Materials Chemistry and Physics 202 (2017) 340–351

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Mechanism of Congo red adsorption on new sol-gel-derived hydroxyapatite nano-particle

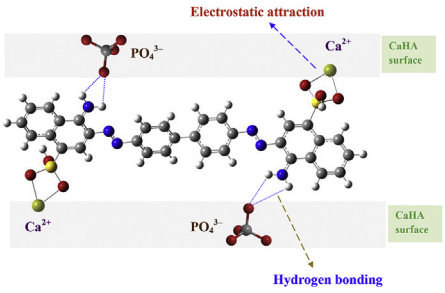
Mohammad Chahkandi

Department of Chemistry, Hakim Sabzevari University, Sabzevar 96179-76487, Iran

HIGHLIGHTS

- Synthesis the new sol–gel derived compound of nano–particles Hydroxyapatite (CaHA).
- CaHA shows high q_m of Congo red adsorption as 487.80 mg g^{-1} in comparision with others.
- Fitting well the adsorption isotherms data with the Langmuir model.
- Kinetic data well fitted with the pseudo–second order equation.
- Exothermic and spontaneous adsorption process as $\Delta G^\circ < 0$ and $\Delta H^\circ < 0$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form
8 July 2017
Accepted 19 September 2017
Available online 21 September 2017

Keywords:
Nano–HydroxyApatite
Congo red
Sol–gel
Kinetics
Adsorption isotherms

ABSTRACT

In this study, an effective adsorbent calcium hydroxyapatite (**CaHA**) having high adsorption capacity about aqueous solution of Congo red dye in ambient temperature is presented. Nano particles of **CaHA** were prepared through a new easy alkoxide–based sol–gel technique. The structural characterization of synthesized **CaHA** were performed by X–ray diffraction (XRD), Fourier transform infrared (FTIR) analysis, thermal behavior (DTA), morphology and elemental analysis *via* scanning electron microscopy (SEM). The nano particle size and micro–strain of **CaHA** were measured using modified Shcerrer equation as Williamson–Hall method and transmission electron microscopy (TEM). XRD pattern shows hexagonal structure of the nano–particle **CaHA** with $P6_3/m$ space group that the size measured through XRD and TEM methods are in good agreement as 25 nm. The equilibrium adsorption capacity (q_m) for 100 ppm CR was measured to be 487.80 mg g^{-1} under optimal conditions. The adsorption isotherms and kinetic data well fitted with the Langmuir model and the pseudo–second order equation with correlation coefficients of 0.9979 and 0.9902, respectively. The calculated structures of CR and its complex including Ca^{2+} and PO_4^{3-} ions show the electrostatic interactions of anionic CR dye and Ca^{2+} site and hydrogen bonding of amine group and phosphate of **CaHA** surface. Thermodynamic parameters ($\Delta G^\circ < 0$ and $\Delta H^\circ < 0$) imply the exothermic and spontaneous adsorption process. Finally, the experimental results suggest that this new synthesized **CaHA** can be good candidate for application in the management of environmental.

E-mail addresses: m.chahkandi@hsu.ac.ir, chahkandimohammad@gmail.com.

https://doi.org/10.1016/j.matchemphys.2017.09.047
0254-0584/

1. Introduction

The dye and organic content of wastewaters discharged industrial are generally high result in severe problems such as delaying the growth of micro–organisms, increasing the chemical oxygen demand (COD), reducing light penetration, and visibility [1–3]. Synthetic dyes having stability, carcinogenic, and toxic properties such as health and visibility problems that cause not completely removed from wastewater as a worldwide major environmental problem [4]. Moreover, their metabolic processes in animals and plants make hazardous aromatic amines that cause problems of environmental pollution. Therefore, many removing techniques including chemical oxidation, adsorption, photo degradation, biodegradation, and electrochemical process are used [5–9]. However, for this purpose the conventional biological treatment processes are not so successful [10].

Congo red (sodium salt of benzidinediazo bis–1–naphthylamine–4–sulfonic acid) (CR) as a most used color in the textile industries, because of its aromatic structure shows high physicochemical, thermal and, optical stability against photo or biodegradation [11]. The good water solubility of CR makes difficult it's discoloring in wastewater and aquatic environment. Among different using methods, adsorption by organic or inorganic adsorbents has been introduced as a most simple, high efficiency, and reusability methods with ease decolorization of textile wastewaters [12]. In recent years, absorbing of different azo dyes including CR using compounds such as the, bentonite, hematite, γ-Fe2O3/SiO2, CuFe2O3, nanoporous silica, mesoporous TiO2, red mud, fly ash, kaolin, leaf powder, marble powder, and activated carbon have been studied [13–17]. The problem is that most of the applied compounds have not sufficient adsorption capacities (less than 100 mg/g) towards CR molecules, therefore in recent years several novel alternative adsorbents such as calcium hydroxyapatite (**CaHA**) bioceramic attract growing interest because of the low–cost, non–toxicity, non–immunogenicity, and high adsorptive capabilities to pollutants [18–25]. **CaHA** shows high stability in physiological conditions [26,27] that makes it a good biomaterials employing in tissue engineering [26].

CaHA possessing two different ionic C and P binding sites on the crystal surface, respectively, rich in calcium ions with positive charge and rich in phosphate ions with negative charge, respectively [28–30]. Therefore, CR as an anionic dye should be adsorbed on C sites through electrostatic interactions. The unsaturated nanoparticles of **CaHA** can bind with other atoms resulted in remarkable adsorption ability. Therefore it has been identified as a good absorbent for many compounds and pollutants like anionic and cationic proteins, heavy metals, phenol, and azo dyes [31–34]. Also, these biomaterials widely used through chromatography to separate different proteins and nucleic acid fragments [35]. There are several works on dyes adsorption of **CaHA** like disperse blue SBL [36], reactive yellow 4 [37], direct yellow 27 [38], and reactive blue 204 and methylen blue (MB) [39], although there are no report, about the adsorption of CR onto sol–gel–derived nanoparticles of HAp. Herein, for the first time the new synthesized sol–gel–derived **CaHA** introduced as an effective adsorbent of CR.

In this work, sol–gel method because of homogeneity of product, capability to make nanoparticles, bioactivity, and low crystallinity of prepared materials with high absorption surface area chose to synthesize nanoparticles of **CaHA**. In followings, the synthesized nanoparticles used for removing CR in water. Finally, the sample characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and particle size estimated by XRD and Transmission electron microscopy (TEM). It should be noted that the experimental results of absorption of CR will be discussed in details about kinetics, equilibrium adsorption isotherms, and thermodynamic parameters.

2. Materials and methods

2.1. HA sol-gel synthesis & physical measurement

Firstly as the novel part of the applied method, triethyl phosphate ($(C_2H_5O)_3PO$, TEP, Fluka) was hydrolyzed for 24 h at R.T. along with the vigorous stirring. In following, an aqueous solution of 3 M $Ca(NO_3)_2{\cdot}4H_2O$ (Merck) was added to 4 M hydrolyzed TEP (Ca/P = 1.67) slowly at a rate of 6 mL/min. Then the respect sol solution was vigorously mixed for 60 min at 80 °C. Finally, a clear solution was obtained that aged at room temperature for 24 h. The progress of sol–gel process was gradually followed with recording the pH values of the aging sol. Next, the aged sol was dried at 150 °C until a white dried gel was obtained. The uncalcined gel structure was analyzed using differential thermal analysis (DTA, Netzsch, Germany) and IR spectroscopy (Buck 500, KBr) in the range of 500–4000 cm^{-1}. The dried gel was ground into fine powder then was heat treated at low calcination temperature 300 °C for 1 h at a constant heat rate of 2 °C/min. Phase identification of the calcined gel of **CaHA** was performed using the X–ray diffractometer (XRD, Philips, X'pert Pro, Cu Kα) at a scanning speed of 1° 2θ/min from 20 to 45°. With the aid of scanning electron microscopy (SEM, S 360, Oxford–England), the morphology of **CaHA** was recorded (Fig. 1 (a)) and its Ca/P molar ratio was measured as 1.98.

2.2. Particle size determination

Particle size and micro–strain of **CaHA** powder with the aid of Scherrer and Williamson–Hall equations [40,41] were calculated. Also, particle size distribution was determined by TEM observations. TEM (Leo 912 AB–Germany) was equipped with a thermionic gun and was operated at 120 kV. TEM sample were prepared as follows: the **CaHA** powder was ultrasonically dispersed for 2 h in absolute ethanol and afterward deposited on a carbonated copper grid.

2.3. Adsorption equilibrium and kinetics measurements

All of the adsorption solutions in the experiment were prepared by dissolving Congo red (CR) (Merck) into ultrapure water. Each experiment was done using the fresh dilutions. In order to study the mechanism of adsorption of CR and determine the optimum adsorption conditions, certain concentrations of **CaHA** samples were treated in 200 mL Erlenmeyer flask containing 100 mL of CR and shaken at 300 rpm on a specified temperature. The effect of dosage was examined in the range of 0.02–0.5 mg (natural pH, contact time for 140 min, temperature at 298 K). The effect of contact time was studied in the time range of 0–140 min (dosage of 60 mg for CR, natural pH, temperature at 298 K). The effect of pH was investigated in the range of 3–10. The initial concentrations of CR rang of 20–150 mg L^{-1} applied to draw of adsorption equilibrium isotherms. CR adsorbed concentrations were determined using a UV–Vis spectrophotometer (UNICO 2800) at its $\lambda_{max} = 485$ nm.

Equilibrium absorbance capacity (q_e (mg/g)) and adsorbed amount of CR per unit mass of the adsorbent at time t were determined using the following equations:

$$q_e = (C_0 - C_e)V / m \quad (1)$$

$$q_t = (C_0 - C_t)V / m \quad (2)$$