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Chemical surface modification of glass beads for the treatment of paper machine process waters

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ABSTRACT

Adsorption of detrimental contaminants on a solid sorbent is proposed to remove these contaminants from process waters to increase water recycling and reduce effluent loads in the papermaking industry. A self-assembly process of attaching (covalent grafting) cationic aminosilane molecules to glass beads was investigated. The existence and the hydrolytic stability of self-assembled monolayers and multilayers were confirmed by X-Ray Photoelectron Spectroscopy and contact angle measurements. Effects of reaction time and curing on aminosilane layer structures are also discussed. The curing step after silanization seems to be crucial in the hydrophobization of the quaternary ammonium silane coated onto glass beads, and curing could affect the final chemical structure of the ammonium groups of grafted organosilane. Results indicated that modified glass beads have a strong hydrophobicity, which is attributed to the hydrophobic property of the longest carbon chain grafted onto the glass surface. Adsorption of a model contaminant (stearic acid) onto chemically modified glass beads was determined using colloidal titration. Hydrophobic interactions could be the main driving force involved between the long carbon chains of stearic acid and the carbon chains of the aminosilane layers on glass bead surfaces. Finally, self-assembly processes applied onto glass beads may have two promising applications for papermaking and self-cleaning systems.

1. Introduction

Cationic polyelectrolytes are extensively used to improve paper properties and the papermaking process. They are used to bond with cellulosic substrates by electrostatic or non-electrostatic interactions, which result in improving product (paper) properties. However, lipophilic extractives released during mechanical pulping will be accumulated in the wet end of the paper machine and have a negative impact on paper machine runnability and product quality. Problems and disturbances such as: pitch deposits on the paper machine, specks in the paper, decreased wet strength, interference with cationic process chemicals, impaired sheet brightness and paper strength, are often caused by lipophilic extractives [1–5]. These extractives are hydrophobic low-molecular-weight compounds; and the various classes of extractives have different chemical behavior during pulping. Some of the esters of these extractives are hydrolyzed during storage [6]. Most of them are released during the mechanical pulping process [6]. It is difficult to remove the lipophilic extractives during neutral and acidic pulping. However, during alkaline processes, such as Kraft pulping, the glycerol esters are completely saponified and free fatty and resin acids are easily dissolved as soaps; although, small amounts remain in the pulp. Conventional approaches for reducing wood-extractive deposits, such as debarking or seasoning of logs, are often insufficient in eliminating pitch troubles. Recent advances in biotechnology have demonstrated the ability of various wood-inhibiting fungi to degrade lipophilic compounds in wood, but these methods appear effective only for certain types of wood and under specific pulping conditions [7]. Furthermore, pitch problems are likely to become more severe with the introduction of more environmentally friendly bleaching processes that have replaced chlorine gas with other reagents such as hydrogen peroxide or ozone [8].

Thus, it is of considerable interest to monitor the removal of lipophilic extractives in papermaking process waters by selective adsorption onto chemically-modified solid sorbents like self-assembled monolayers and multilayers. Covalent molecular assembly is advantageous because each layer in the assembled film can be covalently linked to the substrate (sorbent) and no excess deposition can take place as it is limited by the access to reactive sites on the layer surface. In this technique, the molecules are transferred to the surface of a solid substrate from the liquid or vapor phase containing a self-assembling material. Subsequently, an organized and packed molecular layer forms on the substrate by reaction with the underlying layer. In terms of stability or strength, multilayer films with covalent interlayer bonding [9–13] are more advantageous since they are robust enough to withstand elevated temperatures, polar solvent attack, mechanical wear and abrasion, etc. Among the molecules used

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in the SAM technique, Aminopropylalkoxysilanes (APS) are widely used as coupling agents [14,15] due to their bifunctional nature.

The application of APS in aqueous media has been rapidly developing because of the increasing relevance of surface chemistry in life and environmental sciences [16–18]. In recent years, the use of the SAM technique has received extensive attention because surface energy is easily controlled, thereby also controlling other properties like self cleaning of the surface [19]. However, most of the literature on aminosilanes has focused on the reaction conditions for preparing covalently attached silane layers with controlled thickness and topography. The hydrolytic stability of the attached aminosilane layers is vital to the application and further derivatives of the functionalized substrates in aqueous media. The importance of the hydrolytic stability of attached silanes has been understood since the early days [14,15,41] for silane applications.

The purpose of this study is to investigate the formation of layers of Trimethoxysilylpropyl trimethylammonium chloride (TMAC) on glass-bead surfaces by chemical modification. This will aid in determining the capacity of glass beads in removing stearic acid from papermaking process waters, and in understanding how silanization techniques can have a greater influence on the wettability of glass substrates.

2. Experimental details

2.1. Materials

Soda-lime glass beads, used as a solid sorbent for the removal of stearic acid, were purchased from Fisher Scientific. The beads are 0.5 and 3 mm in diameter and have a density of 2.6 g/cm^3 at 25 °C. The organosilane (cationic coupling agent) used for the silanization technique was N-Trimethoxysilylpropyl N,N,N-trimethylammonium chloride ($C_9H_{24}ClNO_3Si$), purchased from United Chemicals, with a concentration of methanol varying between 47 and 58% by weight. Stearic acid was purchased from ANACHEMIA LTD, Montreal; and was diluted in a 0.1 M potassium hydroxide solution for 4 hours (0.5 g/200 mL). Stearic acid concentration values between 25 and 500 mg/L were used in the adsorption experiments.

Poly-diallyldimethylammonium chloride (p-DADMAC-$C_8H_{16}NCl$), used for colloidal titration, was purchased from Aldrich. It has a density of 1.04 g/cm^3 at 25 °C, a charge density of 5.1 meq/g and a molecular weight (average) of 4.4×10^5 g/mol. All chemicals were of reagent grade and were used without further purification.

2.2. Experimental procedure

2.2.1. Cleaning of glass beads

Glass beads were cleaned thoroughly for at least one hour by immersion into freshly prepared Piranha solution [3:1 H_2SO_4 (98%)/H_2O_2 (30%)] at 90 °C (Caution: piranha solution is a very strong oxidant and reacts violently with many organic materials, it must be handled with extreme care). The substrates were then rinsed with copious amounts of deionized water, and dried in a clean oven under vacuum at 120 °C for 1 h and immediately used for solution phase silanization. The resulting cleaned surfaces were hydrophilic as was proven by contact angle measurements with water, giving values close to 7°.

2.2.2. Silanization

After cleaning and pre-treatment, glass beads were put thought a silanization treatment by dipping them in 50 mL of deionized water containing 1 mL of TMAC at 80 °C for different durations (20 min and 5 hours). The substrates were then rinsed with deionized water and dried at 120 °C for 1 h in a clean oven. Just after cooling, substrates were characterized using X-ray photoelectron spectroscopy XPS analysis and contact angle measurements.

2.2.3. Hydrolytic stability of silanized glass beads

Freshly silanized glass beads were immersed in deionized water for up to 3 days at room temperature. Then, they were shaken in water for 30 min; rinsed with deionized water and dried at 100 °C for 1 h before characterization.

2.2.4. Adsorption isotherms

Chemically modified glass beads (exposed to only 20 min of silanization) were then used in the removal of stearic acid by adsorption. The adsorption of stearic acid (adsorbate) on prepared adsorbents was studied at room temperature (22 °C) using the batch method. 50-mL Teflon tubes were filled with a known volume (20 mL) of adsorbate solution of varying initial concentrations and shaken with a fixed dose of adsorbent (2 g of silanized glass beads) for a specified period of contact time in a temperature-controlled shaking assembly. After equilibrium, the concentration of the adsorbate in the supernatant was determined by polyelectrolyte titration. The amount of stearic acid adsorbed (q (t) in mg/g) was determined from the concentration of excess adsorbate in the supernatant as follows:

$$q(t) = (C0 - Cf) \times \frac{v}{m}$$

C0 and Cf are the initial and final concentrations of the adsorbate in solution (mg/L), V the volume of solution (L) and m is the mass of the adsorbent (g). The reproducibility of our measurements was determined by repeating the experiments at least three times under the same conditions. Average values have been reported. Adsorption was studied as a function of contact time, initial concentration and temperature.

2.3. Instrumentation

2.3.1. XPS

XPS measurements were performed with a Kratos Ultra electron spectrometer (Kratos Analytical) using monochromatic Al Kα X-ray source (15 kV, 5 mA). The low-resolution survey scans were taken with a 1 eV step and 160 eV analyzer pass energy; high-resolution spectra were taken with a 0.1 eV step and 40 eV analyzer pass energy. The analysis area was less than 1 mm^2 and measurements were taken at two different locations on each of the touching faces of glass beads. The collected data was analyzed using Vision software version 2.1.3 and CASA XPS version 2.3.

2.3.2. Scanning electron microscopy (SEM)

The SEM images of typical samples were obtained with a JEOL JSM-5500 Scanning Electron Microscope. Samples were gold coated using an Instrumental Scientific Instrument PS-2 coating unit. The SEM operating voltage was at 15.0 kV.This technique was used to describe the morphology and the topography of the samples' surfaces.

2.3.3. Contact angle measurements

Contact angle (CA) measurements were carried out on the surface of the glass beads before and after silanization in order to determine the change in wettability. The water sessile drop contact angle measurements were carried out on the glass beads using an FTA4000Microdrop instrument (First Ten Angstroms, USA). CA was calculated by averaging the angle measurements of at least ten glass beads, taking into account the geometric shape of spherical beads.

2.3.4. Colloidal titration

The quantity of stearic acid adsorbed on chemically modified glass beads was determined using colloidal titration based on measuring the charge density of the polyelectrolytes. To determine the end point, a Mütek Charge Titrator (PCD03) was used [21]. The charge density of the stearic acid was titrated with standard p-DADMAC (1 meq/L or