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Green synthesis and optimization of nano-magnetite using *Persicaria bistorta* root extract and its application for rosewater distillation wastewater treatment

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ABSTRACT

The aim of this research is to synthesize magnetite nanoparticles, using *Persicaria bistorta* root extract as the reducing agent, and to test its adsorption properties in the treatment of rosewater distillation wastewater. Taking advantage of Taguchi method, effect of synthesis parameters, including molar concentration of $FeCl_2$, concentration of plant extract, temperature, and pH on crystallite size and magnetization strength is studied. Based on the successful synthesis of magnetite nanoparticles and characterization experiments, *Persicaria bistorta* root extract can be considered as a proper alternative as the reducing agent. Data analysis shows that crystallite size and magnetization are positively correlated with concentration of $FeCl_2$ and pH, while inversely related to temperature and independent of plant extract concentration. The optimum values achieved for concentration of $FeCl_2$, temperature, and pH are 0.15 M, 70 °C, and 11, respectively, with the production of nanoparticles with magnetite size of 45.5 nm and magnetization value of 62.5 emu/g. In addition, the application of as-synthesized magnetite nanoparticles as an adsorbent for treatment of rosewater distillation wastewater proved its high adsorption capacity for chemical oxygen demand (COD) up to 149 mg/g. Adsorption data also shows a good fitness with Langmuir and Freundlich isotherm models.

1. Introduction

Rosewater is flavor water achieved by distillation of rose flower and is widely produced in Middle East countries like Iran and Bulgaria to be used in food, medicinal and perfume industries (Rusanov et al., 2014). About 10,000 t rosewater is annually produced in Iran which produces 4000 t of wastewater. The wastewater produced from rosewater industry contains flower debris and complex organic compounds like polyphenol materials which are nonvolatile and remain in the waste stream during distillation. Polyphenols have antimicrobial properties and are considered as bio-contaminants (Rusanov et al., 2014). As the chemical oxygen demand (COD) test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically (Tchobanoglous et al., 2014), COD of this wastewater is very high in the range of 15,000–30,000 mg/l. Most of this wastewater is commonly discharged in waste lagoons or drainage system which leads to serious environmental concerns like decreasing the amount of dissolved oxygen in receiving waters (David et al., 2015). Hence, this wastewater must be treated before being discharged into the environment.

Heretofore, different techniques are implemented for COD removal of distillery spent wash stream including anaerobic treatment (Rao, 1972; Jhung and Choi, 1995; Akunna and Clark, 2000; Pathade, 2003; Mohana et al., 2009), chemical oxidation (Mohana et al., 2009; Apollo et al., 2013; David et al., 2015), coagulation (Pandey et al., 2003; Kalyuzhnyi et al., 2005; Thakur et al., 2009; Mohana et al., 2009), membrane processes (Rai et al., 2008; Yamini and Malini, 2009; Mohana et al., 2009), and adsorption (Lalov et al., 2000; Satyawali and Balakrishnan, 2007; Mohana et al., 2009), among which, adsorption is examined as an uncomplicated and cost-effective method (Azadi et al., 2018). In adsorption, adsorbent plays a key role to increase the capability of process.

Different materials have been employed as adsorbent in COD removal including agricultural by-products (Karimi-Jashni and Saadat, 2014; Saadat et al., 2016; Azadi et al., 2018), activated carbon (Satyawali and Balakrishnan, 2007; Pan et al., 2011; Verma et al., 2014; Nayl et al., 2017), and Fe_3O_4 magnetic nanoparticles (Fe_3O_4 MNPs) (Gharloghi et al., 2016). Fe_3O_4 MNPs have drawn significant interest in

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different employments due to their biocompatibility, biodegradability, and non-toxicity (Yew et al., 2016; Hu et al., 2006). Achieving higher performance requires magnetite nanoparticles (NPs) to be spherical, with narrow size distribution and moderate size besides high crystallinity, large surface area having super-paramagnetic characteristics (for maximal protein or enzyme binding), high magnetic saturation, and good dispersion in aqueous media (Guo et al., 2009). Fe_3O_4 NPs are inseparable upon applying a magnetic field. However, below the critical size of 20 nm super-paramagnetic characteristics are prevailed becoming separable upon the application of a magnetic field (Lu et al., 2007). Therefore, the synthesis procedure for Fe_3O_4 NPs is very important requiring control over the synthesis parameters which affect the final properties (Worawong et al., 2014).

Synthesis of Fe_3O_4 MNPs has been performed using chemical approaches including co-precipitation (Laurent et al., 2008; Martínez-Mera et al., 2007), sol-gel (Laurent et al., 2008; Albornoz, and Jacobo, 2006; Worawong et al., 2014), hydrothermal (Laurent et al., 2008; Wan et al., 2005) and hydrolysis-thermolysis (Laurent et al., 2008; Kimata et al., 2003). However, application of expensive organic solvents in these procedures is very inefficient in terms of ecofriendly requirements and being highly hazardous to the environment. Therefore, it is critical to design an economical and efficient process for synthesizing Fe_3O_4 MNPs with high saturation magnetization (SM) values (Guo et al., 2009). Thus green synthesis of nanoparticles has been suggested as an alternative for chemical methods both costly efficient and environmental friendly (Venkateswarlu et al., 2013). Using plant extracts in the synthesis of nanoparticles is a green chemistry route interconnecting nanotechnology and biotechnology. In this method, plant extracts are used for the bio-reduction of metal salts to provide nanoparticles (Alghuthaymi et al., 2015).

Recently, several researchers have synthesized Fe_3O_4 MNPs via green chemistry approach. Yew et al. (2016) used seaweed as a reducing agent to synthesize Fe_3O_4 MNPs, with an average size of 14.7 nm. Venkateswarlu et al. (2013) used plantain peel extract for the green synthesis of Fe_3O_4 MNPs with sizes below 50 nm. Venkateswarlu et al. (2014) used Syzygium cumini seed extract as the reducing agent for the synthesis of Fe_3O_4 MNPs.

Persicaria bistorta belongs to the family of Polygonaceaes. As the main active ingredients in bistort are tannins ($C_{76}H_{52}O_{46}$), existing in great quantities in the rootstock (15–36%). The dehydrated rootstock in the species of extract has been generally used to prevent both internal and external bleeding (Klimczak et al., 2017). The title "tannin" is commonly applied to any large polyphenolic mixture composed of adequate hydroxyls and carboxyl functional groups. These mixtures create strong complexes with several macromolecules and play the role of the decreasing agent in the synthesis of Fe_3O_4 NPs. A successful green route for the synthesis of Fe_3O_4 MNPs using *Persicaria bistorta* root extract as the reducing agent is proposed in this study for the first time.

Parameters such as pH, initial concentration of ferric salt, temperature, and reducing agent concentration greatly affect the size and magnetization of Fe_3O_4 MNPs. Therefore, an important issue in green synthesis of Fe_3O_4 MNPs would be the optimization of parameters such that nanoparticles with the smallest size and highest magnetization are produced through the least number of experiments with minimum extra financial cost. Literature shows that, this has never been performed and its influence on the green synthesis of Fe_3O_4 MNPs should be investigated. Thus, taking advantage of Taguchi method, the synthesis of NPs with respect to parameters including the molar concentration of $FeCl_2$, plant extract concentration, synthesis temperature, and pH on particles size and magnetization is optimized. Moreover, based on the literature, no treatment method has been used for rosewater distillation wastewater, so far. Only in one case adsorption resins have been used for the recovery of polyphenols from rose oil distillation wastewater (Rusanov et al., 2014). So in this study, as-synthesized magnetite (Fe_3O_4) nanoparticles have been used as an adsorbent for adsorption process in the treatment of rosewater distillation wastewater. Besides, kinetics and isotherm of adsorption process in COD removal from rosewater distillation wastewater using magnetite nanoparticles as adsorbent have been investigated.

2. Materials and methods

2.1. Materials

Iron (II) chloride tetrahydrate ($FeCl_2$.4H2O ≥ 99%) and Sodium hydroxide (NaOH) are purchased from Merck Co. All the chemicals were used without further purification. *Persicaria bistorta* root was supplied by a local medicinal herbs shop in Shiraz city, Iran. All the aqueous solutions were prepared using deionized water. Filtration of *Persicaria bistorta* root extract was performed using Whatman filter No. 42. The pH was measured with a Metrohm 654 pH meter (Metrohm, Herisau, Switzerland). The Chemical Oxygen Demand (COD) was determined using a colorimetric method (5220D analytical method provided in the standard methods) using a UV–Visible Spectrophotometer HACH- DRB5000 (Federation of Water Environment and APHA, 2005). The wastewater used in this study was collected from a rosewater distillation factory in Kashan, Iran. The average COD of this wastewater was ~ 17,500 mg/l.

2.2. Experimental design

Taking advantage of Taguchi method, designing experiments and optimizing the synthesis of magnetite nanoparticles have been done regarding the effect of parameters including molar concentration of $FeCl_2$, concentration of plant extract, temperature, and pH on size and magnetization value (using Design Expert 7.0.0 and minitab 16 softwares). Taguchi method is a comprehensive approach based on a fractional factorial design that yields a stable response (Yang and El-Haik, 2003; Cavazzuti, 2012) using orthogonal arrays outlined to explore the entire parameter space with a small number of experiments. Taguchi method is employed based on four synthesis parameters including molar concentration of $FeCl_2$, ratio of water to plant extract (v/v), synthesis temperature (°C), and pH. The total number of experiments can be determined using (Lande and Gaidhani, 2015):

$$N_{Taguchi} = 1 + \sum_{i=1}^{NV} (L-1) \tag{1}$$

Where, $N_{Taguchi}$ and NV indicate the number of experiments to be conducted and number of variables, respectively. L is also the number of experimental levels. According to Eq. (1), nine experiments are required in this study.

The main parameters investigated in the experimental data include molar concentration of $FeCl_2$ in the set of values (0.1, 0.15. 0.2), water to plant extract ratio in (0, 0.5, 1) (v/v), synthesis temperature in (50, 60, 70) (°C), and pH in (9, 10, 11). The ranges of these parameters are selected based on the pretests and previous studies (Venkateswarlu et al., 2014, 2013; Yew et al., 2016; Alibeigi and Vaezi, 2008). All the experiments have been repeated three times and their average result is reported with an average relative error less than 5%.

2.3. Preparation of Persicaria bistorta root extract

Persicaria bistorta root was thoroughly rinsed with double distilled water to remove any impurities. Chopped *Persicaria bistorta* root was blended (5 g of the chopped root with 100 ml double distilled water) into a 250 ml round bottom flask, and refluxed for 1 h at 70 °C until the color of the solution changed from watery to light reddish brown. The resultant extract was left to cool down to room temperature and filtered.