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Synthesis of carboxymethyl starch-*g*-polyvinylpyrolidones and their properties for the adsorption of Rhodamine 6G and ammonia

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ABSTRACT

Carboxymethyl starch-*g*-polyvinylpyrolidones (CMS-*g*-PVPs) were prepared by grafting of carboxymethyl starch (CMS) with *N*-vinylpyrolidone (NVP) using different initiators. The grafting percentage of all the modified starches was determined and the modified starch (CMS-*g*-PVP-5) with maximum grafting percentage was characterized by elemental analysis, ^{1}H NMR and FT-IR spectroscopy. Crystallinity and thermal properties of CMS-*g*-PVP-5 were analysed by XRD and TGA, respectively. CMS-*g*-PVP-5 was then utilized for the adsorption of Rhodamine 6G (dye) from water under different *p*H, temperature, adsorbate doze and adsorbent concentration. This modified starch showed good adsorption ability towards Rhodamine 6G. CMS-*g*-PVP-5 was also applied for the adsorption of ammonia gas and proved an exciting adsorbent for ammonia.

1. Introduction

Nowadays various kinds of dyes are being used in different industries such as cosmetics, food, plastics, printing, textiles, leather, etc. About 15% of these dyes are drained into water, which make the water unfit for use (Ali, 2012; Jin, Sun, Xu, & Xu, 2015). Dyes are undesirable, even in a very small amount because these are not only toxic to human beings but also to aquatic organisms and affect water quality (Reddy & Lee, 2013; Tan, He, Song, Fu, & Shi, 2016; Yu et al., 2016). Rhodamine 6G, a monocationic xanthene dye which has wide applications (dying and tracing agent) in industries, is carcinogenic, neurotoxic and causes reproductive and chronic toxicity to human and other animals (Bhaskar et al., 2016; Shen & Gondal, 2017; Zaleschi, Secula, Teodosiu, Stan, & Cretescu, 2014). Similarly, smoke aerosols of burning cigarette contain thousands of dangerous chemicals which have cardiovascular, respiratory and carcinogenic health effects (Brewer et al., 2016; Cheruel, Jarlier, & Sancho-Garnier, 2017). Ammonia is one of the chemicals which causes serious damages to mankind including respiratory tract diseases, lung diseases and permanent blindness (Chen et al., 2016; Lemus et al., 2016; Pandey, Goswami, & Nanda, 2013; Takahashi et al., 2016). Several methods have been adopted to remove these dyes from wastewater such as adsorption, coagulation and membrane filtration. Similarly, ammonia content in cigarette smoke can be minimized by using various techniques. Among all the available methods and techniques for the removal of dyes from wastewater and ammonia from smoke, adsorption was found to be most efficient and cost effective method. Various organic and inorganic adsorbents used for the adsorption of dyes and ammonia are activated carbon, carbon nanotubes and polymeric materials (Ali, 2012; Pourjavadi, Nazari, & Hosseini, 2015). However, these adsorbents are either costly or non-biodegradable and may act as secondary pollutants (Ahmaruzzaman & Gupta, 2011; Haroon et al., 2016). Inexpensive plant biopolymers, such as starch and cellulose have been used as effective flocculants (Gross & Kalra, 2002). However these biopolymers need to be modified before use. Similarly, copolymers of PVP have been successfully used for the adsorption of various dyes like Methyl Violet (Şolpan & Kölge, 2006), Crystal Violet (Zhang, Zhou, ö Wang, 2006), Safranine-T (Çöle, Gök, ö Güçlü, 2013), Cibacron Blue, Methyl Orange and Congo Red (Can, Kirci, Kavlak, ö Güner, 2003) etc. A lot of work has been done on grafting of polyvinylpyrolidone (PVP) on biopolymers and its applications. Starch-*g*-PVP has been prepared using AIBN as initiator, however the grafting percentage was very low in this case (Kahya, Şanlı, Ünal, ö Camurlu, 2009). Carboxymethylcellulose-*g*-PVP (CMC-*g*-PVP) was synthesized in aqueous solution using AIBN as initiator. The grafting percentage was very high in this case but its adsorption application was not studied (Yiğitoğlu, Işıklan, ö Özmen, 2007). PVP was also grafted on cellulose membrane with high grafting percentage in aqueous system using cerium ammonium sulfate as initiator (Ibrahim, Flefel, ö El-Zawawy, 2002). Similar cellulose-*g*-PVP (C-g-PVP) was also prepared in homogeneous and heterogeneous media using gamma radiation as

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initiator. This C-*g*-PVP was then used for the adsorption of Acid Red 1, Methylene Blue and heavy metals like cobalt, nickel and copper. However adsorption efficiency of this modified biopolymer for the basic dye was very low (Aly, Sokker, Hashem, ö Hebeish, 2005). Chitosan-*g*-(*N*-vinylpyrrolidone)/montmorillonite composite was also prepared and used for the adsorption of Rhodamine 6G from aqueous solution (Vanamudan, Bandwala, ö Pamidimukkala, 2014). Other Biopolymers, modified with component other than PVP have also been used for the adsorption of dyes. Hydroxyethyl starch-*g*-poly-(*N,N*-dimethyl acrylamide-*co*-acrylic acid) has been synthesized and used as an efficient dye removing agent (Kolya ö Tripathy, 2013). Similarly, for the adsorption ammonia for smoke pyrolyzed starch carbon, oxidized with HNO_3 and H_2SO_4 has been used (Shen, Zhang, Jiang, ö Liu, 2010). Amylose grafted poly(acrylic acid) (Am-*g*-PAA) has been prepared and applied for the adsorption of ammonia in gaseous form in cigarette filter (Chen et al., 2016).

A few reports are available in which an environmental friendly modified starch is used as an adsorbent for the adsorption of ammonia. There is a need of time to develop and synthesize environmental friendly adsorbents, which are easy to prepare, low in cost and high efficient for the adsorption of ammonia and dyes. In this paper, we synthesized novel carboxymethyl starch-*g*-polyvinylpyrolidones (CMS-*g*-PVPs) by grafting of carboxymethyl starch (CMS) with *N*-vinylpyrrolidone (NVP). The synthesized modified CMS with maximum grafting efficiency (CMS-*g*-PVP-5) was used for the adsorption of Rhodamine 6G from wastewater under different conditions of temperature, adsorbent dose, adsorbate dose and *p*H. CMS-*g*-PVP-5 was also used for adsorption of ammonia gas from the gaseous mixture.

2. Experimental section

2.1. Materials

CMS (with degree of substitution (DS) of 0.34 and viscosity (2 wt% solution) of 3 cP) and azobisisobutyronitrile (AIBN) were purchased from Aladdin, China. NVP and Rhodamine 6G were purchased from J & K Chemical Ltd., China. NVP was distilled under reduced pressure to remove inhibitors from it before use. Acetone, tris (acetylacetonate) cobalt (III), potassium persulfate (KPS), ammonia, HCl, ethanol and methanol were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the reagents used in the experiments were of analytical grade.

2.2. Synthesis

Synthesis of CMS-g-PVPs was carried out in a three necked flask equipped with reflux condenser, argon gas inlet and a magnetic stirrer. The synthetic procedure for all CMS-g-PVPs was same, only difference was the use of different initiators and temperature. Therefore, the synthesis of CMS-g-PVP-5 was taken as an example. In a typical procedure 2.0782 g of CMS was taken in the reaction flask and 100 mL distilled water was added to it to prepare the CMS solution with viscosity of 3 cP. The mixture was stirred at 450 rpm for 30 min at 50 °C under argon gas atmosphere. The mixture was cooled to room temperature in 45 min. 82.9 (0.5 mmol) mg AIBN (1 wt% of the weight of the reactants) was added to CMS solution and the reaction mixture was stirred for 30 min at 60 °C to form free radicals on the surface of CMS. 7.45 mL of NVP was added to the obtained reacting mixture and the resulting reaction mixture was further stirred for 5 h under argon gas. The product was precipitated in methanol and washed with ethanol (500 mL) for 5 times to remove homopolymer (PVP) and unreacted NVP because the PVP and NVP were soluble in ethanol while the modified starch was not soluble in ethanol. The obtained product was dried in oven for 24 h and stored in desiccator for characterization and application.

The synthesis of homopolymer (PVP) was also carried out to study the comparative characterization of the prepared PVP with the modified CMS. For synthesis of PVP, 100 mL water was taken in three necked flask. 7.45 mL (70 mmol) NVP was dissolved in it, followed by addition of 82.4 mg (0.5 mmol) AIBN. Then the solution mixture was heated at 60 °C for 5 h to synthesize homopolymer PVP. After 5 h, the reaction was stopped and the homopolymer was separated by precipitation in acetone. The precipitated PVP was washed further 3 times with water and precipitated in acetone and finally the PVP was placed in oven for drying.

2.3. Characterization

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Advanx-400 DMX NMR spectrometer using D_2O as a solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 IR spectrometer. Elemental analysis was done on Vario MICRO V 1.9.5 2010-12-2 Elementar analysensysteme GmbH. X-ray analysis was done with XPert PRO (Cu Kα, λ = 1.54 Å). Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were performed on TA-Q500 (Mettler-Toledo). The concentration of dye was determined using Varian CARY 100 Bio UV/Visible spectrophotometer. The *p*H analysis was performed by using a PHS-3C *p*H meter.

2.4. Adsorption experiments

Adsorption experiments of Rhodamine 6G were carried out in a series of 100 mL Erlenmeyer's flasks. The desired dose of the CMS-*g*-PVP-5 was put in 50 mL aqueous solution of Rhodamine 6G at specific temperature. The resulting solution was stirred at 400 rpm using a magnetic stirrer. After desired time, solution mixture was centrifuged to separate CMS-*g*-PVP-5 and the residual solution was analyzed by UV/Visible spectrophotometer to determine the concentration of Rhodamine 6G. The concentration of Rhodamine 6G in solution was determined by comparing the results with standard line. Standard line was obtained by using different concentrations of Rhodamine 6G (8 mg/L, 16 mg/L, 24 mg/L, 32 mg/L, 40 mg/L, 48 mg/L and 56 mg/L). The absorbance of these Rhodamine 6G solutions was measured and the graph was plotted between absorbance and concentrations of Rhodamine 6G.

For the adsorption of ammonia, 170 mL of ammonia aqueous solution (10.36 mol/L) was taken in a two necked flask. One end of the flask was connected to argon gas inlet and the other end was connected with the flow meter to control the flow of gas. This flow meter was then connected with four glass filter tubes in which three tubes were filled with cotton filter containing different amounts of CMS-*g*-PVP and one tube (blank) was filled with cotton filter having no CMS-*g*-PVP. Each filter tube was further connected with flask containing 100 mL of 0.05 mol/L solution of HCl which was further connected with flask containing 100 mL of water. Argon gas was passed through ammonia solution which took ammonia along with it. This gaseous mixture was then passed through flow meter, where the flow of gas was controlled at specific flow rate (0.15 m^3/h). The gaseous mixture with controlled flow rate was allowed to enter through 4 filter tubes. The adsorbent samples filled in the filter tubes adsorbed some amount of ammonia from gaseous mixture and the remaining gas was entered in the HCl solution, where unadsorbed ammonia was dissolved. After specific adsorption time, *p*H of the HCl solution was determined by a *p*H meter.

3. Results and discussion

3.1. Synthesis

The experimental details for the synthesis of CMS-*g*-PVPs are given in Table 1 and synthetic reaction is shown in Scheme 1. The CMS-*g*-PVPs were synthesized by 'grafting from' approach in which initiating sites were formed on the main chain of CMS from where PVP chain