

Removal of Acid Orange II from Aqueous Solution by Mesoporous Silica Nanospheres Using Starch and Yeast as Pore Forming Agents

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Abstract- Acid Orange II (AO8) is an anionic dye that is characterized by the presence of one azo group. Compared to its use in wide variety of cheap materials, the studies pertaining to its removal from waste water are very limited. Keeping environmental impact in mind, the main aim of this study is to evaluate the effectiveness of adsorption of acid orange by amino functionalized silica nanospheres synthesized using starch and yeast as pore forming agents. Furthermore, a kinetic and thermodynamic study of the adsorption of AO8 from aqueous solutions onto amino-functionalized mesoporous silica nano spheres was investigated under variable conditions of pH, dye concentration and temperature.

Key words - Acid Orange II (AO8), starch, yeast, Mesoporous silica nanospheres .

I. INTRODUCTION

During the treatment of wastewater, removal of color produced by the dyes is one of the main problems encountered by most of the industries such as textile, paper, printing, leather, food, cosmetics, etc. Dyes released from the industrial effluents, makes water unfit for consumption, by imparting color. Being carcinogenic these dyes pose a great damage to human beings and also to aquatic life by blocking transmission of light. Moreover, this dye is highly soluble in water and is capable of generating toxic intermediates during degradation which are carcinogenic [1,2]. Hence, its removal has been attempted by adsorption, as this technique do not produce any toxic products, is cost effective and is easy in operation. Different adsorbents have been reported for the removal of dyes , for instance, Mohammed et al.[3] used CTAB modified FSM-16 , Park et al.[4] used polyelectrolyte impregnated mesoporous silica, Anbia et al.[5] made use of penta ethylene hexamine functionalized SBA-3 as an excellent adsorbent for anionic dyes. The azo dye AO7, commonly called Orange II is a widely used synthetic dye and is used as a model substrate for the aromatic azo dyes. Since it neither shows biological degradation nor light irradiation and chemical oxidation, therefore, its degradation studies are very important. Different research articles report different methods, like Daneshvar et al. [6] used electrocoagulation method while Bandara et al.[7] used photo-Fenton reactions in the presence of natural sunlight, Inoue et al. [8] used ultrasound while Ray et al. [9] carried out photo catalytic oxidation in presence of TiO₂ waves. At present, the major techniques of removing dyes from waste water are activated carbon method or light degradation and even biological treatment method. All these methods have certain drawbacks like activated carbon method is not very effective, light-degradation treatment is energy consuming and biological process are difficult to control once started

[10]. Other methods like flocculation, carbon adsorption and reverse osmosis are not efficient in causing complete destruction of dye pollutants [11]. Since last two decades, mesoporous silica has found its application as an efficient adsorbent [12-14]. Several efforts of modifying silica with functional groups like amino, carboxyl and imidazole have been carried out to achieve specific properties like porosity, pore volume and surface area. Mahmoodi et al. [15]; Wang and Lee. [16] observed that the interactions between adsorbates and amino/ carboxylic-containing functional groups grafted on MCM-41 acts as an efficient adsorbent for the removal of Acid blue 25 and Methylene blue dyes from waste water. There are many studies regarding synthesis of mesoporous silica with large pore size but a very few studies involve the use of polysaccharides that could the end properties like structure and pore size of mesoporous material. The purpose of this study is not only to synthesize but also control the pore size of mesoporous material like silica by a green route where bio-template like starch is used as pore forming agent in presence of biologically derived foaming agents like yeast. The present work is an attempt to remove the organic anionic dye molecules via the application of the modified mesoporous silica material.

II. EXPERIMENTAL

A. Reagents

Sodium silicate (Merck), 25% ammonia solution (purity 99.5%, Merck), ethanol (purity 99.5%, Merck) were used without purification. Dry Yeast and soluble starch used as a template were obtained from Himedia. Deionized water and active dry yeast were used throughout the experiment. All chemicals, reagents used were of analytical grade and were used as received without further purification.

B. Synthesis of mesoporous silicates

The synthesis of mesoporous silica material was carried out with little modification in the method reported elsewhere [17]. A mixture of alcohol and water was used as a solvent for suspending yeast with sodium silicates. Ammonia was used as a catalyst. 20 ml of sodium silicate in ethanol was added to a mixture of ammonium hydroxide in water (10 ml) in a two-necked 500-ml round-bottomed flask fitted with a thermometer and reflux apparatus. The mixture was stirred for 30 minutes at room temperature under nitrogen. Once the solution became clear and homogeneous the reaction mixture was refluxed at 65° C for 5 hours. To this solution, starch-yeast slurry was added with slow stirring. Later the reaction mixture was subjected to sonication at 40°C for an hour. The samples were then dried in a vacuum oven at 110°C. Drying was continued until a constant weight was achieved. This was followed by calcination at a slow temperature increase (1° C/min) up to 550°C for 6 hours to get SY.

C. Preparation of Starch- yeast Slurry

For adding yeast, it was first dissolved thoroughly in (1:1) distilled water by weight. The resulting yeast solution was introduced with stirring into an appropriate amount of starch to form slurry. The slurry was later poured into a 250 ml beaker and covered with a glass cover and simultaneously heated to 40°C inside an oven for 2-3 hours so that fermentation sets in and foaming develops. In all the performed experiments the amount of starch was kept constant at 50% with respect to sodium silicate, while yeast was taken with respect to starch (50% by wt). The sample is abbreviated as SY50. Besides this other samples without yeast (SS) and without starch (SY) were also prepared for comparison purpose using same procedure.

D. Synthesis of Amino Functionalized Silica (FSY)

FSY50 was prepared as per the method of Ho et al. [18] in which 2.5 g of calcined SY was refluxed with 2.5 g of 3-aminopropyltrimethoxy silane (APTMS) in a 100 ml RBF containing 50 ml of n-hexane for about 6-7 hrs. Later the mixture was washed with isopropanol and dried at room temp. To this reduced solution, starch-yeast slurry was added with slow stirring for six hours. % Weight of added starch was calculated from the reaction stoichiometry, assuming complete conversion of TEOS to silica. By-products were separated using rotary evaporator and later subjected to washing at least 5-6 times with water to remove un-reacted yeast/starch. The samples were further dried in a vacuum oven at 110 ° C. Drying was continued until a constant weight was achieved. This was followed by calcination at a slow temperature increase (1° C/min) up to 550 °C for 6 hours to get FSY.

E. Material Characterization

Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer. UV measurements were

performed using Shimadzu Spectrophotometer. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K α radiation of 0.15406 nm wavelength. The nitrogen sorption experiments were performed at -196 °C on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were out-gassed at 120°C for 6 h. The BET specific surface areas were calculated using adsorption data in a relative pressure range of P/P₀ = 0.05–0.25. Pore size distribution curve was calculated using BJH method. The total pore volumes were estimated from the amounts adsorbed at a relative pressure (P/P₀) of 0.99. Scanning electron microscopy (SEM) was performed using Jeol, JSM 5600 microscope operated at 15 kV. The samples were coated with Au prior to SEM examination.

F. Adsorption Experiments

1) *Adsorption Isotherms experiments:* The thermodynamic and kinetic study of the adsorption of azo-dye AO8 onto functionalized silica (FSY50) was investigated by varying dye conc, pH and temperature. For finding the effect of temperature and pH on adsorption, experiments were conducted at various temperatures (25, 30 and 35°C) and initial pH (2–11), respectively. The dye was first dissolved in distilled water to prepare solutions of varying concentrations (10–200 mg/litre). The initial pH value was adjusted with 0.1N NaOH /HCl using a pH meter. For adsorption study, 0.3 g/L of FSY50 was added to 50 ml of dye solution of desired concentration under stirring for pre determined time intervals. For finding the residual AO8, the solution and solid phase were separated by centrifugation. The % of AO8 removed was calculated by the following equation:

$$R = (C_0 - C_e / C_0) \times 100 \dots \dots \dots (1)$$

The equilibrium adsorption of metal ion solution by amino functionalized silica was measured after 5 hrs of contact time. The amount of AO8 adsorbed per gram of the adsorbent was calculated by the difference between the initial and the final readings using equation (2).

$$q_e \text{ (mg/g)} = (C_0 - C_e \text{ (mg/L)} \times V \text{ (L)} / W \text{ (g)} \dots \dots \dots (2)$$

where q_e is the equilibrium adsorption capacity of adsorbent in mg of dye /g of adsorbent, C_0 and C_e are the initial and equilibrium concentration of dye in mg/L respectively, V is the volume of dye and W is the weight of adsorbent in gram. The analysis of equilibrium data was carried out using linear form of Langmuir, Freundlich equations. The linear forms of the Langmuir and Freundlich equations are

$$C_e / q_e = 1 / Q_{ob} + C_e / Q_o \dots \dots \dots (3)$$

$$\log q_e = \log k_f + 1/n \log C_e \dots \dots \dots (4)$$

For kinetic studies, AO8 having initial concentrations of 50, 100 and 150 mg L⁻¹, were treated with 0.3 g / L⁻¹ of FSY at a constant temperature of 298 K. Mixtures were withdrawn at appropriate time intervals and residual concentration was estimated using UV spectrophotometer at a wave length of 486 nm. (50, 100 and 150 mg L-

1).Variation of amount absorbed was studied with respect to time for three initial dye concentrations (50, 100 and 150 mg L⁻¹).

III. RESULT AND DISCUSSION

A. XRD Studies

The relative crystallinity of the as-prepared samples was investigated by XRD. Figure 1, shows the main diffraction peak for SY50 lying in the 2θ range from 23-30 ° signifying the presence of mesoporous structure. The broad peak also suggest poor crystallinity and high water content. The intensity of this peak did not change even on functionalization. The addition of high amount of starch probably inhibits the crystallization of silica.

B. Morphology

SEM was used to investigate the microstructure of the samples. Fig.2 (a,b) shows the SEM images of silica obtained by using starch and yeast as pore forming agent .Porous mass is clearly visible in Fig 2a. The porous structure and stability did not change much on functionalization. Fig 2b shows the increase in bonding sites due to functionalization

C. IR

The FTIR spectra in Fig 3 a,b shows functional groups on the surface of SY50 before and after functionalization. A broad band between 3220-3700 cm⁻¹ can be attributed to the O-H stretching bonds of silanol groups. The vibrations of Si-O-Si (asymmetric and symmetric stretching) appears at 1078 cm⁻¹ and 790 cm⁻¹ stretching)[19]. Two adsorption peaks at 2935 cm⁻¹ and 1582 cm⁻¹ confirms the grafting of -NH₂ groups on the surface of SY50 after amine functionalization. O-H stretching bonds gets replaced with -CH₂ groups after functionalization, which can be seen by a decrease in peak intensity of peaks around 3500 cm⁻¹ and 1687 cm⁻¹.

D. Surface Area and Porosity

The pore structure parameters such as the specific surface area, pore size and pore volume for silica microspheres are listed in Table 1. The porosity of the synthesized silica with and without yeast was investigated by nitrogen sorption analysis. A remarkable increase in surface area, pore size and pore volume

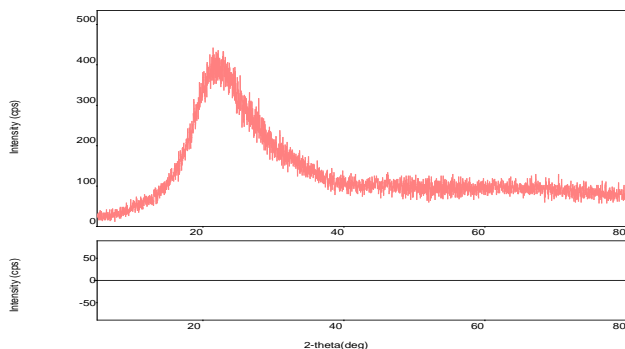


Fig. 1 XRD pattern of silica(SY50) calcined at 550 °C

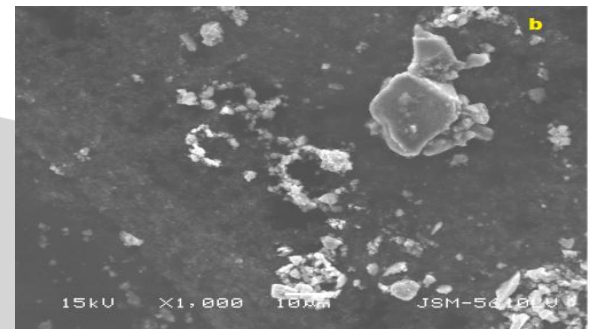
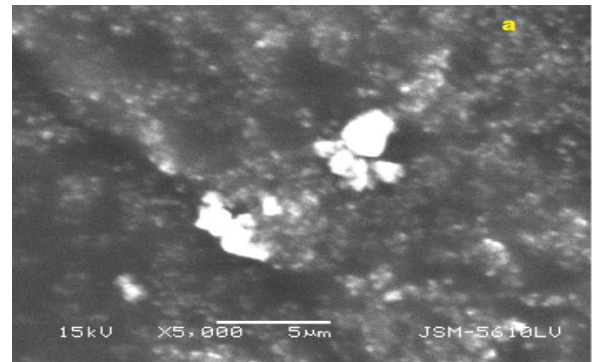


Fig. 2 SEM images of prepared silica:(A) SY50 (B) FSY50

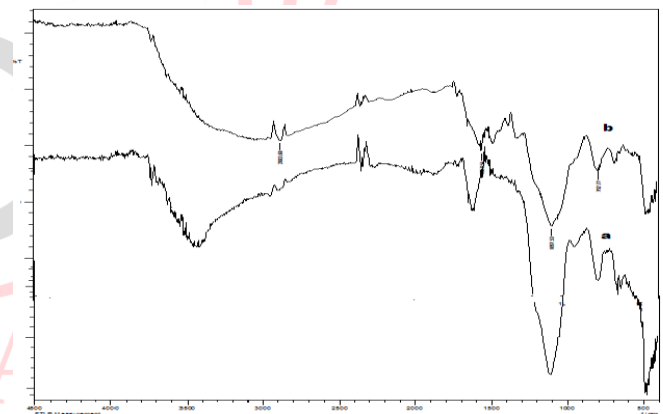


Fig.3 FTIR spectra of (a) silica (SY50), (b) Functionalized silica (FSY50)

TABLE I

| Sample Name | Weight % of added starch | Weight % of added Yeast | Pore diameter (nm) | BET Surface area (m ² /g) | Pore volume (cm ³ /g) |
|-------------|--------------------------|-------------------------|--------------------|--------------------------------------|----------------------------------|
| SS | 50 | 0 | 26.3 | 112.5 | 0.267 |
| SY | 0 | 50 | 11.9 | 23.6 | 0.114 |
| SY50 | 50 | 50 | 7.98 | 341.1 | 0.866 |
| FSY50 | 50 | 50 | 2.99 | 51.7 | 0.139 |

Textural characteristics of silica and functionalized silica was seen on adding yeast. The highest increase in surface area

was observed for samples containing 50% yeast along with starch. This was hence considered an optimum dosage. The increased surface area can be attributed to the formation of spherical, isolated nanospheres with increased density of pores leading to higher pore volume and surface area in the silica matrix. The large pore diameter of FSY50 allows bigger size dye molecules of AO8 to enter the channels that are otherwise restricted [20].

E. Adsorption Isotherm

The adsorption studies was carried out at different pH ranging from 1 to 10 using adsorbent dose 0.3g/L, and at 25oC. The maximum sorption was observed at pH 5 due to highest interactions at that pH with a positively charged surface. Figure 4 shows equilibrium adsorption isotherms for AO8 at three different temperatures. The equilibrium adsorption capacity of AO8 studied at different temperatures showed an increase with increasing temperature. The adsorption was quite rapid initially but slows down gradually and ultimately attains

TABLE II LANGMUIR AND FREUNDLICH CONSTANTS FOR AO8

| Temp (°C) | Langmuir Isotherm | | | Freundlich Isotherm | | |
|-----------|-------------------|-------|----------------|---------------------|----------------|----------------|
| | Q _{max} | b | R ² | n | K _f | R ² |
| 25°C | 195 | 0.058 | 0.987 | 2.01 | 17.23 | 0.768 |
| 30°C | 206 | 0.088 | 0.991 | 2.32 | 26.36 | 0.821 |
| 35°C | 257 | 0.19 | 0.99 | 2.46 | 41.07 | 0.835 |

an equilibrium value at around 60 min. This trend may be attributed to an increase in contact between the sorbate and sorbent during the early stage of absorption when all the available sites were vacant. The Langmuir and Freundlich isotherm equation was used to analyse equilibrium adsorption data shown in Table 2. The linear plot of specific adsorption (Ce/qe) against the equilibrium concentration (Ce) (Fig. 5) shows that the adsorption obeys the Langmuir model.

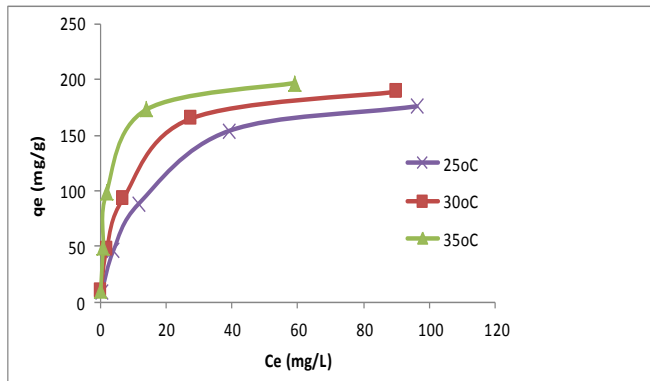


Fig. 4 Equilibrium adsorption isotherms of AO8 at 25°C, 30°C and 35°C

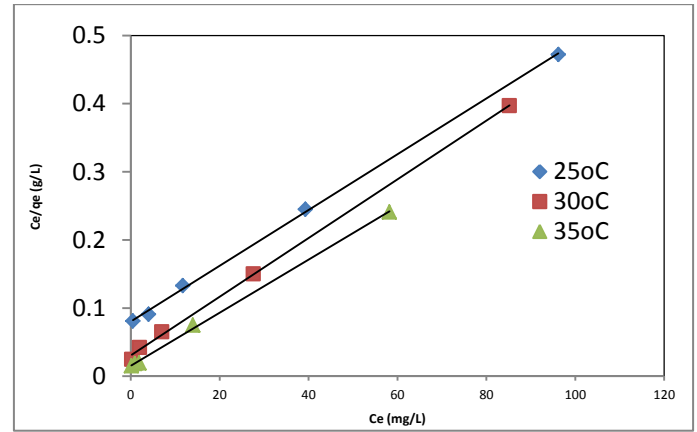


Fig. 5 Langmuir isotherm model of AO8 adsorption onto FSY50 at 25°C, 30°C and 35°C

Table III - Comparative adsorption capacities of various silica based adsorbents used for AO8 adsorption

| Type of Adsorbent | Maximum adsorption capacity (mg/g) | Ref |
|---|------------------------------------|------|
| magnetic silica with amine groups | 48.98 | [21] |
| nanostructured TiO ₂ /SiO ₂ | 40% photocatalytic degradation | [22] |
| Mesoporous CeO ₂ Synthesized from Mesoporous MCM-48 Silica | Photocatalytic degradation | [23] |
| Fe-Cu bimetallic nano particles on hollow mesoporous silica spheres | 78.9% removal efficiency | [24] |
| (H ₅ FeW ₁₂ O ₄₀ 10H ₂ O)/silica structured fabrics | photobleach 85% | [25] |
| Silver Impregnated TiO ₂ /SiO ₂ composite | 89 % removal | [26] |

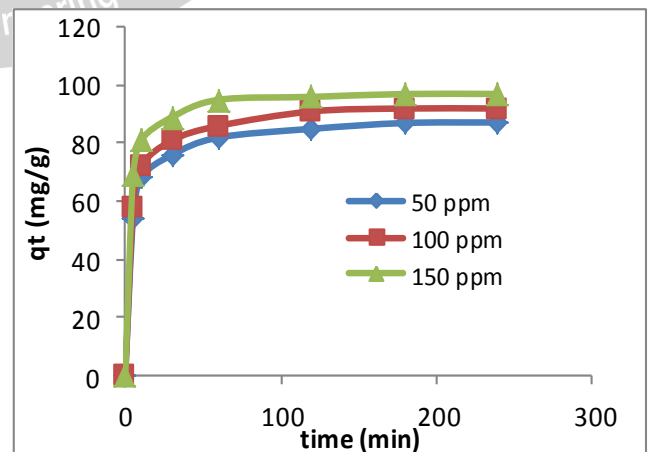


Fig.6 Variation of adsorption capacity with time for 50, 100 and 150 mg/L of AO8

The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot. As seen from Table 2, the Langmuir isotherm fits well with the experimental data with R^2 being 0.99. Since the Langmuir equation assumes that the surface is homogenous, hence there must be a homogenous- distribution of active sites on FSY50. The maximum adsorption capacity of AO8 dye corresponding to the complete monolayer coverage (mg/g) on the FSY50 spheres prepared in this work was 257 mg/g. This value was found to be much higher than that reported for other silicates. Table 3 gives a comparative data of adsorption capacity of various silica based adsorbents [21-25].

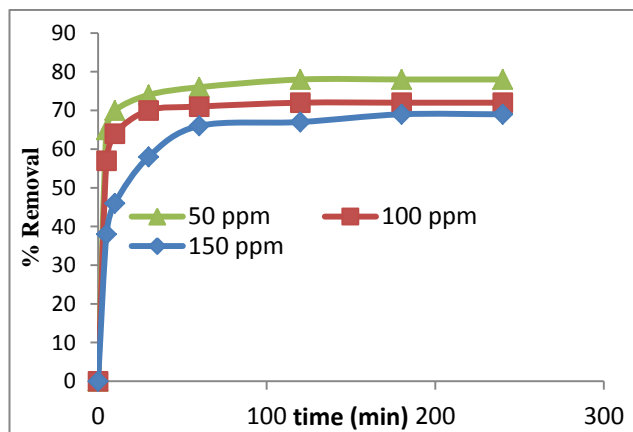


Fig.7 Percentage removal of AO8 on FSY50 adsorbent as a function of contact time

F. Adsorption Kinetics

The adsorption performance of the FS particles for the removal of AO8 from water was investigated by the batch type adsorption kinetic experiments. Fig. 6 shows the adsorption capacity as a function of contact time at different initial AO8 concentrations. A fast initial adsorption was seen followed by a relatively slow adsorption for various initial AO8 concentration ranging from 50, 100 and 150 mg/L. The highest removal efficiency of about 78% was achieved in 120 min as seen from Fig 7, when AO8 concentration was 150 mg/L. The initial rapid adsorption might be attributed to electrostatic attraction that resulted in fast transportation of dye from solution onto the surface of adsorbent. At pH 5, AO8 gets adsorbed on the surface of FSY50 due to electrostatic attraction between the positively charged silica surface and sulfonic acid groups of the AO8 molecules. Apart from this, large values of surface area and pore volume results in high adsorption affinity of FS.

IV. CONCLUSION

In the present work, a simple and eco-friendly procedure has been adopted for the synthesis of silica microspheres using polysaccharides. The use of starch and yeast could satisfactorily be used as a pore forming agent so as to accommodate large sized pollutants like dyes. The surface area and porous properties of these mesoporous structures can be significantly improved by simply adjusting the ratio of starch band yeast. . The equilibrium adsorption data are

well fitted by Langmuir isotherm equation giving the maximum adsorption capacity of 257 mg/g. These mesoporous particles with high surface area and pore volume showed good adsorption performance to remove AO8 dye from water. This work may be further extended for a variety of other heavy metal ions, organic molecules and dyes.

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