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Ionic liquid based periodic mesoporous organosilica: An efficient support for removal of sunset yellow from aqueous solutions under ultrasonic conditions

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ABSTRACT

The efficiency of an ionic liquid based periodic mesoporous organosilica (PMO-IL) in the removal of sunset yellow from aqueous solutions using ultrasonic assisted adsorption method was investigated. The PMO-IL was first characterized by nitrogen sorption and TEM techniques. The optimized conditions (0.013 g of adsorbent, 32 mg L^{-1} of sunset yellow at 2 min of sonication time and pH 7) were obtained by central composite design (CCD). Fitting the equilibrium data show the suitability of the Langmuir model with second-order equation to control the kinetic of the adsorption process and good reusability (5 cycles) of PMO-IL for adsorption of dye.

1. Introduction

Synthetic colorants are a very important class of food additives that are widely used in food and therefore they are given high priority by the food industry [1]. However, some of these colorants pose a potential risk to human health, especially if they are consumed in excess. Because of their high organic matter concentrations and their intense colors, the effluents discarded by the food industry are an important source of pollution for water bodies [2]. Consequently, their removal from such industrial effluents is challenging requirement to produce a safe and clean environment [3]. Sunset yellow (SY) is a pyrazolone dye used in common food products such as beverages, candies, dairy products, pharmaceuticals and bakery products (Fig. 1). The presence and content of SY must be controlled since the related industries often release large amount of these dyes into effluents [4,5]. Many technologies, including flocculation, coagulation, precipitation, biosorption, membrane filtration, electrochemical techniques and adsorption have been used for the removal of dyes from industrial effluent [6–9]. Among them, adsorption process is a general used technique due to its high efficiency, non-toxicity, easy available adsorbents, high capacity and keeping quality of water undisturbed compare to conventional waste water treatment method with potential for adsorbent regeneration [10,11].

Nowadays nanometer materials due to their special physical and chemical properties have great attention and application in different fields [12–14]. On the other hand, ordered mesoporous silica materials have been in the center attention due to their especial properties such as high thermal and mechanical stability, superior surface area, high regularity and uniformity of the mesochannels, as well as tunable their pore sizes which facilitate the diffusion of substrates inside the pores [15]. These materials can be synthesis by hydrolysis and condensation of the tetraalkoxysilane units in the presence of a surfactant template under acidic and/or basic conditions [16]. To increase the potential applications of such materials in the catalysis, adsorption, optical devices, electrochemistry, biochemistry, chromatographic separation, etc., they have been modified by several functional groups [17]. This modification accomplishes via grafting and/or sol–gel methods [18]. In grafting, the functional group chemically attaches into/onto the surface of ordered mesostructure, while sol–gel approach contains hydrolysis and co-condensation of tetraalkoxysilane with an organic functional group in the presence of surfactant template under acidic or basic conditions. However, these methods suffer from

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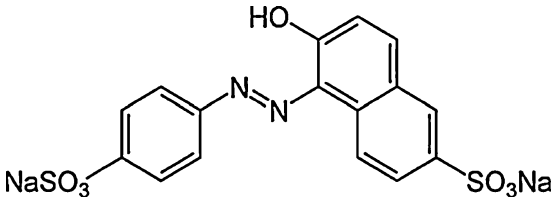

Fig. 1. Chemical structure of SY.

some problems including low loading, low stability and non-uniform distribution of functional group in the material network. To overcome aforementioned limitations, more recently a new class of organic–inorganic materials called periodic mesoporous organosilicas (PMOs) have been discovered and reported [19–21]. The especial properties of PMOs such as excellent thermal and mechanical stability, high loading of uniformly distributed organic functional groups, tunable their physical and chemical properties and their high surface area made them attractive materials for several practical applications in the different area of chemistry and material sciences [22]. Up to now several reports of PMO applications in catalysis, optical and mechanical chemistry, device chemistry, etc. have been reported by using of different organic functional groups as precursor [23]. However, according to our knowledge, there is no any report of application of these materials in the adsorption of dyes to now. Accordingly, herein we have developed for the first time, the efficiency and reusability of an ionic liquid based periodic mesoporous organosilica (PMO-IL) material in the removal of sunset yellow dye has been investigated.

Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation with formation, growth and collapse of micrometrical bubbles as useful tool in intensifying the mass transfer process and breaking the affinity between adsorbate and adsorbent [24]. Acoustic streaming induced by the sonic wave is the movement of the liquid, which can be considered to be the conversion of sound to the kinetic energy. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles [25]. These phenomena increase the rate of mass transfer near the surface. Ultrasound, and its secondary effect, cavitation (nucleation, growth and transient collapse of tiny gas bubbles) improve the mass transfer through convection pathway that is emerged from physical phenomena such as micro-streaming, micro-turbulence, acoustic (or shock) waves and microjets without significant change in equilibrium characteristics of the adsorption/desorption system [26].

Designing and optimization of experiments and evaluation of the variables influence need to apply methods to be able for simultaneous optimization while consider the interaction of variables. Statistical design of experiment can be preferred to decrease the number of experiments and considered the interaction between variables [27].

The PMO-IL was synthesized and subsequently characterized via different techniques such as TEM, BET and spectroscopic analysis. The removal of SY from wastewater was investigated via ultrasonic power as a novel, simple, sensitive and rapid/assisted adsorption method followed by UV detection. At first the influence of pH on the removal of SY was optimized, then the influence of important variables (sonication time, initial SY concentration and amount of adsorbent) were investigated and optimized by central composite design (CCD) combined with response surface methodology (RSM) using the desirability function (DF) as maximize criterion of the response. The adsorption rates were evaluated by fitting the experimental data to conventional kinetic models such as pseudo first and second-order and intraparticle diffusion models.

2. Experimental

2.1. Instruments

Liquid NMR was obtained on a DMX-250 MHz Bruker Advance (Germany) instrument using $CDCl_3$ as solvent and TMS as internal standard. The nitrogen sorption analysis was accomplished using a Belsorp-BEL, Inc. analyzer at 77 K (Japan). Prior to the measurement, the materials were degassed at 373 K for 12 h. The surface area of the PMO-IL nanomaterial was calculated by BET method and the pore size distribution was calculated from the adsorption branch of the isotherm using Barrett–Joyner–Halenda (BJH) method that is a well-known method for calculating pore size distribution of porous materials. Transmission electron microscopy (TEM) image was taken on a FEI Tecnai 12 BioTWIN microscope operated at 120 kV. The pH measurements were carried out using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss) and the dyes concentrations were determined using Jusco UV–vis spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 431 nm. An ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System, Italy) at 40 kHz of frequency and 130 W of power was used for the ultrasound-assisted adsorption procedure.

2.2. Materials and reagents

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. The following chemicals were commercially available: sodium imidazolide (90%, Fluka, USA), 3-chloropropyltrimethoxysilane (98%, Merck, Germany), tetramethoxysilane (96%, Fluka, USA) and Pluronic P123 (Fluka, USA). NaOH and HCl with the highest purity were purchased from Merck (Darmstadt, Germany). The stock solution (200 mg L^{-1}) of SY (Merck, Germany) was prepared by dissolving 20 mg of each solid dye in 100 mL double distilled water and the working concentrations daily were prepared by their suitable dilution.

2.3. General procedure for the synthesis of 1,3-bis(trimethoxysilylpropyl)imidazolium chloride (BTMSPICl)

BTMSPICl was synthesized via our previous reported procedure [28]. Typically, sodium imidazolide (20 mmol) and 3-chloropropyl-trimethoxysilane (20 mmol) were added in a flask containing absolute THF (100 mL) and stirred for 24 h at 65 °C under argon atmosphere. After cooling the reaction solution to room temperature, the solvent was removed under vacuum and the obtained mixture was transferred to a new flask containing a toluene solution of 3-chloropropyl-trimethoxysilane (20 mmol) and refluxed for 48 h. After cooling reaction solution to room temperature, the obtained mixture was first completely washed with toluene (5 × 40 mL) and then super dry CH_2Cl_2 (20 mL) was added to precipitate and remove of sodium chloride side product. The supernatant dichloromethane solution was transferred in another well-dried flask and a yellow viscous ionic liquid (BTMSPICl) was obtained after removal of the solvent and drying under reduced pressure. The spectral data for BTMSPICl is as following: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.10 (s, 1H, NCHN), 7.43 (d, 2H, J = 1.8 Hz CHCH), 4.36 (t, 4H, J = 7.2 Hz, NCH_2), 3.55 (s, 18H, 6 OCH_3), 2.03 (m, 4H, $CH_2CH_2CH_2$), 0.63 (t, 4H, J = 8.2 Hz $SiCH_2$). ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): δ = 136.1 (NCHN), 122.1 (CHCH), 51.8 (NCH_2), 50.8 (OMe), 24.1 ($CH_2CH_2CH_2$), 5.8 ($SiCH_2$).