



Facile synthesis of aluminium cobalt oxide for dye adsorption



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ABSTRACT

A new adsorbent aluminium cobalt oxide (CS-ACO) was synthesized by solution combustion technique. The synthesized product was characterized by various techniques. The adsorption capacity of CS-ACO was higher than that observed with commercial activated carbon. Four anionic dyes namely – Congo red, Orange G, Indigo carmine and Methyl blue were adsorbed on CS-ACO. Congo red showed the maximum adsorption per unit weight of adsorbent. The effect of pH and adsorbent loading on the adsorption kinetics and equilibrium was determined. The controlling mass transfer regimes during the course of adsorption were also identified.

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Introduction

Adsorption has wide applications ranging from the removal of suspended particles, metal ions, colloids, microbiological contaminants to purification of petroleum fractions [1–5]. The commercially important adsorbents are activated carbon, silica gel, zeolites or molecular sieves and activated alumina [6]. Activated carbon is the microcrystalline, non-graphitic form of carbon obtained by calcination of the nutshell, peat, lignin, rice hull or coal [7,8]. Zeolites are aluminosilicates of metals that are used for the separation of paraffins, *iso*-paraffins, aromatics, *p*-xylene/*o*-xylene/*m*-xylene [9,10]. Carbon molecular sieves are mainly used for nitrogen production by employing the pressure swing adsorption [11]. Silica gel is the modified form of silica containing hydroxyl groups (silanol) and is used for moisture adsorption [12].

Dyes find their application mainly in textile and leather industries. Nearly 10% of the used dyes are discharged into water bodies as a result of fixation of spent dye baths, residual dye liquors and post-washing of dye treated fabrics. Dyes are carcinogenic compounds and lead to the arrested development of lives in water bodies. Therefore, it is important to develop adsorbents that can remove the dye from water.

About 80% surface area of activated carbon lies in the pores having size (10 Å) less than the molecular size of the dyes (typically 5–35 Å), making them inaccessible for dye molecules. The unavailability of significant area leads to poor efficiency [13].

Further, activation of carbon requires treatment with expensive chemicals and high temperature [14,15]. Current studies have used magnetic nanoparticles coated with organic layers to obtain the desired effect [16,17]. However, in this work, the emphasis has been to develop a new material that can be used for the adsorption of dyes.

Solution combustion is a highly exothermic and self-propagating redox reaction [18]. It is a rapid process of liberation of large amount of gases leading to the formation of product in nanosize regime [19]. The synthesis of metal oxides via combustion route is well reported. Most of the reported adsorbents are metal oxides and many oxides such as ZnO, SnO₂, TiO₂–SiO₂, ZrO₂, Co₃O₄ have been used for adsorption [20–23].

This is the first study that has investigated the synthesis and adsorption capacity of combustion synthesized aluminium cobalt oxide (CS-ACO). The synthesized product was characterized by various techniques. Four anionic dyes belonging to different classes – Congo red (diazo), Orange G (monoazo), Indigo carmine (indigo) and Methyl blue (triarylmethane) were used for adsorption studies. The equilibrium isotherms, the effect of adsorbent loading and the kinetics of adsorption were determined and discussed.

Experimental details

Materials

Analytical grade aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O – Merck, India) and cobaltous nitrate hexahydrate (Co(NO₃)₂·6H₂O – S.D. Fine Chemicals) were used for synthesis as received. The dyes, Congo red (CR) and Orange G (OG) were

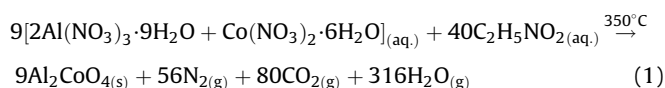
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procured from S.D. Fine Chemicals, India; Indigo carmine (IC) was obtained from Rolex Labs, India and Methyl blue (MB) was from Merck, India. Activated carbon, NaOH pellets and 35% HCl were obtained from Merck, India. Double distilled water, filtered through a Millipore filter (0.22 μm) was used for all purposes.

Synthesis of adsorbent

Solution combustion technique was used to synthesize the aluminium cobalt oxide (CS-ACO). Solution combustion is a well-practiced technique to prepare metal oxides in nanosize range. In the typical synthesis procedure, aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved separately in water in the molar ratio of 2:1, respectively. The mixture was used as oxidizer for the combustion. Glycine was dissolved in deionized (DI) water and used as fuel. The reaction based on oxidizer to fuel stoichiometric (molar) ratio can be written as Eq. (1).



The stoichiometric amount of precursors was mixed and kept at $350 \pm 15^\circ\text{C}$ in a preheated furnace. The progress of reaction was continuously monitored till the solid product was formed. During combustion, the release of 452 mol of gas in a short time of 10 min makes the final product highly porous and voluminous. The combustion was smouldering type. The grey colour product was ground for half an hour before subjecting to adsorption.

Characterization of adsorbent (CS-ACO)

The prepared product was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), surface area determination using BET analysis and ζ potential measurement.

Powder X-ray diffraction (XRD) was carried out using X-ray diffractometer (Rigaku SmartLab, Japan) equipped with detector Scintillator NaI (photomultiplier with preamplifier). The instrument was operated at 40 kV and 30 mA. The powder specimen was exposed to $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The scanning was done in the 2θ range of $10\text{--}80^\circ$ at a scan rate of $2^\circ/\text{min}$. For SEM analysis, the powder specimen was dispersed in ethanol and drop-casted on silicon wafer. High resolution field emission scanning electron microscope (Ultra 55, Carl Zeiss, Germany) equipped with EDAX was used to observe the morphology (at 8–70K magnification) and atomic percent of elements present in the sample, operating at the accelerating voltage of 5 kV. The TEM (Tecnai T20, FEI, US) images were obtained at 160 kV. Prior to the imaging, the sample was dispersed in ethanol for 20 min of sonication. It was then drop casted on carbon coated Cu grids and was left for 12 h for drying. To identify the oxidation state of cobalt in the prepared sample, XPS (Axis Ultra, Kratos, UK) was recorded using monochromatic $\text{Al K}\alpha$ radiation. The surface area of adsorbent was determined by surface area analyser (Nova 1000, Quantachrome, US). In order to understand the mechanism of adsorption, the zeta potential of adsorbent CS-ACO was measured (Brookhaven, ZetaPALS, US). Prior to the measurement, CS-ACO (0.4 g L^{-1}) was sonicated at its natural pH.

Adsorption experiments

The adsorption of dyes was carried out in dark to avoid photolysis at the natural pH. Natural pH was measured in aqueous

media without any addition of external ions. A stock 1 solution of 2000 ppm was prepared and kept in dark. This was used for adsorption studies after appropriate dilution. For comparison, adsorption of dyes was also studied on activated carbon. The amount of adsorbent was kept constant at 0.4 g L^{-1} unless otherwise mentioned. The solution was continuously stirred at 500–600 rpm to maintain homogeneity throughout the solution.

The samples were taken out at suitable intervals for the measurement of concentration of dye in liquid phase. The aliquots were centrifuged to remove the adsorbent particles and the absorbance was measured using UV–vis spectrophotometer (UV 1700, Shimadzu, Japan) at the characteristic wavelength (λ) of the dye (CR-497 nm, OG-480 nm, IC-610 nm, MB-600 nm). The calibration based on Beer Lambert's law was used to convert absorbance to concentration. The absorbance varied proportionally with dye concentration as $\text{absorbance} = A \times \text{concentration}$. The values of A were 0.0124, 0.0176, 0.0155 and 0.0285 for CR, OG, IC and MB respectively, and this calibration is valid up to dye concentration of 50 mg L^{-1} . For higher concentrations, dilution was carried out and accordingly the concentration was obtained by multiplying with dilution factor.

Results and discussion

Characterization of CS-ACO

X-ray diffraction

The XRD pattern of CS-ACO revealed the formation of cubic lattice as shown in Fig. 1. The pattern was found to match with Al_2CoO_4 (JCPDS card no. 82-2245) [24,25]. The absence of CoO (JCPDS card no. 75-0393) and Al_2O_3 (JCPDS card no. 78-2427) shows that metal oxides are not phase separated. The Scherrer equation ($D = 0.89\lambda/\beta_{1/2}\cos\theta$, where λ is the wavelength of X-ray, θ is the diffraction angle and $\beta_{1/2}$ represents the peak full width half maxima) was used to calculate the crystallite size. The crystallite size was found to be 16 nm. To investigate the presence of Al in the compound, further analysis (EDAX analysis) was carried out.

Scanning electron microscopy

The SEM micrographs of synthesized product are shown in Fig. 2. Fig. 2(a) and (c) show that the adsorbent has flake-like morphology. The highly porous structure of the particles is visible from Fig. 2(b) and (d). An interconnected network of pores of size

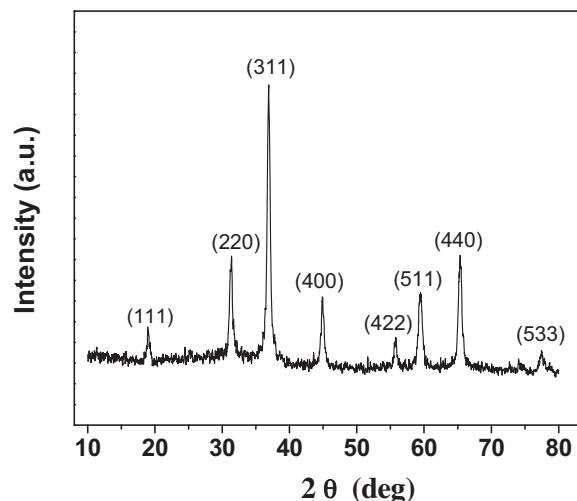


Fig. 1. XRD of CS-ACO. Numerics inside parentheses represent plane parameter (hkl) corresponding to the peak.

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