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A Study on Synthesis of Zeolite and Removal of Amido Black dye by adsorption with Zeolite

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Abstract

Investigations have been undertaken to determine whether cheap, commercially available materials (natural zeolite and bentonite) hold promise in the treatment of wastewaters from the textile industry. The initial findings indicate that zeolite synthesized from fly ash has high adsorptive capacity for dyes and it is relatively cheap. The adsorption of two basic dyes (Amido Black and Thionine) onto granular activated carbon as well as zeolite from fly ash and bentonite has to be studied as single equilibrium isotherms. The effectiveness of each adsorbent has to be measured in terms of its adsorption capacity towards individual constituents of the effluent. The adsorption isotherm would be described by the Langmuir and Freundlich isotherm equations. The parameters in the adsorption isotherms will be estimated from the experimental equilibrium data using non-linear regression analysis. Using these data, the selection of the best adsorbent can be done for design purposes.

Keywords: Natural Zeolite, bentonite, Amido Black, Thionine, Langmuir, Freundlich, granular activated carbon

1. Introduction

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated carbon is the most popular adsorbent and has been used with great success, but is expensive [6]. A full description of low cost adsorbents for waste and wastewater treatment: a review has been presented by S.J.T. Pollard et al (2007) [11]. A number of studies have been reported with regard to the adsorption equilibrium of dye removal processes using various adsorbents. In most adsorption systems of dyestuffs-adsorbent, Langmuir [3,9,10], Freundlich [2,9,10], and Redlich-Peterson [1,6,7,8,10] isotherms have been applied to describe equilibrium between liquid–solid phases. Two intra-particle diffusion mechanisms are involved in the adsorption rate (a) diffusion within the pore volume known as pore diffusion, and (b) diffusion along the surface of pores known as surface diffusion [13]. Some of the investigators have applied the pore diffusion model with and without film resistance [3]. McKay has developed homogeneous solid phase diffusion model to describe systems dyes on bagasse pith (2011) [7]. The homogeneous solid phase diffusion model has been developed based on external mass transfer and surface diffusion by M.S.El-Geundi [1]. He has applied this model for adsorption of basic dyes onto natural clay in a batch adsorber. The branched pore kinetic model was used to describe the adsorption of cobalt phthalocyanine dye onto active carbon and basic dyes onto natural clay [2].

Research has already been carried out using different treatment technologies e.g. chemical coagulation-flocculation [2], different types of oxidation processes [3], biological processes [4], membrane based separation processes [5–7], adsorption [8] etc. for the removal of colored dye from wastewater. Research is focused on the use of low-cost, reusable, locally available, biodegradable adsorbents made from natural sources. Natural and modified clays, zeolite from fly ash and bentonite are being considered as alternative low-cost adsorbents. Adsorption of organic molecules to an adsorbent depends on various factors like temperature, pH of the solution, the structure and concentration of the adsorbing molecule, the ionic strength of the suspension, and the structure of the adsorbent. Experimental investigations have been carried out to adsorb Amido Black dye from aqueous medium using zeolite as an adsorbent. Characterization of zeolite is to be done by measuring

- Particle size distribution using particle size analyzer
- BET surface area using BET surface analyzer
- Structural analysis using X-ray diffractometer
- Microscopic analysis using scanning electron microscope.

- The effects of initial dye concentration, contact time, zeolite loading, stirring speed, pH, and temperature are to be studied for the adsorption of Amido Black in batch mode.
- Comparison of adsorption capacity of zeolite with other adsorbent such as activated carbon

The aim of this work is to study the ability of zeolite synthesized from fly ash to remove the acidic dye Amido Black from aqueous solutions. This adsorbent was chosen because of its cheapness and abundance.

II Description of Materials

A. ZEOLITES

The types of zeolites formed on treatment are very much selective to reaction parameters and also the raw material compositions. The synthesis of various zeolites from fly ash and their properties mainly depend on the effect of reaction time, reaction
temperature, alkalinity and fly ash composition.

Zeolites are crystalline, micro-porous, hydrated aluminosilicates that are built from an infinitely extending three-dimensional network of $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedral linked to each other by the sharing of oxygen atom. Generally, their structure can be considered as inorganic polymer built from tetrahedral TO_4 units, where T is Si^{4+} or Al^{3+} ion. Each oxygen (O) atom is shared between two T atoms.

$Mx/n[(AlO_2x(SiO_2)y] \cdot wH_2O$, where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite, y/x can be raging from 10 to 100.

The adsorption of dyes onto zeolites has been extensively investigated by some researcher but only a few studies have been reported about the adsorption of dye onto fly ash-based zeolites .A comparison of the adsorption capabilities of Amido Black with other larger dyes over zeolites and activated carbon will provide valuable information about adsorption mechanisms and the structure of the zeolites. The structure of zeolite is given in fig.1.

Adsorption and adsorption processes are important fields of study in physical chemistry. They form the basis for understanding phenomena such as heterogeneous catalysis, chromatographic analysis, dyeing of textiles, and clarification of various effluents.

Dyes are defined as colored substances which when applied to fibers give them a permanent color, i.e. resistant to action of light, water and soap. Practically every dyestuff is made from either one or more of the compounds obtained by the distillation of the coal tar. The chief of these are Benzene (C_6H_6), Toluene ($C_6H_5.CH_3$), Naphthalene ($C_{10}H_8$), Anthracene ($C_{14}H_{10}$), Phenol (C_6H_5OH), Cresol (C_7H_7OH), Acridine ($C_{13}H_9N$), and Quinoline (C_9H_7N). Wastewaters from dyeing and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluent has been the target of great attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problems. Recent estimate indicates that 20% of dyes enter the environment through effluent that result from the treatment of industrial wastewater. The existing technologies have certain efficiency in the removal of dyes but their initial and operational costs are very high. On the other hand, low cost technologies do not allow the desired degree of color removal or have certain disadvantage. Oxidation and adsorption are two major technologies that are used for wastewater treatment in the textile industry. Among oxidation methods, UV/Ozone and UV/H_2O_2 treatments are technologies for decolorizing wastewater. Adsorption is rapidly becoming a prominent method of treating
aqueous effluents and it has been extensively used in industrial processes for a variety of separation and purification purposes. Adsorption of dyes by zeolites has evolved into one of the most effective physical process for the decolorization of textile wastewater. This process has been found to be superior to other

techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances.

B. TYPES OF ZEOLITE

The following table presents the most common types of zeolites in table 1.

C. AMIDO BLACK DYE

Amido black 10B is an amino acid staining diazo dye. Its molecular formula is $C_{22}H_{14}N_6Na_2O_9S_2$. Amido Black 10B is a synthetic acid dye containing both NN and CC chromophore groups (pyrazolone dye). It is a dark red to black powder soluble in water and used as a stain for protein-containings. Its chemical designation is 4-amino-5-hydroxy- 3-[(4-nitrophenyl) azo]- 6-(phenylazo)- 2,7-naphthalene disulfonic acid disodium salt. Acid dyes are water-soluble dyes employed mostly in the form of sodium salts of the sulfonic or carboxylic acids. They are anionic which attach strongly to cationic groups in the fibre directly. They can be applicable to all kind of natural fibres

like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. However, they are not substantive to cellulosic fibres. They are also used in paints, inks, plastics and leather. Chemical structure of Amido Black dye is shown in fig.2.

III. Experimental Methodology

Process flow diagram for synthesis of zeolite from fly ash is shown in fig.3.

A. ZEOLITE SYNTHESIS:

Before any treatment, the raw fly ash samples were first screened through a BSS Tyler sieve of 80-mesh size to eliminate the larger particles. The unburnt carbon (4–6%) along with other volatile materials present in fly ash were removed by calcination at 800 (± 10) ℃ for 2 h.Mixture of sodium hydroxide and fly ash (calcined and HCl treated) in a pre-determined ratio, was milled and fused in a stainless steel tray at different temperatures ranging from 500–650 ℃ for 1 h. The sodium hydroxideto fly ash ratio (by weight) was varied from 1×0–1×5. The resultant fused mixture was then cooled to room temperature, ground further and added to water (10 g fly ash/100 ml water). The slurry thus obtained was agitated mechanically in a glass beaker for several hours. It was then kept at around 90 ℃ for 6 h without any disturbance. The flow diagram of the synthesis process is shown in figure 3.

The resultant precipitate was then repeatedly washed with distilled water to remove excess sodium hydroxide, filtered and dried. The sodium hydroxide added to the fly ash not only works as an activator, but also adjusts the sodium content in the starting material.

IV. Results and Discussion

A. DETERMINATION OF λ_{max} FOR AMIDO BLACK DYE SOLUTION

To determine the wavelength that corresponds to maximum absorbance (λ_{max}), a standard solution of Amido Black in distilled water was scanned through a wavelength range of 200–700 nm using a UV–Visible spectrophotometer. Maximum absorbance value was noticed at a wavelength of 618 nm (Figure 1). The same value was also used in several literatures (Qiu et al., 2009). Therefore, λ_{max} for amido black was taken as 618 nm. A plot of absorbance versus wavelength for Amido Black dye solution is given in fig.4.

B. CALIBRATION CURVE FOR AMIDO BLACK DYE SOLUTION

Absorbance values were determined at various known concentrations of the dye solution to obtain a calibration curve for Amido Black dye solution. As shown in figure 2, a linear fit to the observed data (absorbance versus dye concentration) yielded a straight line with a slope of 0.0658. This calibration curve can be used for the determination of unknown dye concentration in the solution after adsorption with zeolite. A calibration curve for amido black dye solution is shown in fig 5.

C. ADSORPTION EXPERIMENTS

The adsorption experiments were carried out for 6 h under continuous agitation at 120 rpm and 20°C. The experimental scheme is as follows.

Six different concentrations of the adsorbent (zeolite) were studied to obtain the optimal concentration of the zeolite for effective removal of the dye from its aqueous solution.

D. CALCULATION OF REMOVAL EFFICIENCY

Dye removal efficiency was determined from the dye concentration in the solution before and after adsorption with zeolite.

$$\text{Removal efficiency, R} = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

$$\text{Adsorption capacity, } q_t = \frac{C_i - C_f}{C_z} \qquad (2)$$

Here,
C_i = initial dye concentration in the solution, mg/L
C_f = dye concentration in the solution after adsorption with zeolite, mg/L
C_z = zeolite loading (adsorbent dosage), g/L
q_t = amount of dye adsorbed per unit weight of zeolite, mg/g

The values of dye removal efficiency and adsorption capacity of zeolite evaluated using the above formulae (Eq. 1–2) for various concentrations of zeolite were presented in table 3.
A plot of dye removal efficiency versus zeolite concentration yielded a non-linear profile as shown in figure 3. From this figure, it can be observed that the removal efficiency increased with increasing the zeolite concentration up to 10 g/L and no significant improvement in the removal efficiency values was observed beyond this value. Hence, the optimal zeolite concentration for Hence, the optimal zeolite concentration for the removal of Amido Black dye was chosen to be 10 g/L. A variation of dye removal efficiency with zeolite concentration is given in fig.6.

As can be seen from figure 5, the adsorption capacity of the zeolite (determined by Eq. (2)) decreased with increasing the zeolite concentration. This observation is also in good agreement with the literature [xx]. It indicates that the adsorption capacity of a zeolite decreases with increasing the zeolite dosage. Hence, it can be concluded that too much of zeolite concentration in the solution is not effective for adsorption and it is also not economical. A variation of adsorption capacity with zeolite concentration is given in fig.7.

Zeolitized fly ash product is successfully used as low cost adsorbent for this anionic dye. Equilibrium and kinetic results obtained in this study may be useful for designing a treatment plant for dye removal from industrial colored effluents.

V. Conclusions

The following conclusions have been derived from the experimental analysis carried out so far.

- Zeolite has been synthesized from low-cost raw material, i.e. fly ash.

- The prepared zeolite has been successfully applied for the adsorptive removal of Amido Black dye from its aqueous solutions.
- The prepared fly ash based zeolite is found to be more effective than the natural zeolite *clinoptilolite* presented in the literature (Qiu et al., 2009).
- The optimum zeolite concentration obtained from the experimental studies for Amido Black is 10 g/L.
- λ_{max} for Amido Black 10B dye solution was found to be 618 nm.

Most important observation in this work is that the zeolite synthesized from fly ash could act as a very effective adsorbent for the removal of Amido Black dye. The removal efficiency increased with increasing the zeolite concentration significantly and reached a value as high as 74% at lower concentrations (up to 10 g/L) where as no significant change was observed at higher concentrations.

Work done so far includes the preparation of zeolite and studying the effect of zeolite loading on the removal of Amido Black dye by varying the zeolite concentration from 0 to 15 g/L.

VI. Acknowledgement

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Table 1

Zeolites	Typical oxide formula
Zeolites A	Na2O.Al2O3.2SiO2.4.5H2O
Zeolites X	Na2O.Al2O3.2.5SiO2.6H2O
Zeolites Y	Na2O.Al2O3.4.8SiO2.8.9H2O

Table 2

Dye Concentration, mg/L	Absorbance, A.U.
5.0	0.329
10.0	0.658
15.0	0.987
20.0	1.316
25.0	1.645
30.0	1.974
35.0	2.303
45.0	2.961
50.0	3.290

Table 3

Zeolite concentration (g/L)	**Solution concentration** (mg/L)	**Adsorption capacity** (mg/g)
0	20.2	–
2.5	14.5	2.3
5	9.1	2.2
7.5	6.5	1.8
10	5.3	1.5
12.5	5.5	1.2
15	4.9	1.0

Table 4

Zeolite concentration (g/L)	**Removal efficiency** (%)
0	0
2.5	28.3
5	54.9
7.5	68.0
10	73.8
12.5	73.0
15	75.9

Figures

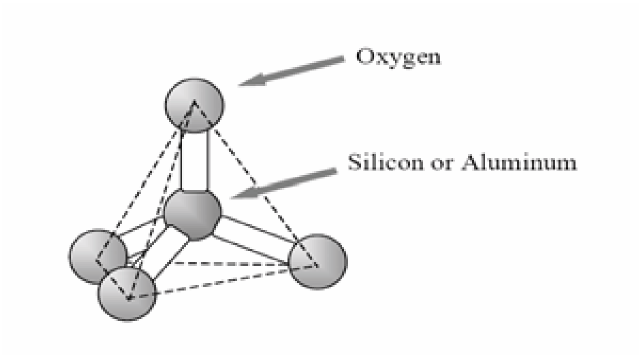


Fig.1

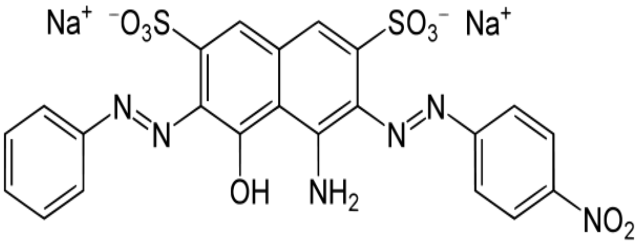
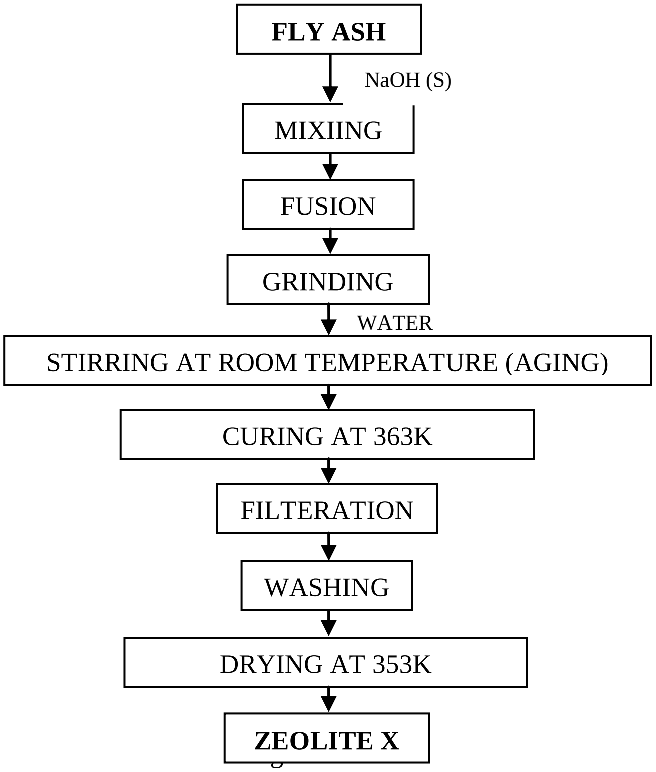


Fig.2


FLY ASH
NaOH (S)
MIXIING
FUSION
GRINDING
WATER
STIRRING AT ROOM TEMPERATURE (AGING)
CURING AT 363K
FILTERATION
WASHING
DRYING AT 353K
ZEOLITE X

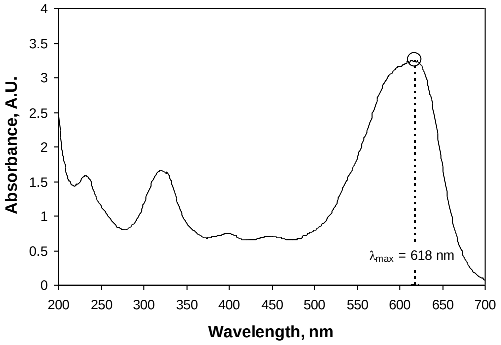

Absorbance, A.U.
4
3.5
3
2.5
2
1.5
1
0.5
0
200
250
300
350
400
450
500
550
600
650
700
Wavelength, nm
λ_{max} = 618 nm

Fig.4

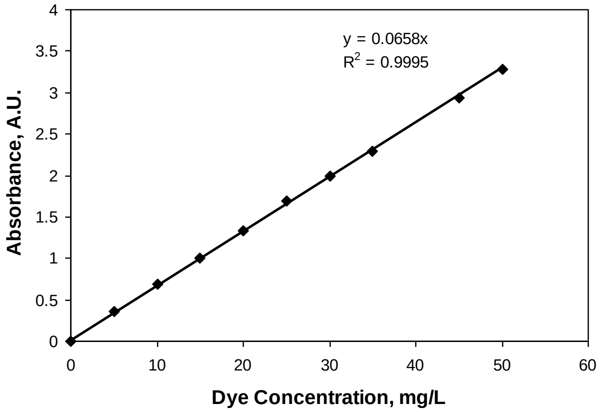


Fig.5

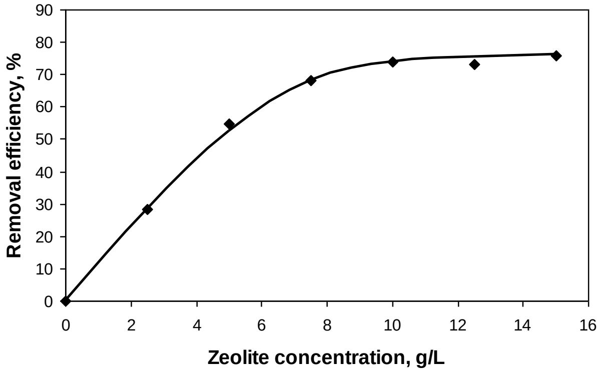


Fig.6

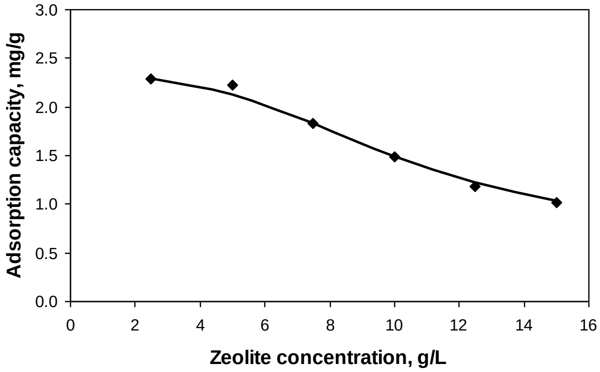


Fig.7

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