doses (w_s) from 0.1 to 10 gm for 0.4 mol/L of glycolic acid at 303–323 K. For the selected dosage, it was found that the adsorption increases with increase in w_s . The reason for this being that higher dosage provides higher surface area and hence more adsorption sites for removal of glycolic acid. The maximum adsorption was obtained to be 27.21%, 22.18%, 20.67% for $T = 303, 313$ and 333 K, respectively (Fig. 3).

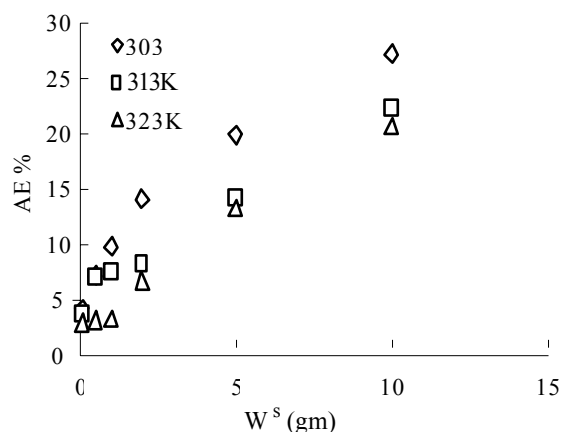


Fig. 3. Effect of the BFA dosage (0.1-10 gm) on the adsorption of GA Using BFA

To study the effect of initial acid concentration on adsorption for glycolic acid, its concentration was varied from 0.2 mol/L to 1.2 mol/L for a fixed BFA (1 g). It can be observed that increasing the initial acid concentration from 0.2 mol/L to 1.2 mol/L percentage acid removed decreases from 11.50 to 4.53 %, 10.05 to 4.43 % and 9.53 to 4.15 % (Fig. 4), on the other hand, glycolic acid uptake per unit mass of BFA increases from 0.0017 to 0.0041, 0.0015 to 0.0040 and 0.0014 to 0.0037 respectively for BFA at 303, 313, 323 K. Thus adsorption using BFA is effective when acid is present in dilute solutions. At higher initial concentrations of acid the ratio of initial moles of glycolic acid to the available surface area is high and hence the fractional adsorption becomes dependent on the initial acid concentration. Further, the decreases in percentage removal efficiency can be explained on the view point of the saturation of BFA surface. At fixed BFA dosage, the available sites become the limiting parameter and hence adsorb the same amount of sorbate. This results in the decrease of the percentage removal of adsorbate with increase in initial acid concentration. Decrease may be caused with the rate uptake of adsorbate is found to increase non-linearly with increasing concentration of solute.

Time for the attainment of equilibrium (t) was determined when the glycolic acid and BFA were contacted with each other in a mechanically agitated contactor (2000 rpm). Time was varied from 0-90 min for the initial acid concentration 0.4 mol/L and 1 g BFA concentration at 303 K (Fig. 5). A quasi stationary state was obtained within 85 minutes of shaking and is independent of BFA dose. Thus based on this study, it can be suggested that 85 minutes is sufficient time for studying the equilibrium characteristics of glycolic acid adsorption using various BFA. It was observed that adsorbent rate is fast at the initial stages of the contact

period, and thereafter, it become slower near the equilibrium. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Further it can be seen that equilibrium could be achieved in 90 minutes.

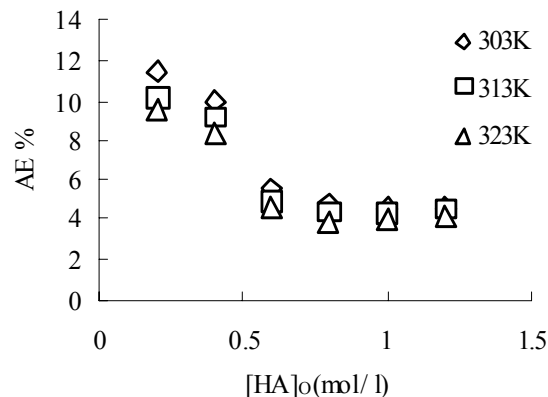


Fig. 4. Effect of acid concentration on the adsorption of GA using BFA

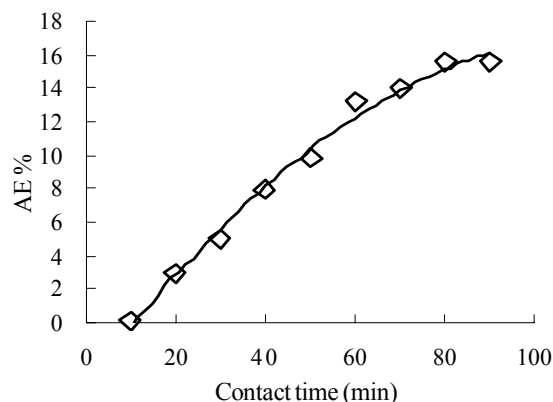


Fig. 5. Effect of contact time on the adsorption of GA using BFA

To study the effect of temperature on the adsorption of GA three different temperatures (303, 313 and 323K) for different initial acid concentration (0.2-1.2 mol/L) and different BFA dosage of (1-10 g) were employed (Fig. 3-4). For a fixed BFA concentration (1 g) it was found that adsorption decreases with increase in temperature for all acid concentrations (Fig. 4). The average decrease in adsorption is 34%. However, for fixed acid concentration, as the amount of BFA increases, the percentage adsorption increases but with the increase in temperature adsorption decreases (Fig.

3). The percentage increase ($I\% = \{AE\% \text{ at } 323 \text{ K} - AE\% \text{ at } 303 \text{ K}\} / AE\% \text{ at } 323 \text{ K}$) was higher at lower BFA concentration and decrease as the amount of BFA is increased. $I\%$ decreases from 27.21 to 4.27 % as BFA concentration was increased from 0.1 g to 10g. The maximum ratio of $[HA]^*/Q_e$ for glycolic acid adsorption using BFA was found to be 21248.78, 21802.50, 23640.54. This value shows that the adsorption efficiency of the BFA decreases with increasing temperature. Thus, it could be understood that the adsorption of GA is exothermic in nature, such like the most of adsorption reactions. The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be determined by using the following equations:

$$\ln K_A = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

$$\Delta G = \Delta H - T \Delta S \quad (4)$$

Where, R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and K_A (mol/g) is the standard thermodynamic equilibrium constant. By plotting a graph of $\ln K_A$ versus $1/T$ the values ΔH° and ΔS° can be estimated from the slopes and intercepts. Values of ΔG° , ΔH° and ΔS° are given in Table 1 and shown in (Fig. 6).

It is observed that the adsorption of GA decreases with increase in temperature. Favorable condition for adsorption of GA is at lower temperature. The decrease in adsorption with increase in temperature is partly due to the weakening of the attractive force between the GA and BFA surface, and partly due to the enhancement of thermal energies of the adsorbate, thus making the attractive force between BFA and GA insufficient to retain the adsorbed molecules at the binding sites. From Table 1, it can be seen that the free energy of the system increases with increase in temperature decreasing the spontaneity of the process. The value of enthalpy and entropy change suggests that, the process is exothermic in nature.

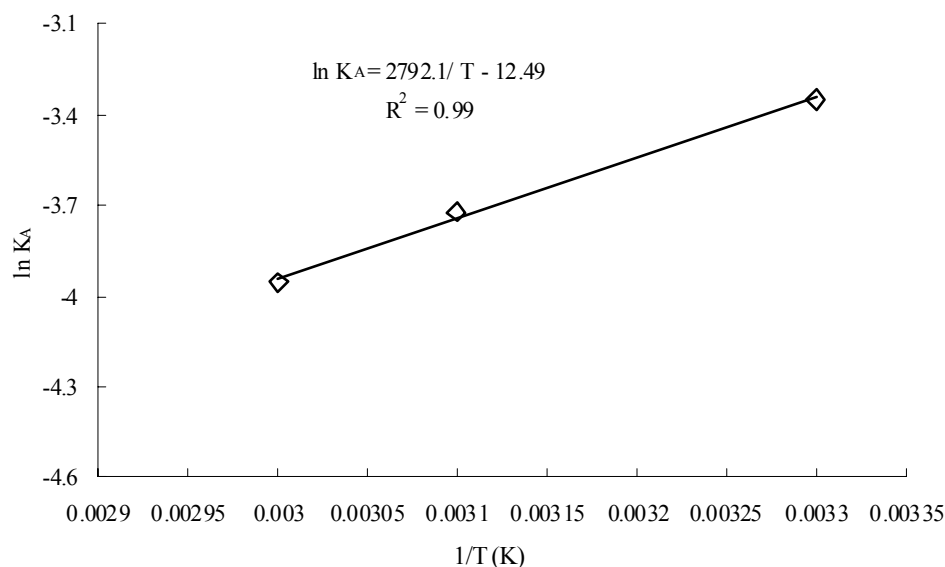


Fig. 6. Effect of $\ln K_A$ vs. $1/T$ for estimation of thermodynamic parameters for adsorption of GA using BFA

Table 1. Thermodynamic parameters for adsorption of GA using BFA

Adsorbent	Temperature (K)	ΔG° (kJ/mol)	ΔS° (kJ/ Kmol)	ΔH° (kJ/mol)
Bagasse fly ash	303	7033589.69	-23213.51	-103.84
	313	7265724.79		
	323	7497859.89		

Langmuir derived a simple adsorption isotherm based on theoretical consideration. The Langmuir equation is defined as:

$$Q_e = \frac{K_A \cdot Q_{\max} \cdot [HA]^*}{1 + K_A \cdot [HA]^*} \quad (5)$$

Where Q_{\max} denotes the maximum adsorbent and Q_e denotes the experimental adsorbent uptake at equilibrium (g/mg). $[HA]^*$ is the equilibrium concentration of solute in the solutions (g/L). K_A is a Langmuir model coefficient and it is related to the affinity between the BFA and GA. The value of K_A and Q_{\max} could be determined by transforming Eq. (5) as (Hall *et al.*, 1996).

$$\frac{[HA]^*}{Q_e} = \frac{1}{Q_{\max} \cdot K_A} + \frac{[HA]^*}{Q_{\max}} \quad (6)$$

The values of K_A & Q_{\max} could be determined from the intercept and slope of the straight line in Eq. (6). Langmuir isotherm was fitted to the experimental data for GA concentration (0.2-1.2 mol/L) and 1 g of BFA for different temperatures (303-323 K). The calculated model parameters determined by least square fit of the experimental sorption data and their corresponding regression coefficients (R^2) are presented in Table 2. The graphical comparison of the isotherm and the experimental data is given in (Fig. 7). The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter (R_L).

$$R_L = \frac{1}{1 + K_L [HA]_0} \quad (7)$$

Table 2. Isotherm parameters for adsorption of GA using BFA

Langmuir Isotherm				Freundlich Isotherm			
T (K)	Q_{\max} (g/ mg)	K_A (l/mg)	R^2	T (K)	K_f	n	R^2
303	0.0048	0.035	0.9674	303	0.00069	2.62	0.9709
313	0.0049	0.026	0.9519	313	0.00051	2.30	0.9800
323	0.0058	0.014	0.8214	323	0.00031	1.93	0.8595

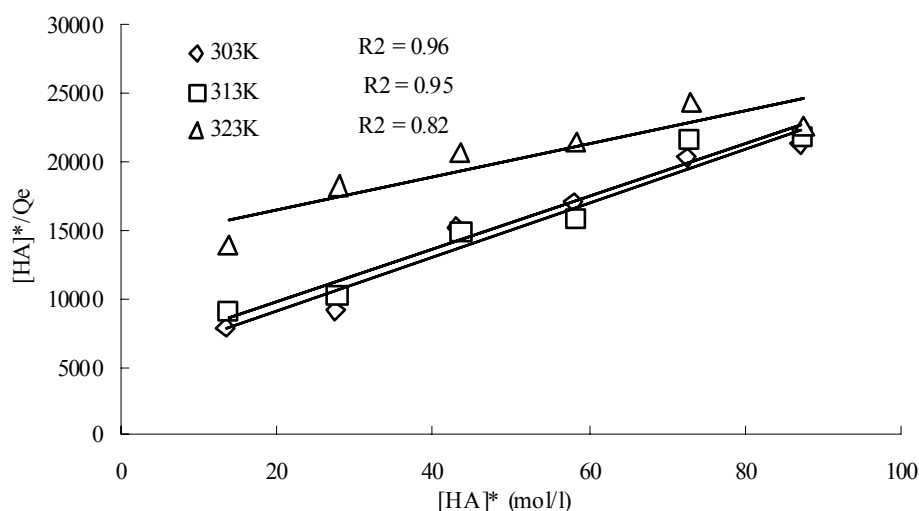


Fig. 7. Fit of Langmuir isotherm for the adsorption of GA at different temperatures using BFA

Where, K_L is Langmuir constant and $[HA]_0$, the initial glycolic acid concentration (mg/L). R_L indicates the type of isotherm that is favorable: $R_L > 1 \rightarrow$ unfavorable; $R_L = 1 \rightarrow$ linear; $0 < R_L < 1 \rightarrow$ Favourable, $R_L = 0 \rightarrow$ Irreversible. Adsorption system is 'favourable' or 'unfavourable' were predicted according to the effect of isotherm shape (Hall *et al.*, 1966). R_L was evaluated using Eq. (7) and was found to vary from 0.96-0.99 at $T = 303K$, 0.97-0.99 at $T = 313 K$ and 0.98-0.99 at $T = 323K$. Thus in all cases it was found to be less than 1 and hence the adsorption is favorable.

Derived empirically in 1912, Freundlich isotherm was the second method employed for studying the equilibrium characteristics (Azizian *et al.*, 2009; Ifikhar *et al.*, 2009)

$$Q_e = K_f \cdot [HA]^*{}^{1/n} \quad (8)$$

Q_e and $[HA]^*$ were the same as describe earlier in Langmuir's isotherm. A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined,

$$\log Q_e = \log K_f + (1/n) \log [HA]^* \quad (9)$$

K_f is the Freundlich capacity factor, (mg adsorbate/g adsorbent) 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 $\log [HA]^*$. Fig. (8), shows the plots of Freundlich equilibrium isotherms for GA adsorption at three different temperatures using BFA as adsorbent. Results of Freundlich equation were presented in Table 2 and Fig. (8). The plot of $\log Q_e$ and $\log [HA]^*$ is a straight

line with slope $1/n$ and intercept $\log K_f$, presenting the Freundlich capacity factor and Freundlich intensity parameter determined by least square fit and their corresponding regression coefficients (R^2). Further, K_f and n was found to decreases with increasing temperature.

R^2 , the magnitude of regression coefficient has been used to assess the fit of the isotherms. Langmuir isotherm fitted to experimental results for GA, provides R^2 values of 0.96, 0.95, 0.82 and Freundlich isotherm provides R^2 values of 0.97, 0.98, 0.86 for different temperatures, 303, 313 and 323 K, respectively. Comparing R^2 values it could be seen that at all temperatures of study, Freundlich found to best represent the data for GA adsorption using BFA.

Kinetics in a time-dependent process and study of kinetics is very important in order to know the rate of adsorption for designing and evaluating the adsorbent in removing the acids from aqueous streams. In order to determine the kinetics of adsorption of glycolic acid onto bagasse fly waste, first order, pseudo-second order, Weber-Morris intraparticle diffusion model and Elovich model were applied. In the cases of liquid phase adsorption systems, surface diffusion is an important phenomenon that describes the intraparticle diffusion. A number of studies on surface diffusion have been carried out to elucidate the mechanism of surface diffusion, and to develop an estimation procedure of surface-diffusion coefficient. A complete understanding of the mechanism is essential to elucidate the diffusion coefficient. However, because of great influence of adsorbates, adsorbents, and solvents, estimation of diffusion coefficient is very difficult. The dependence of this coefficient, on

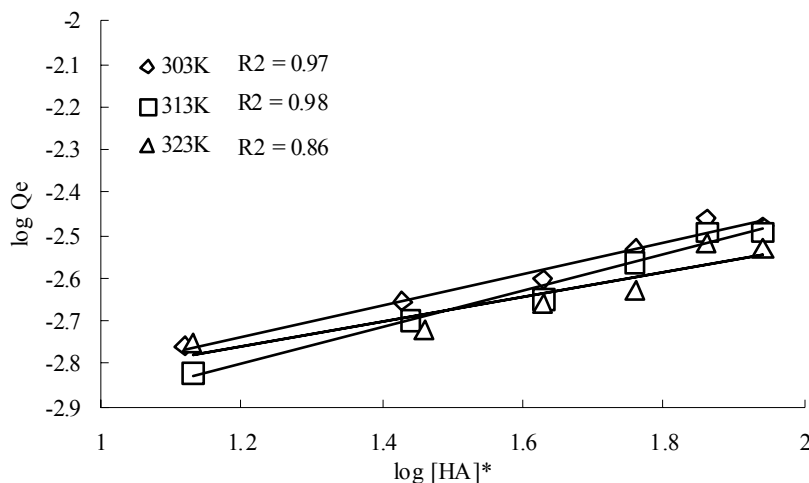


Fig. 8. Fit of Freundlich isotherm for the adsorption of GA at different temperatures using BFA

temperature and the amount adsorbed, can be investigated as characteristic features of surface diffusion. For the estimation of surface-diffusion coefficient, numerous diffusion models are developed in literature.

The Elovich model equation is generally expressed as (Low, 1960):

$$\frac{dQ_t}{dt} = \alpha \cdot \exp(-\beta \cdot Q_t) \quad (10)$$

Where α is the initial adsorption rate (mg/g.min) and β is the desorption constant (g/mg). To simplify the Elovich equation, $\alpha\beta t \gg 1$ is assumed and by applying the boundary conditions $Q = 0$ at $t = 0$ and $Q = Q_t$ at $t = t$ equation becomes:

$$Q_t = \beta \cdot \ln(\alpha \cdot \beta) + \beta \cdot \ln(t) \quad (11)$$

A plot of q_t versus $\ln(t)$ should yield a linear relationship (Fig. 9). The constants are listed in Table 3. The Elovich equation, which has been shown to be useful in describing chemisorption on highly heterogeneous adsorbents, give a good account of adsorption of glycolic acid with $R^2 = 0.98$ for BFA.

First order model:

The Langmuir rate equation may have been the first rate equation for the sorption of solid- liquid systems.

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (12)$$

After the integration of Eq. (12), the equation can be linearized as (Lagergren, 1898)

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (13)$$

Where, k_1 is the first order rate coefficient (1/min). In this model the limiting phenomenon is intra-particle mass transfer resistance.

The equation for the pseudo-second order model is shown below,

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (14)$$

Where, k_2 is the pseudo second-order rate coefficient (mg/g.min). If Eq. (14) is integrated, a linear equation is obtained (Ho and McKay, 1998). This equation is

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (15)$$

The initial sorption rate, Γ (mg/g min) at $t \rightarrow 0$ is defined as;

$$\Gamma = k_s Q_e^2 \quad (16)$$

The values of k_2 and calculated Q_e are obtained from the slope of the plot t/Q_t versus t . Γ and k_2 are obtained from the intercept. In this model, the limiting phenomenon is the adsorption mechanism, not the transfer of mass resistance. The first order and the pseudo-second-order model parameters are shown in Table 3 and plot of both models can be seen from (Fig. 10-11).

First order and pseudo-second-order models were investigated for GA, calculated from linear regression

Table 3. Kinetic parameters for the removal of GA using BFA

Elovich model		
α (mg/g.min)	β (g/mg)	R^2
$-6 \cdot 10^{-4}$	5000	0.9554
W-M Intra particle diffusion model		
k_{id} (mg/(g.min ^{0.5}))	I (mg/g)	R^2
0.00003	-0.00046	0.9864
Pseudo First order		
Q_e	k_1 (min ⁻¹)	R^2
0.950	0.798	0.9201
Pseudo second order		
Q_e	k_2 (mg/g.min)	R^2
0.0242	$3.8 \cdot 10^{-4}$	0.9810

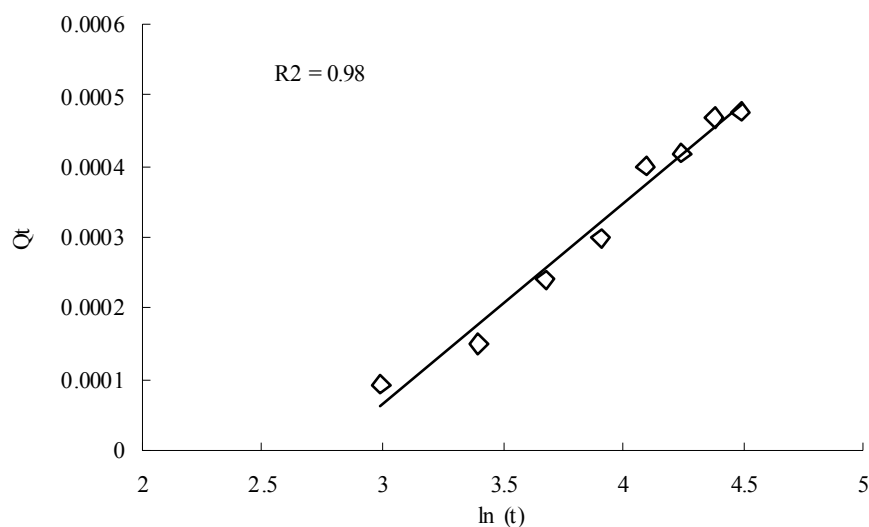


Fig. 9. Elovich equation fit for the adsorption of GA (0.4 mol/l) using GA using BFA

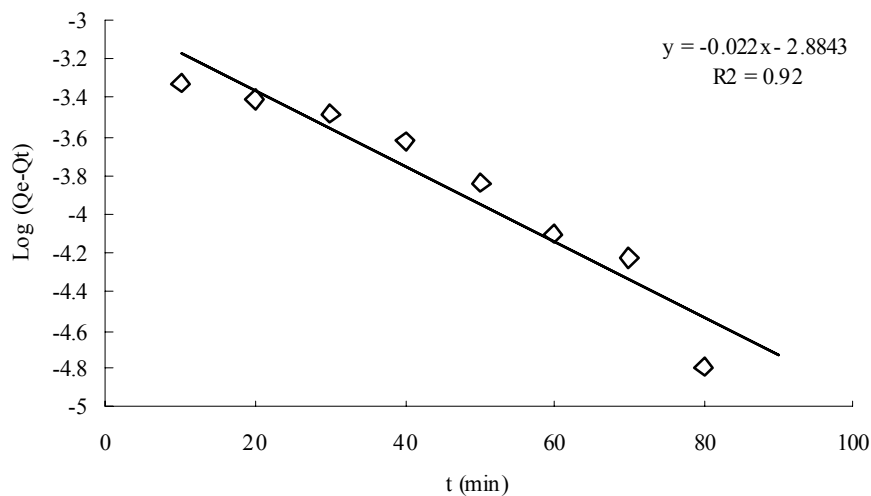


Fig. 10. First order equation fit for kinetic adsorption of the GA (0.4 mol/l) using BFA

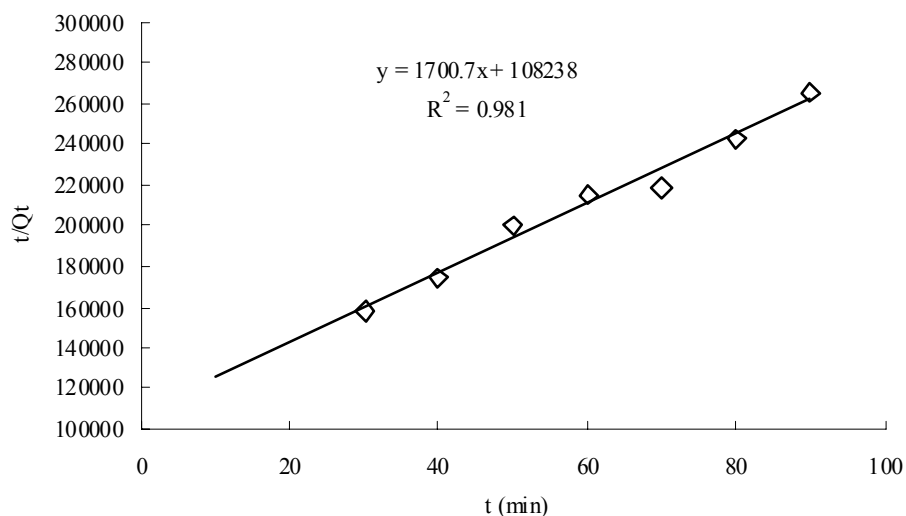


Fig. 11. Pseudo second order equation fit for kinetic adsorption of the GA (0.4 mol/l) using BFA

and regression coefficient for first order is R^2 0.92 and for second order 0.98 for BFA shown in (Fig. 10-11). The values stated above that each of the sorption process can be described using the second order kinetic model with fairly high correlation coefficients.

Weber and Morris intra-particle diffusion model:

Intra-particle diffusion can be estimated by using the Weber-Morris intra particle diffusion model (Rajoriya *et al.*, 2007)

$$Q_t = k_d t^{1/2} + I \quad (17)$$

In Eq. (17), k_d is the intra-particle diffusion rate coefficient and I give an idea about the thickness of the boundary layer. These values can be found by a plot, q_t versus $t^{1/2}$. As seen in (Fig. (12)) the straight lines deviate from the origin. The difference between final mass transfer rate and initial mass transfer rate may cause the deviations of straight lines. Also this deviation can show the pore diffusion is not the only rate-controlling step. I and k_d values are shown in Table 3.

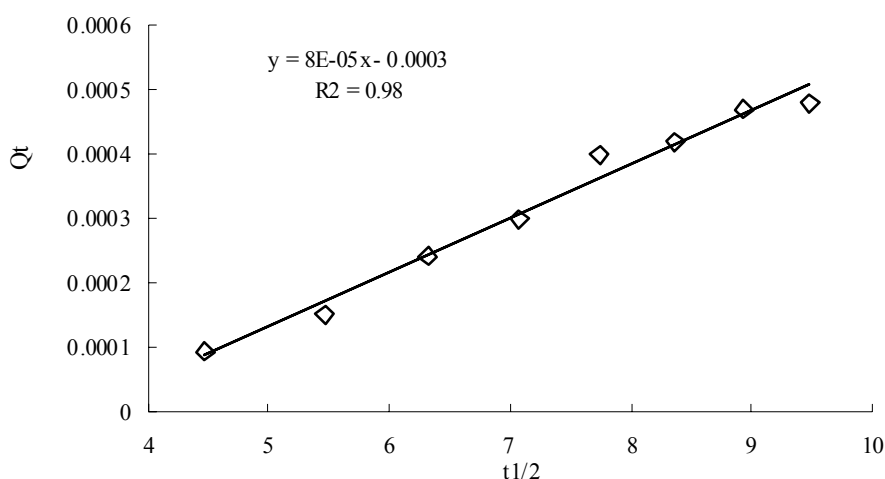


Fig. 12. Weber and Morris intra particle diffusion equation fit for adsorption of GA (0.4 mol/l) using BFA

CONCLUSION

Equilibrium and kinetic adsorption of glycolic acid recovery from dilute solution were investigated. For the selected dosage, it was found that the adsorption increases with increase in BFA doses when dosage was varied from 0.1-10 g and decreases with increase in acid concentration when acid concentration was varied from 0.2 mol/L to 1.2 mol/L. A quasi stationary state was obtained within 85 minutes of shaking in a CSTR used for kinetic study and is independent of BFA dose. Adsorption decreases with increase in temperature for all acid concentrations. Equilibrium isotherms: Langmuir and freundlich isotherms provides R^2 values of 0.96, 0.95, 0.82 and 0.97, 0.98, 0.86, respectively for different temperatures, 303, 313 and 313 K, respectively. Freundlich found to best represent the data for GA adsorption using BFA. Kinetic model such as the Elovich equation, give a good account of adsorption of glycolic acid with $R^2 = 0.98$ for BFA. First order and pseudo-second-order models were investigated for GA adsorption and regression coefficient for first order were found to be R^2 0.92 and for second order 0.98 for BFA. Intra-particle diffusion

can be estimated by using the Weber-Morris intra particle diffusion model

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