



Simultaneous removal of benzene polycarboxylic acids from water by polypyrrole composite filled with a cellulosic agricultural waste



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ABSTRACT

The polypyrrole composite filled with a cellulosic agricultural waste (*Nut-shells of Argan*) was prepared by chemical oxidative polymerization. PPy/*Nut-shells of Argan* (PPy/NA) composite was used as an eco-friendly adsorbent for the removal of three polycarboxy-benzoic acids (hemimellitic, trimellitic, and pyromellitic acids) from single, binary, and ternary systems. The effects of parameters influencing the adsorption process including initial pH, adsorbent dose, contact time, initial concentration of polycarboxy-benzoic acids, and temperature were investigated. The kinetics studies indicated that the pseudo-second-order kinetic model well better described the adsorption kinetics for single systems. The adsorption equilibrium data from single, binary, and ternary systems were successfully described by the Langmuir isotherm model. The comparison of equilibrium adsorbed amounts in single and multi-component systems shows an antagonism effect. The obtained results indicate that the affinity of studied polycarboxy-benzoic acids on the surface of PPy/NA composite followed the order pyromellitic acid > trimellitic acid > hemimellitic acid. The thermodynamic parameters show that the nature of adsorption is spontaneous and endothermic.

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1. Introduction

The aquatic humic substances derived from the biodegradation of natural organic matter (plant and animal residues) constitute almost half of the dissolved organic carbon in freshwater. The carboxylic and phenolic functional groups are most abundant in dissolved humic substances (humic and fulvic acids) [1]. The physicochemical and biological transformations of humic substances generally produce the carboxylic acids of low molecular weight such as polycarboxy-benzoic acids (BPCAs) [2–4]. The removal of these compounds from natural waters in drinking water treatment plants is a major challenge because they are pollutant models for biodegradation of natural organic matter. Also, BPCAs present in industrial effluents of various manufacture fields such as resins, plasticizers, dyes, printing inks, and polymers [5]. It should be recalled that the BPCAs can cause severe damage to the pulmonary tract, skin, eyes, mucous membranes, etc [6]. However,

the water containing these compounds may seriously disrupt aquatic ecosystems and drinking water quality.

Several wastewater treatment technologies have been used for the removal of organic pollutants in aqueous solutions. The widely used treatment methods are: chemical precipitation, coagulation, membrane filtration, photocatalytic degradation, and adsorption [7–10]. Among these techniques, adsorption presents the easiest method to implement, allows producing treated water with high quality, and low cost. The most commonly used adsorbent for the removal of organic and inorganic pollutants in aqueous solution is activated carbon, but the high cost of carbon activation and regeneration after adsorption limits its more use [11–13].

Recently, the polymer composites reinforced with natural fillers have attracted considerable attention for multifunctional applications, because of their various advantages such as low cost, natural abundance, good physicochemical properties, renewability, biodegradability, recyclability, and environment friendliness [14,15]. Conducting polymers are widely used in various research fields such as: protection of metal surfaces against corrosion, gas sensors, catalysts and adsorbents, etc [16–20], because of their relatively high electrical conductivity, good stability in the environment, and ease of synthesis. Polypyrrole (PPy) is one of the most stable conductive polymers in air and water [21,22]. According to literature, a variety of organic and inorganic materials

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including sawdust [23], rice husk [24], Sorghum vulgare [25], chitosan [26], α -cellulose [27], porous carbon [28], Fe_3O_4 [29], Al_2O_3 [30], TiO_2 [31] and montmorillonite clay [32] were coated with PPy and are used as effective adsorbents for wastewater treatment. However, various hazardous pollutants such as methylene blue [33], carmoisine [34], phosphate [35], nitrate [36], Cr (VI) [23] and Zn (II) [37] were successfully removed from aqueous solutions by PPy/sawdust composites.

The objective of this work was to evaluate the efficiency of removing hemimellitic (benzene-1,2,3-tricarboxylic acid), trimellitic (benzene-1,2,4-tricarboxylic acid), and pyromellitic (benzene-1,2,4,5-tetracarboxylic acid) acids in aqueous solutions by adsorption their on the PPy coated *Nut-shells of Argan* (PPy/NA) synthesized by chemical oxidative polymerization. The effects of pH, contact time, initial concentration of polycarboxy-benzoic acids, adsorbent dose, temperature, and carboxylic functional groups (the position and number) of the adsorbate molecules on the adsorption efficiency, were studied in detail. The adsorption isotherms, kinetic models and thermodynamic parameters were used to describe the mechanism involved in the adsorption process. Moreover, the wastewaters commonly contain a mixture of several pollutants. For this reason, the adsorption ability of PPy/NA composite for removing simultaneously several adsorbates has been investigated in single, binary and ternary systems.

2. Materials and methods

2.1. Chemicals

Pyrrole monomer was purchased from Sigma-Aldrich and was distilled prior to use. Anhydrous iron chloride (FeCl_3), hemimellitic acid, trimellitic acid, pyromellitic acid, hydrochloric acid (HCl), sodium hydroxide (NaOH), acetone and methanol were all of analytical grade and used as received (Sigma-Aldrich). The *Nut-shells of Argan* (NA) were naturally collected from a rural region of southwestern Morocco (Tiznit – Souss Massa).

2.2. Synthesis of PPy/NA composite

The NA particles were mashed in an electric grinder (SM 100 Retsch Germany). Sieving of NA was made with a vibrating screen (Fritsch, Germany); particle sizes less than $125\ \mu\text{m}$ were recovered for the next step. Extraction of the soluble organic matter of crushed NA is a significant step to ensure the better deposition of PPy on the NA. For this, an amount (10 g) of NA particles was extracted twice with water (75 mL) then stirred for 24 h at room temperature. Then the matrix was placed in 25 mL of methanol in an ultrasonic bath (45 kHz) for 45 min with progressive variation in the temperature from 20 to 50°C . In addition, a washing of NA with acetone (200 mL) was carried out under the same conditions of extraction of methanol [38,39]. The matrix of NA was dried at 60°C for 4 h.

The PPy/NA composite was prepared by in situ chemical polymerization of pyrrole monomer on the NA surface as follows: 2 g of NA particles were suspended in 50 mL of 0.1 M pyrrole monomer solution under magnetic stirring for 3 h. Then, the mixture was stirred with ultrasonic vibration for 30 min to ensure good deposition of pyrrole monomer on the surface NA particles. After that, 50 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution with monomer/oxidant molar ratio = 1/2 was slowly added into the pyrrole solution containing the NA particles to start the polymerization of pyrrole monomer. The polymerization reaction was carried out at room temperature for 4 h. At last, the resulting composite was collected by filtration, then washed several times with distilled water and ethanol to remove impurities (traces of monomer and oxidant), and finally

dried at 60°C for 12 h [23,40]. The PPy/NA composite was milled before use; the particle size is less than $200\ \mu\text{m}$.

2.3. Adsorption tests

The study of the adsorption of trimellitic, hemimellitic, and pyromellitic acids on the PPy/NA was performed at different conditions such as solution pH (2–12), contact time (5–120 min), adsorbent dose (0.1 – $2\ \text{g L}^{-1}$), temperature (20 – 50°C), initial concentration (20 – $200\ \text{mg L}^{-1}$), and adsorption in binary and ternary systems. The pH of solution was adjusted by addition of HCl (1 M) or NaOH (1 M). Concentrations before and after adsorption tests were determined by UV–vis spectrophotometry (UV 2300 spectrophotometer). The maximum absorption wavelengths of trimellitic, hemimellitic, and pyromellitic acids are 210, 205, and 215 nm, respectively. The adsorbed amount and the adsorption efficiency were calculated using the following equations:

$$Q = \frac{(C_0 - C)}{R} \quad (1)$$

$$\% \text{ Efficiency} = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

where Q (mg g^{-1}) is the adsorbed quantity of adsorbate per unit mass of adsorbent, C_0 (mg L^{-1}) is the initial concentration, C (mg L^{-1}) is the concentration after adsorption, and R (g L^{-1}) is the weight of adsorbent per liter of aqueous solution.

The concentration ratios of trimellitic, hemimellitic, and pyromellitic acids were prefixed at 1:1 and 1:1:1 in adsorption experiments for binary and ternary mixtures, respectively. The sum of the initial concentrations of components in multi-component systems was varied in the range of 20 – $200\ \text{mg L}^{-1}$. The equilibrium concentration of each component in binary and ternary systems was determined by the method of Al-Duri et al. [41]. For this, the calibration constants (in single systems) and the optical densities (multi-solute systems) at maximum absorption wavelength of each adsorbate were determined. These constants were employed to estimate the concentration of individual component after adsorption in binary and ternary mixtures for trimellitic, hemimellitic, and pyromellitic acids.

2.4. Data evaluation

2.4.1. Kinetic modeling

In order to investigate the adsorption kinetics of the trimellitic, hemimellitic, and pyromellitic acids on the PPy/NA in aqueous solution (single system), we applied three kinetic models widely used to describe the adsorption process, pseudo-first-order model [42], pseudo-second-order model [43], and intraparticle diffusion [44]. The linear form expressions of the pseudo-first-order and pseudo-second-order, and intraparticle diffusion models are represented by Eqs. (3), (4), and (5), respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

$$Q_t = k_{\text{int}} t^{1/2} \quad (5)$$

where Q_t and Q_e are, respectively, the adsorbed quantities (mg g^{-1}) at any contact time t (min) and at equilibrium. k_1 (min^{-1}),

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