

Removal of β -Naphthalenesulfonic Acid from Aqueous Dilute Solution Using Bagasse Fly Ash*

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Abstract Bagasse fly ash was converted into an inexpensive adsorbent and utilized for the removal of β -naphthalenesulfonic acid in dilute solution. The effect of pH, temperature, adsorbent concentration, and co-existed acids on the removal of β -naphthalenesulfonic acid was examined. The adsorption data have been correlated with both Langmuir and Freundlich adsorption models. Thermodynamic parameters obtained indicate the feasibility of the process, and kinetic studies provided the necessary mechanistic information of the removal process.

Keywords adsorption, bagasse fly ash, β -naphthalenesulfonic acid

1 INTRODUCTION

Current production of β -naphthol involves a process which is not environment friendly under the current environmental regulation, for its producing a large amount of β -naphthalenesulfonic acid (NSA) wastewater and causing environmental pollution. The removal of NSA from wastewater can be carried out by ion exchange, solvent extraction, reverse osmosis, chemical oxidation, and by adsorption. Adsorption is effective for treatment of wastewater. Commercially activated carbon has long been used as a standard adsorbent. In spite of its widespread use in various cleaning procedures, activated carbon remains expensive; therefore, the development of low-cost alternative adsorbents has been the focus of recent research. Bagasse fly ash, a waste of sugar industries, causes a disposal problem. It is used as space filler in building materials, but to date, wider application of this waste is being searched. Recently, bagasse fly ash has been converted into an effective adsorbent for the removal of metal ions and phenols^[1,2]. The aim of the present research is to use the bagasse fly ash to remove NSA from aqueous dilute solution and report the results on the removal of NSA.

2 EXPERIMENTAL

2.1 Materials and measure

All reagents used were of AR grade (Beijing chemical plate). Stock solution of NSA ($0.03 \text{ mol}\cdot\text{L}^{-1}$) was prepared in double-distilled water. Bagasse fly ash was obtained from a sugar manufacturer at Changchun, China. This material was best treated with excess of hydrogen peroxide at 60°C for 24 h to oxidize the adhering organic matter. The resulting product was then washed with distilled water and

dried at 100°C for 24 h, and then sieved before being used to obtain particles of uniform mesh size. Finally, the product was stored in a vacuum desiccator.

pH was measured by a model CT No.CL46 pH meter. X-ray measurements were made by a Philips X-ray diffractometer employing nickel filtered Cu-K α radiation. Surface area of the sample was measured by a Model QS-7 Quantasorb surface area analyser (USA Fisons Instruments Company). Scanning electron microscopy was performed using a Philips SEM501 electron microscope. The ZPC of adsorbent was determined by potentiometric titration^[3]. The concentration of NSA in solution was determined with Shimadzu high performance liquid chromatography. The adsorbed phase concentration was calculated according to

$$q = (c_0 - c)\rho V/W \quad (1)$$

2.2 Adsorption experiment

A series of 200 ml test flasks filled with 50 ml of NSA solution of various concentration at desired pH and temperature. An empirical amount of adsorbent ($0.2 \text{ g}\cdot\text{ml}^{-1}$) was then added into each test flasks and agitated intermittently for 24 h. Preliminary investigation showed that the equilibrium was attained in 8–10 h. The liquid obtained on centrifugation was analyzed for adsorbate concentration.

2.3 Kinetic experiment

A number of test flasks containing 50 ml of solutions containing of known concentrations ($0.03 \text{ mol}\cdot\text{L}^{-1}$, $0.015 \text{ mol}\cdot\text{L}^{-1}$, and $0.005 \text{ mol}\cdot\text{L}^{-1}$, respectively) were placed in a thermostated shaking assembly. When the desired temperature was reached, a known amount of adsorbent was added to each test flasks. At specified intervals the solution in the specified flasks were separated from the sorbent materials

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and the concentration of NSA was measured.

3 RESULTS AND DISCUSSION

3.1 Characteristics of bagasse fly ash

Chemical composition and characteristics of the bagasse fly ash determined by standard methods of chemical analysis^[3] are SiO₂: 61.44; Al₂O₃: 14.50; CaO: 2.82; Fe₂O₃: 4.86; MgO: 0.71; and the loss on ignition: 17.12 (%). The adsorbent prepared from bagasse fly ash was found to be of "L" type as classified earlier^[1], *i.e.*, it lowers the pH when kept in deionized water. It is quite stable in water, salt solutions, acids and bases. The X-ray diffraction pattern of the product provide d-spacing values that reflect the presence of minerals like goethite, mullite, kaolinite, α -quartz, γ -alumina, *etc.* in the adsorbent. The surface area of the adsorbent as calculated by the BET method was 440 m²·g⁻¹. A SEM photograph at 320 × magnification clearly reveals the porous texture of the adsorbent. The porosity of adsorbent was 0.36(fraction).

3.2 The effect of pH

Figure 1 depicts the variation of adsorption with the initial pH. The NSA is strongly adsorbed at pH 1.5. The variation of adsorption with pH can be explained by considering the point-of-zero charge (ZPC, the value of pH required to give zero net surface charge) of the bagasse fly ash. The main constituents of bagasse fly ash are silica and alumina. The ZPC of silica is 2.3, while that of alumina is 8.2^[1]. Accordingly the surface of bagasse fly ash would have high positive charge density below pH 5.8, *i.e.*, ZPC of the bagasse. So, bagasse fly ash has a strong adsorption in low pH. With increasing pH, the negative charge density on the surface increases, resulting in the decrease in adsorption.

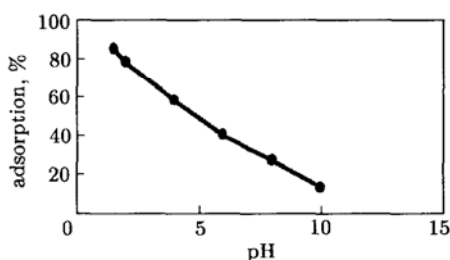


Figure 1 Effect of the initial pH on the adsorption of NSA on bagasse fly ash (temperature 20°C, particle size 200–250BSS mesh, NSA concentration 0.03 mol·L⁻¹, adsorbent dose 0.2 g·L⁻¹)

3.3 The effect of particle size

Various fractions of particle size, *e.g.*, 100–150, 150–200, 200–250, 250–300 BSS mesh, was tried, and the removal of NSA is 70%, 84%, 94%, and 95%, respectively. The reason is that it is beneficial for

smaller particle size to increase the rate of NSA interdiffusion in the bagasse fly ash. The removal of NSA increases with the increasing of mesh size. However, the difference in the percentage of removal with 200–250 and 250–300 BSS mesh is very small. Furthermore, because of the handling problems with smaller particle size, especially in the column experiments, the particles of mesh size 200–250 are selected for all the subsequent adsorption tests.

3.4 The effect of co-existed acids

The effect of ionic interaction on the adsorption process has been interpreted, using the ratio of the adsorption capacity of the ion in a single-component system (q_0) to that in a multi-component system (q_m)^[1].

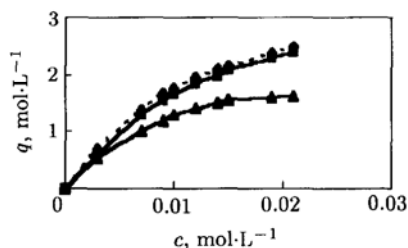


Figure 2 Comparative adsorption of NSA in the absence (---) and in the presence (—) of H₂SO₄ and H₂SO₃ (temperature 20°C, particle size 200–250BSS mesh, adsorbent dose 0.2 g·ml⁻¹, pH 1.5)
◆— NSA; ■— sulfurous acid; ▲— sulfuric acid

Figure 2 shows that the presence of sulfuric acid (H₂SO₄) would reduce the uptake ($q_m/q_0 < 1$) of NSA significantly by 30%, while a slight decrease by 3% in the scavenging efficiency of the adsorbent in the presence of sulfurous acid (H₂SO₃) is observed. It can be explained on the basis of a dual site adsorption mechanism for dibasic acids^[4,5]. In this case the adsorbing anion is SO₄²⁻ which is attached to two protonated sites of bagasse fly ash. Adsorption capacity for NSA decreases when H₂SO₄ is present due to the competition of adsorbable components for the available sites. H₂SO₄ competitively displaces NSA from limited adsorption sites available on bagasse fly ash at higher concentration, while H₂SO₃, as a weak acid, has only a slight effect on adsorption of NSA on bagasse fly ash.

3.5 Adsorption isotherms

All the isotherms (Fig. 3) are regular in shape, indicating a possible application of Langmuir equation. Furthermore, the adsorption decreased with an increase in temperature, indicating that the process is exothermic^[6].

Freundlich and Langmuir isotherms have been employed to study the adsorption behavior of NSA.

$$\text{Freundlich isotherm } q_e = K_F C^{1/n} \quad (2)$$

$$\text{Langmuir isotherm } q_e = Q^0 b C_e / (1 + b C_e) \quad (3)$$

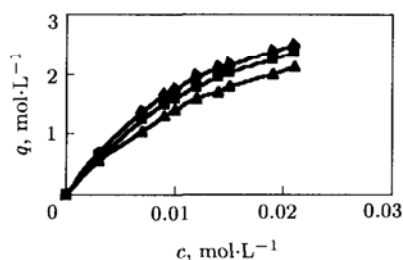


Figure 3 Adsorption isotherms of NSA on bagasse fly ash at different temperatures (temperature 20°C, particle size 200–250BSS mesh, adsorbent dose 0.2 g·ml⁻¹, pH 1.5)
 ◆ 20°C; ■ 30°C; ▲ 40°C;

Eqs. (2) and (3) were fitted to the experimental sorption data for NSA, and the parameters of each sorption model are tabulated in Table 1.

Table 1 Freundlich and Langmuir constants for the adsorption of NSA

$T, ^\circ\text{C}$	Freundlich model			Langmuir model		
	$1/n$	K_F	RR	Q^0 mol·L ⁻¹	b L·mol ⁻¹	RR
20	0.53	19.41	0.989	4.13	1221.5	0.956
30	0.59	22.80	0.994	4.08	1067.7	0.932
40	0.64	25.59	0.991	3.79	888.9	0.960

It can be seen from the correlation coefficients (RR) in Table 1 that the Freundlich model agree with the experimental data much better than the Langmuir model.

The change in standard Gibbs free energy (ΔG^0) is $-17.34 \text{ kJ}\cdot\text{mol}^{-1}$, $-17.52 \text{ kJ}\cdot\text{mol}^{-1}$, $-17.67 \text{ kJ}\cdot\text{mol}^{-1}$ at different temperatures. The changes in standard enthalpy (ΔH^0) and entropy (ΔS^0)^[2] are $-12.18 \text{ kJ}\cdot\text{mol}^{-1}$ and $17.61 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$, respectively. The negative free-energy changes indicate the feasibility of the process and its spontaneous nature without any induction period. Negative ΔH^0 value reflects the exothermic nature of the process, and ΔS^0 value suggests that no noticeable change in the structure of bagasse fly ash takes place during the adsorption.

3.6 Kinetics

Preliminary investigations on the rate of removal of NSA by bagasse fly ash indicate the process to be quite rapid. Nearly 77% of the sorption capacity is realized within the first hour of contact when the initial concentration is $0.03 \text{ mol}\cdot\text{L}^{-1}$. The initial rapid adsorption gives way to a very slow rate of approach to equilibrium as shown in Fig. 4. The effect of the initial concentration ($0.03 \text{ mol}\cdot\text{L}^{-1}$, $0.015 \text{ mol}\cdot\text{L}^{-1}$, and

$0.005 \text{ mol}\cdot\text{L}^{-1}$) of NSA on adsorption phase concentration was presented in Fig. 4.

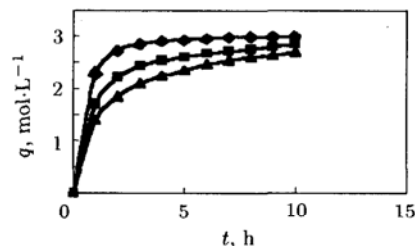


Figure 4 The variation of adsorbed phase concentration with time (temperature 20°C, particle size 200–250BSS mesh, adsorbent dose 0.2 g·ml⁻¹, pH 1.5)
 $c_0, \text{ mol}\cdot\text{L}^{-1}$: ◆ 0.03; ■ 0.015; ▲ 0.005

NOMENCLATURE

b	Langmuir constant
c	equilibrium concentrations, $\text{mol}\cdot\text{L}^{-1}$
c_e	equilibrium concentration of NSA in the solution, $\text{mol}\cdot\text{L}^{-1}$
c_0	initial concentrations, $\text{mol}\cdot\text{L}^{-1}$
K_F	Freundlich constant
$1/n$	Freundlich constant
Q^0	solid phase concentration corresponding to complete coverage of available adsorption sites, $\text{mol}\cdot\text{L}^{-1}$
q_e	equilibrium concentration of NSA on the adsorbent, $\text{mol}\cdot\text{L}^{-1}$
q	adsorbed phase concentration, $\text{mol}\cdot\text{L}^{-1}$
V	volume of the solution, L
W	mass of the wet resin particles, g
ρ	apparent density, $1280 \text{ g}\cdot\text{L}^{-1}$

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