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Silica-polymer hybrid materials as methylene blue adsorbents

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ABSTRACT

Nanohybrid materials have emerged as effective adsorbents for the removal of contaminants from the polluted water bodies. In this study we report two new hybrid materials as adsorbents for methylene blue from its aqueous solutions. Nanohybrid materials were prepared from methacrylic acid and methyl methacrylate or 2-hydroxyproypl methacrylate by emulsifier–free emulsion polymerization using 3–aminopropyltriethoxysilane (APTES) as silane coupling agent, and tetraethoxysilane (TEOS) and polyvinyl alcohol (PVA) as silica component precursor and polymeric colloid stabilizer, respectively. Adsorption was studied as a function of various factors, including contact time using two cationic dyes methylene blue (MB) and malachite green and one anionic dye Congo red. Since the results obtained suggest more affinity of the adsorbents for MB than other two dyes, hence the former was selected to assess the effect of variation of temperature, pH and concentration, which control the dye adsorption process. The hybrid materials exhibited high adsorption capacity both in the cumulative as well as in the reusability studies. Experimental data was subjected to different kinetic models and adsorption isotherms to understand the adsorption mechanism.

1. Introduction

Discharge of dyes from different industries causes severe damage to the living beings with hazardous health disorders including carcinogenic and mutagenic changes [1]. The dyes have complex chemical structures and are stable to light, heat and oxidation. Dyes are not easily biodegradable though their degradation with fungi has been reported [2–4]. Consequently, different physico–chemical methods like coagulation [5], ultra–filtration [6], electro–chemical [7], adsorption and photo–oxidation [8] have been extensively reported for the removal of various dyes from wastewater [9]. However, adsorption is more cost-effective and a number of low cost adsorbents for dye removal, including activated carbon [10–12], activated sludge [13–15], biowaste [16–24], and clays [25,26], have been reported in literature. Out of the reported adsorbents polymeric hybrid materials, comprising of inorganic and organic components, where the latter is a polymer, are highly promising materials as adsorbents for metal ions [27–32] and dyes [31–35]. High efficacy of the hybrid materials, than the mono or individual components used separately, results from the synergetic effect of the two components into the secondary matrix. Among these the hybrids materials synthesized from silica as one component and polymer as the other component have been reported to be efficient dye adsorbents [34,35].

In the present work, new poly(methacrylate)/silica hybrid materials were synthesized and used for the removal of methylene blue (MB), a cationic dye, from its aqueous solutions. Its removal by different adsorbents has been reported elsewhere [10,23,36–40]. There is scanty information on its removal by silica–polymer hybrid materials. The hybrid materials reported in this work are new and not reported elsewhere. The polyacrylate–based silica hybrid materials have been reported elsewhere using monomers styrene, butyl acrylate and methacrylic acid with tetraethoxysilane (TEOS) as the Si precursor [41]. However, in the present study hybrid materials were synthesized from a binary monomer system containing methacrylic acid (MAA) and methyl methacrylate

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Table 1
Composition of hybrid materials.

Hybrid	Composition
H_{MMA}	MAA (2.0 g) + MMA (2.0 g) + APTES (0.2 g) + TEOS (0.50 g) + PVA (4.0 g)
H_{HPMA}	MAA (2.0 g) + HPMA (2.0 g) + APTES (0.2 g) + TEOS (0.50 g) + PVA (4.0 g)

(MMA) or 2-hydroxypropyl methacrylate (HPMA). Synthesis was carried out by emulsifier–free emulsion polymerization using 3–aminopropyltriethoxysilane (APTES) as silane coupling agent, and TEOS and polyvinyl alcohol (PVA) as the silica component precursor and polymeric colloid stabilizer, respectively. The removal of MB from its aqueous solutions was studied as a function of time, temperature, pH and concentration. The reusability of the synthesized hybrid materials was also investigated.

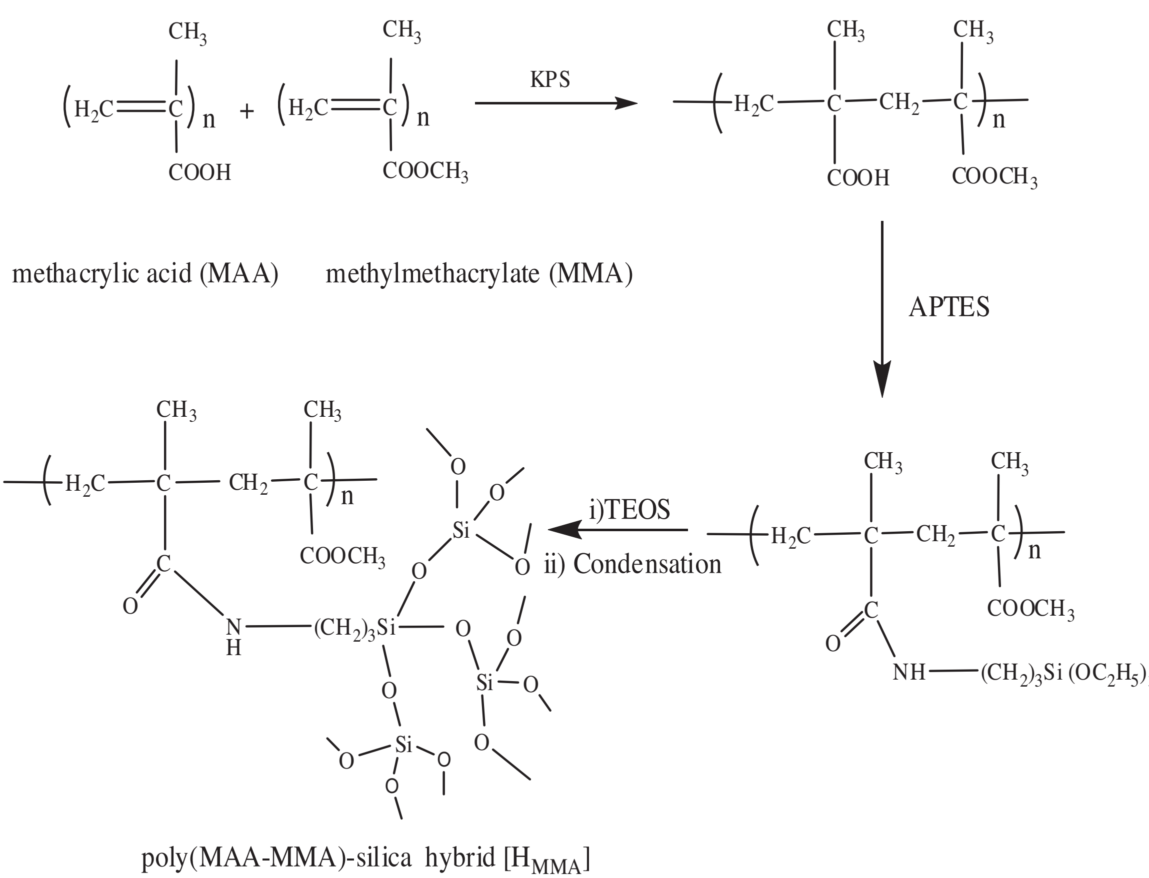
2. Materials and methods

2.1. Materials

Methacrylic acid (MAA), methylmethacrylate (MMA), 2-hydroxypropyl methacrylate (HPMA) (Merck, Schuchardt, Germany), 3-aminopropyltriethoxysilane (APTES), tetraethoxysilane (TEOS) (Himedia, Mumbai, India), polyvinyl alcohol (PVA) (CDH Lab reagents, New Delhi, India), potassium persulfate (KPS), sodium hydroxide (SD fine Chem. Ltd., India), methylene blue (MB), malachite green (MG), Congo red (CR) (Alpha Chemika, Mumbai, India), all of analytical grade, were used as received. The concentration of MB in the sorption experiments were determined with Photolab 6600 UV–vis spectrophotometer and pH values were measured with pH meter (Eutech 20).

2.2. Synthesis of hybrid polymers

Silica–based hybrid materials were synthesized via emulsifier-free emulsion polymerization method by modifying an earlier reported protocol [41]. Firstly, PVA (10% w/v in water) was taken in a reaction flask that was fitted with a reflux condenser, mechanical stirrer and a digital thermometer. After stirring at 350 rpm for 30 min, in the next step, monomers (MAA and MMA or MAA and HPMA), APTES and TEOS were added into the vessel. Solution of initiator (KPS) was prepared in water and added slowly, within 1 h, to the reaction vessel maintained at 80 °C. After the addition, the polymerization system was kept undisturbed at 85 °C for 2 h. The hybrid materials thus obtained were designated as H_{MMA} and H_{HPMA}, respectively. The details of the materials used and the proposed mechanism for the synthesis of hybrid materials are presented in Table 1 and Scheme 1, respectively.



Scheme 1. Proposed mechanism for the synthesized hybrid materials.