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A. N. Anozie^a; E. E. Okuhon^a; F. N. Osulale^b; J. K. Adewole^a

^a Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria ^b Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomosho, Nigeria

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Dehydration of Ethanol-Water Mixture Using Activated Carbons from Sawdust and Palm Kernel Shells

A. N. Anozie,¹ E. E. Okuhon,¹ F. N. Osuolale,² and J. K. Adewole¹

¹Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria

²Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomosho, Nigeria

This work was carried out to determine the optimum conditions for preparing activated carbons from sawdust and palm kernel shells (PKS); the maximum initial water concentration in feed solution to produce anhydrous ethanol using the adsorbents; and the effects of initial water concentration on water removal efficiency, selectivity, and adsorption capacity. The sawdust was chemically activated with ammonium chloride as catalyst while the PKS was carbonized and steam activated. Different particle sizes of the activated carbons were used in the study. The optimum conditions for preparing the activated carbons were established. It was found that only the activated sawdust particle sizes could break the ethanol-water azeotropic composition in feed solutions containing 5–9% (v/v) water to produce anhydrous ethanol. Powdered activated sawdust particles had the highest adsorption capacity compared to all the other particle sizes. The water removal efficiency, selectivity of water-to-ethanol adsorption, and adsorption capacity were higher at low initial water concentrations.

Keywords activated carbon; anhydrous ethanol; ethanol-water mixture; palm kernel shells; particle size; sawdust

INTRODUCTION

The highest ethanol concentration that can be obtained by simple fractional distillation is about 95% (w/w) because it forms an azeotrope with water at this composition. Azeotropic distillation has been used to overcome this problem for large scale production of anhydrous ethanol (1). However, the inherent drawbacks such as the addition of a third component (called an entrainer) to the mixture, large cost of entrainer recovery, the inevitable entrainer losses, and choices of materials of construction make the production of anhydrous ethanol by azeotropic distillation on a small scale not feasible. On a small scale, anhydrous ethanol can be obtained by an adsorption operation. In that operation, a solute is selectively retained on the surface of a solid adsorbent. The underlying

mechanism of attachment could be physical, chemical, or electrostatic in nature. Adsorbents are characterized by very large adsorbing internal surface area per unit weight of the material (2). Frequently used commercial adsorbents include silica gel and activated carbons (3). Silica gel can be used to completely dehydrate the 95% ethanol mixture to absolute alcohol (4).

There has been a growing research interest in producing activated carbons from industrial and agricultural by-products and sometimes biological materials. Examples of such materials are—palm kernel fiber (5), oil palm fiber (6), jackfruit peel (7), coconut husk (8), carica papaya (9), rice husk ash (10), flyash (11), eggshell waste (12), bamboo (13), marine green macroalga (14), and algal *Spirogyra* (15). Activated carbons derived from these materials are not only cheaper but are environmentally friendly as well (16). Activated sawdust has been successfully applied for the removal of: toxic metal Cr (VI) from aqueous solutions (17), Cu (II) ions from solutions (18), and dyes from textile effluents (19). Similarly, activated carbon produced from tamarind wood has been applied efficiently for the removal of Cr (VI) from waste water (20). Activated carbons produced from palm kernel shells have been applied for the removal of odor from water in household water filters (21), and in gas-phase adsorption (22).

The pore structure of an adsorbent is highly influenced by the parameters of its production such as catalyst-to-carbon ratio, activation time, activation temperature, and particle size. It is necessary to establish the optimal conditions for the production of high efficiency activated carbons. The response surface method of optimization has been employed to derive the best batch process parameters for the production of activated carbons (8,23–25).

Freundlich and Langmuir developed adsorption isotherms for liquid-phase adsorption. The Freundlich isotherm (26) is empirical and is given by the equation:

$$q = KC^n \quad (1)$$

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Address correspondence to A. N. Anozie, Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria. E-mail: ananozie@yahoo.com

where q is defined as the adsorption capacity and is the amount of solute adsorbed per unit weight of adsorbent, C is the equilibrium concentration of the solute in solution, while K and n are empirical constants. K is proportional to the active surface area of the adsorbent, and n is adsorption exponent. The smaller the value of n , the more effectively the solute is removed from solution or held by the adsorbent. The Langmuir isotherm (26) has a theoretical basis and is given by the equation:

$$q = q_o C / (K + C) \quad (2)$$

where q_o and K are empirical constants.

In this study the adsorption capacity was evaluated with experimental data using the equation:

$$q = (C_o - C)V\rho/W \quad (3)$$

where C_o is the initial concentration of water in solution (volume fraction), C is the adsorption equilibrium water concentration in solution (volume fraction), V is the initial volume of the solution (cm^3), ρ is the density of water (g/cm^3), and W is the mass of carbon (g). The water removal efficiency, η (%) (27), was evaluated using the equation:

$$\eta = (C_o - C)100/C_o \quad (4)$$

where concentration terms are in percent volume.

It is important that the adsorbent used in a particular adsorption system adsorbs the desired component and rejects, or only slightly adsorbs, the other component. For the ethanol-water system, it is desirable to adsorb the water and not the ethanol. The relative separation, or selectivity, between two components A and B in an adsorption system, is defined as:

$$\alpha_{AB} = X_A Y_B / X_B Y_A \quad (5)$$

where X_A is the mole fraction of component A in the adsorbed phase, X_B is the mole fraction of component B in the adsorbed phase, Y_A is the mole fraction of component A in the fluid phase, and Y_B is the mole fraction of component B in the fluid phase. Equation (5) gives the selectivity of water-to-ethanol adsorption, and the selectivity of ethanol-to-water adsorption, α_{BA} , is the reciprocal of Eq. (5).

Very little work has been done on the use of activated carbons for the dehydration of ethanol to produce anhydrous ethanol. The objectives of this study were to determine: (a) the optimum conditions for the production of activated carbons from sawdust by chemical activation method and from palm kernel shells by steam activation method for the sorption of water from ethanol; (b) the maximum initial water concentration for the production of anhydrous ethanol using the activated carbons; and (c)

the effects of initial water concentration on water removal efficiency, selectivity, and adsorption capacity.

MATERIALS AND METHODS

Preparation of Chemically Activated Carbon from Sawdust (ASD)

Sawdust sample was obtained from a local sawmill in Ile-Ife town. It was dried and ground to about 0.14 mm using CYCLOTEC sample mill (Model 1093, TECATOR CD, Sweden). The catalyst was ammonium chloride. For a given catalyst-to-sawdust mass ratio, a paste of the mixture formed was allowed to stand for 2 hours and then dried. The dried material was transferred into a crucible and activated. After activation, the resultant activated carbon was rinsed with water to leach out all traces of ammonium chloride. It was oven dried at 105°C for three hours and then ground to a fine powder of particle size S_0 (0.063–0.100 mm). The powdered activated carbon was mixed with dilute molasses as binder, allowed to stand for two hours, and was formed into briquettes manually. The briquettes were dried in an oven at a temperature of 140°C for two hours. To completely free the briquettes of any traces of molasses, the briquettes were carbonized at a temperature of 550°C for ten minutes. The Seliwanoff test was carried out on the carbonized briquettes to further detect any traces of molasses. The molasses-free briquettes were crushed and sieved to give particle sizes of S_1 (1.180–2.057 mm), S_2 (2.057–2.812 mm), S_3 (2.812–3.350 mm), and S_4 (3.350–4.000 mm).

Preparation of Steam Activated Carbon from Palm Kernel Shells (APKS)

Fresh palm kernel shells obtained from a market in Ile-Ife were washed and then dried. The method of Ogedengbe et al. (21) was adopted for the carbonization. Accordingly, the palm kernel shells were carbonized in a metal crucible at 500°C until the cessation of white fumes from the crucible signifying the removal of all the organic matter in the palm kernel shells. Subsequently, they were subjected to rapid cooling by soaking them in water to make more pores available and thus increase their internal surface area. A weight loss of about 70% was noted in the carbonized shells. Thereafter, it was crushed and sieved into four different particle sizes: P_1 (1.180–2.057 mm), P_2 (2.057–2.812 mm), P_3 (2.812–3.350 mm), and P_4 (3.350–4.000 mm). A measured volume of the carbonized palm kernel shells taken from one size group was steam activated in a custom made metal furnace. The activated carbon was allowed to cool in air and later boiled for 2.5 hours in water to dissolve out all the inorganic constituents and other impurities. The cleaned, activated palm kernel shells were finally oven dried at a temperature of 120°C for 1.5 hours.

Procedure for Adsorption Experiments

The adsorption experiments for powdered activated sawdust were carried out in tightly sealed sample bottles. The known weight of the powdered activated sawdust and the known volume and concentration of ethanol-water mixture in a sample bottle were brought to equilibrium by means of a gyratory shaker (Model G25-R, Brunswick, England) at a temperature of 25°C, a speed of 250 rpm, and for 12 minutes. The solution was centrifuged and the supernatant liquid removed for refractive index and density measurements.

For the granulated activated carbons from sawdust and palm kernel shells, the experimental runs were carried out in an adsorption column. The column was packed with a known weight of granulated activated carbon from one size group and different concentrations of ethanol-water mixture were poured through. The concentrations of ethanol-in-water were determined using both the refractive index and density methods for pre- and post-column samples.

For refractive index measurements, an Abbe refractometer (Model 60, Abbe, England) was employed. An ethanol-water refractive index calibration table was prepared by determining the refractive indices of ethanol-water mixtures at different concentrations. The mixtures were prepared from absolute ethanol and distilled water. In preparing the mixtures, large volumes of ethanol and water were used in order to minimize errors. It was noted that at very high ethanol concentrations, the sensitivity of the refractometer to changes in concentration decreased. Therefore, only density measurements were used in such ranges. Specific gravity bottles were used for the density measurements. Literature values of ethanol-water density measurements were read off (28). The purity of the anhydrous ethanol obtained was tested using gas chromatographic techniques.

Determination of Optimum Conditions for Preparing ASD and APKS

In preparing chemically activated powdered sawdust, the catalyst-to-sawdust ratio, the activation temperature and activation time were varied in order to determine the optimal values. Chemical activation of the sawdust was carried out at varying catalyst-to-sawdust mass ratios of 1:2, 1:1, and 2:1; varying activation temperatures of 500, 600, 700, and 800°C; and varying activation times of 1, 1.5, 2, 2.5, and 3 hours.

For steam-activated palm kernel shells, since the optimum carbonization parameters had been established (21), three activation parameters were investigated, namely, activation temperature, activation time, and particle size. Steam activation was carried out at varying activation temperatures of 600, 700, 800, 900, and 1000°C; varying

activation times of 2, 3, 4, 5, and 6 hours; and varying particle sizes P_1 , P_2 , P_3 , and P_4 .

The ranges of values for the parameters investigated were chosen based on literature. To investigate a parameter, the others were fixed and the parameter under investigation was varied. After preparing the activated carbons at the varying conditions, adsorption experiments were carried out to determine the best operating conditions which gave the highest adsorption equilibrium concentration of ethanol in solution and the highest selectivity of water-to-ethanol adsorption.

Production of Anhydrous Ethanol and Effects of Initial Water Concentration on Water Removal Efficiency, Selectivity, and Adsorption Capacity

Each particle size group of the activated carbons (prepared at the optimum conditions for high performance) and ethanol-water mixtures having 5, 6, 7, 8, and 9% (v/v) initial water concentration were employed in adsorption experiments to determine the maximum initial water concentration and adsorption capacities for the production of anhydrous ethanol. Similarly, each particle size group of the activated carbons and ethanol-water mixtures having 10, 20, 30, 40, and 50% (v/v) initial water concentration were employed in adsorption experiments to determine the effects of initial water concentration and particle size on the water removal efficiency, selectivity, and adsorption capacity.

RESULTS AND DISCUSSION

Optimum Conditions for Production of ASD

In the production of powdered ASD, the effects of varying catalyst-to-sawdust mass ratio on the adsorption equilibrium concentration of ethanol and on the selectivity of water-to-ethanol adsorption are presented in Table 1 (Data Row 1). It was observed that the highest adsorption equilibrium concentration of ethanol and the highest selectivity of water-to-ethanol adsorption occurred at catalyst-to-sawdust mass ratio of 1:1 and this represents the optimum (local) catalyst-to-sawdust mass ratio. This shows that below or above this ratio under- or over-activation takes place. Increasing the catalyst-to-carbon mass ratio above the optimum value has been found to reduce performance of activated carbon (7).

During the production of powdered ASD, the effects of varying activation temperature on the adsorption equilibrium concentration of ethanol and on the selectivity of water-to-ethanol adsorption are also presented in Table 1 (Data Row 2). It was observed that the optimum (local) activation temperature is 600°C. As the activation temperature increased, increase and subsequent decrease in the adsorptive performance indicators may be explained from the fact that during activation, increase in temperature

TABLE 1

Effects of varying production parameters of powdered ASD on adsorption equilibrium concentration of ethanol and selectivity of water to ethanol adsorption*

Catalyst to sawdust ratio	Activation temperature (°C)	Activation time (hr)	Adsorption equilibrium concentration of ethanol (% v/v)	Selectivity of water to ethanol adsorption, α_{AB}
1:2	600	2	66	1.94
1:1			69	2.23
2:1			68	2.13
1:1	500	2	67	2.03
	600		69	2.23
	700		64	1.78
	800		61	1.56
1:1	600	1	65	1.86
		1.5	66	1.94
		2	69	2.23
		2.5	68	2.13
		3	66	1.94

*Mass of adsorbent = 3.0 g, Initial volume of feed solution = 20 cm³, Initial concentration of feed solution = 60% ethanol (v/v).

favors the opening up of pores and thus enhancing the adsorptive performance (8). Further increase however, in activation temperature may cause structural alteration of the activation surface.

In the production of powdered ASD, the effects of varying activation time on the adsorption equilibrium concentration of ethanol and on the selectivity of water-to-ethanol adsorption are again shown in Table 1 (Data Row 3). It was observed that the optimum (local) activation time is 2 hours. As the activation time increased, the increase and subsequent decrease in the adsorptive performance indicators may also be explained as due to under- and over-activation with time. It was observed that the variation of time did not show much effect on adsorptive performance as compared to variation of activation temperature (29).

Optimum Conditions for Production of APKS

During the production of APKS, the effects of varying activation temperature on the adsorption equilibrium concentration of ethanol and on the selectivity of water-to-ethanol adsorption, for all the particle sizes, are shown in Table 2 (Columns 1–5). As the activation temperature increased, the adsorption equilibrium concentration of ethanol and the selectivity of water-to-ethanol adsorption first increased with increase in temperature and later decreased. The explanation of the observed trend is similar to that of ASD. It was observed that the optimum (local) activation temperatures for the particle sizes P_1 , P_2 , P_3 , and P_4 were 700, 800, 800, and 900°C, respectively. This showed that the optimum activation temperature increased with increase in particle size. The highest adsorption

equilibrium concentration of ethanol of 67% and selectivity of water-to-ethanol adsorption of 2.03 were obtained for particle sizes P_1 and P_2 at their optimum activation temperatures.

In the production of APKS, the effects of varying activation time on the adsorption equilibrium concentration of ethanol and on the selectivity of water-to-ethanol adsorption, for all the particle sizes, are also shown in Table 2 (Columns 1, 6–9). As the activation time increased, the adsorption equilibrium concentration of ethanol and the selectivity of water-to-ethanol adsorption first increased with rise in activation time and later decreased. This initial increase and subsequent decrease in the adsorptive performance indicators may be due to initial availability of more adsorption sites at the onset of the activation process (10). It was observed that the optimum (local) activation times for particle sizes P_1 , P_2 , P_3 , and P_4 were 4, 4, 4, and 5 hours, respectively. This showed that the optimum activation time was constant for three particle sizes and different only for the largest particle size. The highest adsorption equilibrium concentration of ethanol of 68% and selectivity of water-to-ethanol adsorption of 2.13 were obtained for particle sizes P_1 and P_2 at their optimum activation time of 4 hours.

The results presented in Table 2 for APKS showed that adsorption is favored by smaller particle sizes. Particle sizes P_1 and P_2 had the highest and the same adsorption equilibrium concentration of ethanol and selectivity of water-to-ethanol adsorption. This may be attributed to the fact that they have a larger internal surface area and shorter diffusion path that favour quick interaction between fluid and adsorbent (23).

TABLE 2
Effects of varying production parameters of APKS on adsorption equilibrium concentration of ethanol and selectivity of water to ethanol adsorption*

Particle size (mm)	Activation temperature (°C)	Activation time (hr)	Adsorption equilibrium concentration of ethanol (% v/v)	Selectivity of water to ethanol adsorption, α_{AB}	Activation temperature (°C)	Activation time (hr)	Adsorption equilibrium concentration of ethanol (% v/v)	Selectivity of water to ethanol adsorption, α_{AB}
P_1 : 1.180–2.057	600	3	63	1.7	700	2	64	1.78
	700		67	2.03		3	67	2.03
	800		65	1.86		4	68	2.13
	900		64	1.78		5	65	1.86
	1000		63	1.70				
P_2 : 2.057–2.812	600	3	64	1.78	800	2	64	1.78
	700		65	1.86		3	67	2.03
	800		67	2.03		4	68	2.13
	900		66	1.94		5	65	1.86
	1000		65	1.86				
P_3 : 2.812–3.350	600	3	62	1.63	800	2	63	1.70
	700		63	1.70		3	66	1.94
	800		66	1.94		4	67	2.03
	900		65	1.86		5	65	1.86
	1000		64	1.78				
P_4 : 3.350–4.000	600	4	62	1.63	900	2	62	1.63
	700		62	1.63		3	62	1.63
	800		63	1.70		4	64	1.78
	900		64	1.78		5	65	1.86
	1000		63	1.70		6	64	1.78

*Mass of adsorbent = 14 g, Initial volume of feed solution = 20 cm³, Initial concentration of feed solution = 60% ethanol (v/v).

Maximum Initial Water Concentration for Production of Anhydrous Ethanol

It was found that all the particle sizes of activated sawdust (ASD) successfully broke the ethanol-water azeotropic composition to produce anhydrous ethanol. On the contrary, it was found that steam-activated palm kernel shells (APKS) could not be used to break the ethanol-water

TABLE 3

Maximum initial water concentrations and adsorption capacities for producing anhydrous ethanol using ASD

Particle size (mm)	Maximum initial water concentration (% vol.)	Adsorption capacity, q (kg. water/kg. carbon)
S_0 : 0.063–0.100	7	0.467
S_1 : 1.180–2.057	9	0.30
S_2 : 2.057–2.812	8	0.22
S_3 : 2.812–3.350	7	0.20
S_4 : 3.350–4.000	5	0.125

azeotropic composition. Table 3 shows the maximum initial water concentrations and adsorption capacities for production of anhydrous ethanol for the particle sizes of activated sawdust. It was observed that briquetted activated sawdust of particle size S_1 produced anhydrous ethanol with the highest maximum initial water concentration of 9% and adsorption capacity of 0.30 g water/g carbon. The powdered activated sawdust of particle size S_0 produced anhydrous ethanol with maximum initial water concentration of 7% and highest adsorption capacity of 0.467 g water/g carbon. Considering the quantities of activated carbons that will be used for adsorption, the powdered activated sawdust (S_0) with highest adsorption capacity will be preferable to the briquetted activated sawdust (S_1) because less activated carbon will be used to produce anhydrous ethanol. Considering the type of unit operation equipment to be used, the powdered carbon will need mixing and centrifuging equipment whereas the briquetted carbon will need a packed bed column.

Furthermore, it was also found that the chromatograms of the anhydrous ethanol produced using the activated sawdust were very much like the one from the original

absolute ethanol, with no extra peaks, indicating that the adsorption bed did not add any extra impurities to the anhydrous ethanol produced.

Effects of Initial Water Concentration on Water Removal Efficiency

The effects of initial water concentration on the water removal efficiency for all the particle sizes are shown in Table 4. It was observed that as the initial water concentration increased the water removal efficiency decreased for all the particle sizes and that the activated sawdust particle sizes (S_0 – S_4) have greater water removal efficiencies than the activated palm kernel shell particle sizes (P_1 – P_4) at 10–30% initial water concentrations. The water removal efficiencies of the two types of activated carbons for all particle sizes were about the same at initial water concentrations of 40–50%. These results showed that chemically activated sawdust performed better than steam activated palm kernel shells in removing water from ethanol-water solutions with low initial water concentrations and both had about the same performance in solutions with high initial water concentrations.

Effects of Initial Water Concentration on Selectivity of Water-to-Ethanol Adsorption

The effects of initial water concentration on the selectivity of water-to-ethanol adsorption for all the particle sizes of the activated carbons are shown in Table 5. The following observations were made:

- the selectivity of water-to-ethanol adsorption of the ASD particle sizes at 10% initial water concentration was much higher than that of the APKS particle sizes,

TABLE 4

Effects of initial water concentration on water removal efficiency

Particle size (mm)	Initial Water Concentration (% vol.)				
	10	20	30	40	50
	Water	Removal	Efficiency	η (%)	
S_0 : 0.063–0.100	70	45	30	17.5	14
S_1 : 1.180–2.057	80	50	33.3	12.5	4
S_2 : 2.057–2.812	70	50	30	20	6
S_3 : 2.812–3.350	80	50	26.7	20	2
S_4 : 3.350–4.000	70	50	30	17.5	6
P_1 : 1.180–2.057	30	30	23.3	17.5	8
P_2 : 2.057–2.812	30	25	20	17.5	8
P_3 : 2.812–3.350	30	25	20	15	8
P_4 : 3.350–4.000	20	20	16.7	12.5	6

TABLE 5

Effects of initial water concentration on selectivity of water-to-ethanol adsorption

Particle size (mm)	Initial Water Concentration (% vol.)				
	10	20	30	40	50
	Selectivity, α_{AB}				
S_0 : 0.063–0.100	32.33	8.09	3.76	2.03	1.32
S_1 : 1.180–2.057	65.67	9.00	4.00	1.86	1.08
S_2 : 2.057–2.812	39.00	9.00	3.76	2.13	1.13
S_3 : 2.812–3.350	49.00	9.00	3.55	2.13	1.04
S_4 : 3.350–4.000	32.33	9.00	3.76	2.03	1.13
P_1 : 1.180–2.057	13.29	6.14	3.35	2.03	1.17
P_2 : 2.057–2.812	13.29	5.67	3.17	2.03	1.17
P_3 : 2.812–3.350	13.29	5.67	3.16	1.94	1.17
P_4 : 3.350–4.000	11.50	5.25	3.00	1.86	1.13

- selectivity was higher at low initial water concentration (10–30%) than at high initial water concentration (40–50%),
- selectivity decreased sharply from 10–30% initial water concentration and decreased gradually from 30–50% initial water concentration for all the particle sizes. Selectivity is a useful performance index in assessing the performance of adsorbents. For the ethanol-water adsorption system, it is desirable that the selectivity of water-to-ethanol should be high and this implies that the initial water concentration should be low.

Effects of Initial Water Concentration on Adsorption Capacity

The effects of initial water concentration on adsorption capacities of the activated carbons of different particle sizes are shown in Table 6. It was observed that the adsorption capacities of the activated carbons increased and then decreased as the initial water concentration increased for all the particle sizes. Activated carbons from sawdust have higher adsorption capacities than activated carbons from palm kernel shells for all the initial water concentrations. Adsorption capacities were much higher at initial water concentrations of 10–30% than at 40–50% initial water concentration. Powdered activated sawdust (S_0) stood out as having the highest adsorption capacity than all the other particle sizes. Therefore, dehydration of ethanol-water mixture must be carried out using powdered activated sawdust carbons. Furthermore, it is not advisable to use ethanol-water mixture exceeding 30% initial water composition for multi-stage adsorptive separation of ethanol-water mixture. The optimum number of distillation and adsorption stages required to bring a fermentation broth from about 8–12% initial ethanol

TABLE 6
Effects of initial water concentration on adsorption capacity

Particle size (mm)	Initial	Water	Concentration (% vol.)		
	10 Adsorption	20 Capacity, q	30 (kg. water/kg. carbon)	40	50
S_0 : 0.063–0.100	0.64	0.90	0.90	0.70	0.58
S_1 : 1.180–2.057	0.34	0.50	0.40	0.25	0.48
S_2 : 2.057–2.812	0.30	0.40	0.45	0.32	0.10
S_3 : 2.812–3.350	0.27	0.40	0.32	0.23	0.03
S_4 : 3.350–4.000	0.23	0.33	0.30	0.18	0.08
P_1 : 1.180–2.057	0.05	0.12	0.14	0.13	0.08
P_2 : 2.057–2.812	0.05	0.11	0.12	0.13	0.07
P_3 : 2.812–3.350	0.05	0.10	0.11	0.11	0.07
P_4 : 3.350–4.000	0.04	0.07	0.08	0.08	0.05

concentration to anhydrous ethanol will be based on economic considerations.

CONCLUSIONS

This study has shown that ammonium chloride is suitable as catalyst for the preparation of activated carbon from sawdust. The optimum (local) conditions for preparing activated sawdust were: catalyst-to-sawdust mass ratio of 1:1, activation temperature and time of 600°C and 2 hours, respectively. The optimum (local) steam activating conditions for preparing activated palm kernel shells were: particle size range of 1.180–2.057 mm, activation temperature and time of 700°C and 4 hours, respectively. It was shown that chemically activated sawdust could be used to break the ethanol-water azeotropic composition in solutions containing 5–9% (v/v) water to produce anhydrous ethanol whereas steam activated palm kernel shells could not be used to achieve the same purpose. The effects of initial water concentration on water removal efficiency, selectivity of water-to-ethanol adsorption, and adsorption capacity showed that dehydration of ethanol-water mixture using activated carbons should be carried out at low initial water concentrations. The optimum number of distillation and adsorption stages required to produce anhydrous ethanol from fermentation broth will be based on economic considerations.

REFERENCES

- Treybal, R.E. (1981) *Mass Transfer Operations*, 3rd Ed.; Mc-Graw-Hill Book Company: Singapore.
- Cooney, D.O. (1980) *Activated Charcoal: Antidotal and Other Medical Uses*; Marcel Dekker: New York.
- Inglezakis, V.J.; Pouloupoulos, S.G. (2006) *Adsorption, Ion exchange and Catalysis: Design of Operations and Environmental Applications*; Elsevier: Amsterdam, 31–54.
- Mantell, C.L. (1951) *Adsorption*; McGraw-Hill: New York.
- Ofomaja, A.E. (2007) Sorption dynamics and isotherm studies of methylene blue uptake onto palm kernel fibre. *Chemical Engineering Journal*, 126: 35–43.
- Tan, I.A.W.; Hameed, B.H.; Ahmad, A.L. (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal*, 127: 111–119.
- Prahas, D.; Kartika, Y.; Indraswati, N.; Ismadji, S. (2008) Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. *Chemical Engineering Journal*, 140: 32–42.
- Tan, I.A.W.; Ahmad, A.L.; Hameed, B.H. (2008) Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. *Chemical Engineering Journal*, 137: 462–470.
- Shaik, B.; Murthy, Z.V.P.; Jha, B. (2009) Sorption of Hg (II) onto Carica papaya: Experimental studies and design of batch sorber. *Chemical Engineering Journal*, 147: 226–234.
- Lataye, D.H.; Mishra, I.M.; Mall, I.D. (2009) Adsorption of α -Picoline onto rice husk ash and granular activated carbon from aqueous solution: Equilibrium and thermodynamic study. *Chemical Engineering Journal*, 147: 139–149.
- Archana, M.; Tripathi, B. (2008) Utilization of flyash in adsorption of heavy metals from waste water. *Toxicological and Environmental Chemistry*, 90 (6): 1091–1097.
- Menzener, Y.L.; Bensmaili, A. (2009) Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chemical Engineering Journal*, 147: 87–96.
- Hameed, B.H.; Din, A.T.M.; Ahmad, A.L. (2007) Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *Journal of Hazardous Materials*, 141 (3): 819–825.
- Pavasant, P.; Apiratikul, R.; Sungkhum, V.; Suthiparinyanont, P.; Wattanachira, S.; Marhaba, T.F. (2006) Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. *Bioresource Technology*, 97: 2321–2329.
- Mohan, S.V.; Ramanaiah, S.V.; Rajkumar, B.; Sarma, P.N. (2007) Biosorption of fluoride from aqueous phase onto algal *Spirogyra* IO1 and evaluation of adsorption kinetics. *Bioresource Technology*, 98: 1006–1011.
- Stavropoulos, G.G.; Zabanitoutou, A.A. (2005) Production and characterisation of activated carbon from olive seed waste residue. *Micropor. Mesopor. Mater.*, 83: 79–85.
- Gupta, S.; Babu, B.V. (2009) Removal of toxic metal Cr (VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chemical Engineering Journal*, 150 (2–3): 352–365.

18. Rahman, M.S.; Islam, M.R. (2009) Effects of pH on isotherms modelling for Cu (II) ions adsorption using maple wood sawdust. *Chemical Engineering Journal*, 149: 273–280.
19. Izadyar, S.; Rahimi, M. (2007) Use of beech wood sawdust for adsorption of textiles dyes. *Pakistan Journal of Biological Sciences*, 10 (2): 287–293.
20. Acharya, J.; Sahu, J.N.; Sahoo, B.K.; Mohanty, C.R.; Meikap, B.C. (2009) Removal of chromium (VI) from wastewater by activated carbon developed from tamarind wood activated with zinc chloride. *Chemical Engineering Journal*, 150 (1): 25–39.
21. Ogedengbe, O.; Oriaje, A.T.; Tella, A. (1989) Carbonization and activation of palm kernel shells for household water filters. *Water International Journal, Canada*, 10: 132–138.
22. Lua, A.C.; Guo, J. (2001) Microporous oil-palm-shell activated carbon prepared by physical activation for gas-phase adsorption. *Langmuir*, 17: 7112–7117.
23. Ravikumar, K.; Pakshirajan, K.; Swaminathan, T.; Balu, K. (2005) Optimization of batch parameters using response surface methodology for dye removal by a novel adsorbent. *Chemical Engineering Journal*, 105: 131–138.
24. Karacan, F.; Ozden, U.; Karacan, S. (2007) Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology. *Appl. Thermal Eng.*, 27: 1212–1218.
25. Bacaoui, A.; Yaacoubi, A.; Dahbi, A.; Bennouna, C.; Phan Tan Luu, R.; Maldonado-Hodar, F.J.; Rivera-Utrilla, J.; Moreno-Castilla, C. (2001) Optimization of conditions for the preparation of activated carbons from olive waste cakes. *Carbon*, 39: 425–432.
26. Geankoplis, C.J. (2006) *Transport Processes and Separation Process Principles*, 4th Ed.; Prentice Hall of India: New Delhi.
27. Kazemipour, M.; Ansari, M.; Tajrobehkar, S. (2008) Removal of lead, cadmium, zinc and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell and apricot stone. *Journal of Hazardous Materials*, 150: 322–327.
28. Perry, R.H.; Green, D.W. (1997) *Perry's Chemical Engineers' Handbook*, 7th Ed.; McGraw-Hill: New York.
29. Sentorun-Shalaby, C.; Ucak-Astarliogu, M.G.; Artok, L.; Sarici, C. (2006) Preparation and characterisation of activated carbon by one step steam pyrolysis/activation from apricot stones. *Micropor. Mesopor. Mater.*, 88: 126–134.