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Synthesis of mesoporous triple-metal nanosorbent from layered double hydroxide as an efficient new sorbent for removal of dye from water and wastewater

Miloš Kostić[a,*], Miljana Radović[a], Nena Velinov[a], Slobodan Najdanović[a], Danijela Bojić[a], Andrew Hurt[b], Aleksandar Bojić[a]

[a] Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, 18 000 Niš, Serbia
[b] Faculty of Engineering and Science, University of Greenwich, Chatham Maritime, Kent ME4 4TB, UK

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ABSTRACT

In this study, co-precipitation synthesis of the mesoporous triple-metal nanosorbent from Fe, Cu, Ni layered double hydroxide (FeCuNi-LDH), on the basis of the data obtained from the TG analysis was carried out. The FTIR spectroscopy and XRD results confirm the formation of CuO, NiO and Fe_2O_3 nanoparticles, while the EDX analysis does not show significant variations on the surface in elemental composition. BET analysis shows that FeCuNi-280 (FeCuNi-LDH calcinated at 280 °C) with mesoporous structure, has larger surface area compared to FeCuNi-LDH and FeCuNi-550 (FeCuNi-LDH calcinated at 550 °C). The value of pH_{PZC} of FeCuNi-280 is found to be 8.66. Obtained FeCuNi-280 material showed the ability for efficient removal of dye Reactive Blue 19 (RB19) from water, with a very high sorption capacity of 480.79 mg/g at optimal conditions: the sorbent dose of 0.6 g/dm^3, stirring speed of 280 rpm and pH 2. The kinetics results of the sorption process were well fitted by pseudo-second order and Chrastil model, and the sorption isotherm was well described by Sips, Langmuir and Brouers–Sotolongo model. FeCuNi-280 was easily regenerated with aqueous solution of NaOH, and reutilization was successfully done in five sorption cycles. The present study show that easy-to-prepare, relatively inexpensive nanosorbent FeCuNi-280 is among the best sorbents for the removal of RB19 dye from water solution and wastewater from textile industry in wide range of pH.

1. Introduction

Environmental contamination by organic pollutants, as reactive textile dyes, has severe and chronic effects on living organisms, and it is one of a major problems that society faces today (Salleh et al., 2011). About 10,000 different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. Some 10–20% of these dyes are discharged into the wastewater stream after use in dyeing and finishing (Zubieta et al., 2008). Dyes are chemically and photolytically stable and originally produced to be resistant to the weather, light, water, and detergents. Reactive dyes are highly soluble in water. As effluents they contain environmentally problematic compounds and influence reduced water transparency and sunlight penetration, thereby altering photosynthetic activity and gas solubility (Bergamini et al., 2009). Reactive Blue 19 (RB19) or disodium salt of 1-amino-2-sulfo-4-(3-sulfoxy-ethyl-sulfophenyl-1-ylamino)-5,10-anthraquinone is one of the very stable and resistant anionic dye: it may be mutagenic and toxic because of the presence of electrophilic vinyl sulfone groups (Moghaddam et al., 2010).

Numerous techniques such as biological treatments, membrane filtration, electrochemical technology, advance oxidation processes and sorption process are used for the removal of dyes from water. Among them, sorption has been frequently used because of its high efficiency, economic feasibility, and operational simplicity (Xiao et al., 2016; Saeed et al., 2005). Many sorbents have been tested in attempts to reduce dye concentrations from aqueous solutions, such as carbon nanotubes (Karimifard and Moghaddam, 2016), paper sludge activated with potassium fluoride (Auta and Hameed, 2014), modified bentonite (Özcan et al., 2007; Gök et al., 2010), hydrolytic and aerobic microorganisms (Wang et al., 2009), g-MnO_2/MWCNT nanocomposite (Fathy et al., 2013), magnetic Fe_3O_4 nanoparticles modified by pyrrole (Shanehsaz et al., 2015), silica (Banaei et al., 2017a, 2017b), chitosan (Nga et al., 2016), MgO nanoparticles (Moussavi and Mahmoudi, 2009; Nga et al., 2013) and biosorbents (Çiçek et al., 2007; Shirzad-Siboni et al., 2014; Zhang et al., 2003).

Layered double hydroxides (LDH), known as anionic clays or hydrotalcite clays, have been investigated because of their tunable charge

* Corresponding author.
E-mail addresses: milos.kostic@pmf.edu.rs, mk484475@gmail.com (M. Kostić).

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density and wide application prospects. LDH have been widely used as catalysts, drug delivery materials, sorption and flame retardants. LDH provide the possibility of a high sorption capacity because of the large surface area, easy manipulation of sorption sites, morphology/pore structure and interlayer ion exchange (Cai et al., 2018). LDH as sorbents are characterized by high sorption capacity, low cost and non-toxicity. After calcination, LDH may be converted into mixed metal oxides. Likewise, the calcined product can be reconstructed into original layered structure in the aquatic environment (Lei et al., 2017; Lv et al., 2006). LDH materials can be represented by the general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+} \times [A^{n-}_{x/n} \times mH_2O]$.

In this study, a novel process of synthesis of a mesoporous triple-metal nanosorbent, has been developed. The structural characterizations of LDH (FeCuNi-LDH) and the nano-triple-metal nanosorbents have been performed through different techniques such as: Brunauer-Emmett-Teller (BET) method, x-rays diffraction (XRD), thermogravimetric analysis (TGA) for the thermal analysis, Fourier transform infrared spectroscopy (FTIR) to confirm the formation of nanosorbents, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) to explore the surface morphology, size of the particles and elemental composition. The effect of different variables, including pH, temperature, sorbent dose, contact time and initial dye concentration was evaluated. The experimental results of RB19 sorption on nanosorbent FeCuNi-280 were analyzed using pseudo-first, pseudo-second-order, intra-particle diffusion and Chrastil's kinetic models and Langmuir, Freundlich, Sips and Brouers–Sotolongo isotherm models. The thermodynamics of the sorption was also evaluated. Regeneration and reusability of sorbent was studied. In order to confirm the efficiency of triple-metal nanosorbent FeCuNi-280 in real conditions, removal of RB19 from wastewater was carried out.

2. Materials and methods

2.1. Reagents

All chemicals were of reagent grade and used without further refinement. HNO_3, NaOH, NaCl, Na_2CO_3, $FeCl_3{\cdot}H_2O$, $FeCl_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, RB19, acetic acid and sodium salt of dodecylbenzene sulfonic acid were purchased from Merck (Darmstadt, Germany). Gleiton P was purchased from Polycoating GmbH (Brühl, Germany). All solutions were prepared with deionized water (18 MΩ).

2.2. Preparation of the nanosorbent

Nanosorbent was prepared by the novel hydrothermal process, using 6.76 g $FeCl_3{\cdot}6H_2O$, 4.97 g $FeCl_2{\cdot}4H_2O$, 4.26 g $CuCl_2{\cdot}2H_2O$ and 5.92 g $NiCl_2{\cdot}4H_2O$, dissolved in 50 ml of 0.1 M HCl solution, respectively. The solution was heated to 80 °C with a reflux condenser and mixed by agitating and ultrasonication (the power of ultrasound was 100 W/dm^3 and agitation speed 400 rpm), in period of 1 h. Then, 2 M NaOH solution was added dropwise, with the monitoring of the pH. The co-precipitation reaction was carried out at 80 °C with vigorous stirring and agitating with ultrasonication with refluxing. A brown colored precipitate was obtained at pH of about 10. After that, the suspension was continuously stirred and agitated with ultrasonication for 1 h. Following this, the mixture was allowed to settle for 2 h without stirring, ultrasonication and heating. The precipitate was washed several times with hot deionized water over a Büchner funnel. Finally, the prepared precipitate was dried at 90 °C for 24 h and abbreviated as FeCuNi-LDH. In the second step, the obtained FeCuNi-LDH was calcined in a furnace by being heated from room temperature to 280 °C and 550 °C with the gradient of 7 °C/min for 1 h. After calcination, the layered hydroxide structure was destroyed and changed into the triple-metal nanosorbent. Finally, the obtained solid aggregates of the triple-metal nanosorbent were crushed into powder and stored in an airtight plastic container for further use. The prepared triple-metal nanosorbents were abbreviated as FeCuNi-280 (calcinated at 280 °C) and FeCuNi-550 (calcinated at 550 °C).

2.3. Analysis and characterizations

RB19 concentration in the samples was determined using the UV–vis technique by the spectrophotometer Shimadzu UV–vis 1650 PC (Shimadzu, Japan), after filtration through a 0.45 μm membrane filter (Agilent Technologies, Germany). The infrared spectrum of nanosorbent FeCuNi was obtained by using a Fourier transform infrared spectrometer (Bomem Hartmann & Braun MB-100 spectrometer). The morphology of the nanosorbent surface was analyzed by SEM (Hitachi SU8030). EDS analysis (Thermo Scientific NORAN System 7, USA) provides elemental information via the analysis of X-ray emissions from the sorbent surface. Elemental composition was analyzed by the Perkin Elmer series II CHNS/O System Analyzer 2400. The specific surface area was measured by a nitrogen adsorption using the Micromeritics Gemini 5 Surface Area Analyzer, USA. Data were collected with a Bruker D8 Advance X-ray Diffractometer (Bruker, Germany) in theta-theta geometry in reflection mode with Cu Kα. TG analysis was performed using TGA Q5000 (TA Instruments, USA).

2.4. Batch sorption experiments

A stock solution of RB19 was prepared by dissolving an accurate quantity of dye in deionized water. The working standard solutions were prepared just before use by the appropriate dilution of the stock solutions. The sorption study was carried out using various RB19 concentration (20–700 mg/dm^3) at pH 2 and the temperature of 20 °C. The effect of pH on the RB19 sorption was studied in the pH range of 2.0–10.0. The pH of each solution was adjusted to the required value with 0.1/0.01 mol/dm^3 $NaOH/HNO_3$ solutions using a pH-meter (H260G, HACH, USA). The effects of FeCuNi-280 concentration on the removal of RB19 were studied by varying the dose of FeCuNi-280 from 0.125 to 1.0 g/dm^3 at 200 mg/dm^3 of the RB19 concentration, at pH 2 and the temperature of 20 °C. The temperature was held at 20.0 °C (± 0.2 °C) by thermostated bath Julabo F12-ED (Refrigerated/Heating Circulator, Germany). All experiments were conducted in triplicate.

The sorption capacity q_t (mg/g) and the removal efficiency (*RE* %) was determined by using the Eqs. 1 and 2:

$$q_t = \frac{(c_0 - c_t) \times V}{m} \quad (1)$$

$$RE\ \% = \frac{c_0 - c_t}{c_0} \times 100 \quad (2)$$

where c_0 and c_t are the initial and final concentrations of the dye in solution (mg/dm^3), V is the solution volume (dm^3) and m is the mass of the sorbent (g).

2.5. Desorption of RB19 and reused of triple-metal nanosorbent

In order to investigate the reusability performance of the triple-metal nanosorbent, five successive sorption–desorption (regeneration) cycles were performed. In adsorption test, 0.15 g of FeCuNi-280 was loaded with 250 cm^3 of RB19 solution with concentration of 200 mg/dm^3 and stirred for 180 min. After that, FeCuNi-280 was separated by centrifugation at 4000 rpm for 5 min and concentration of RB19 was determined in filtrate. To regenerate the adsorbent, the used FeCuNi-280 was contacted with 250 cm^3 of desorption solutions (0.1 M NaOH and 1 M NaCl), with stirring for 1 h. The sorption–desorption process was repeated for five times. The desorption efficiency (*DE* %) was calculated as follows:

$$DE\ \% = \frac{m_{\text{desorbed RB19}}\ [\text{mg}]}{m_{\text{previously sorbed RB19}}\ [\text{mg}]} \times 100 \quad (3)$$