Journal of Water Process Engineering 11 (2016) 152–161

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Surface modified spinel cobalt ferrite nanoparticles for cationic dye removal: Kinetics and thermodynamics studies

Manjot Singh, Harmanjit Singh Dosanjh, Harminder Singh *

Department of Chemistry, Lovely Professional University, Punjab-144411, India

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 5 May 2016
Accepted 10 May 2016
Available online 25 May 2016

Keywords:
Adsorption
Ferrites
Nanoparticles
Surface modification
Crystal violet

ABSTRACT

Present study is an endeavour to explore adsorption potential cobalt ferrite nanoparticles which were synthesised by combustion method and its surface modification was done by a SDS surfactant to make it suitable for the removal of cationic dye. Characterization was carried through FTIR, SEM and XRD analysis. Batch adsorption studies were carried out for removal of crystal violet cationic dye by SDS coated cobalt ferrite. Various parameters like initial concentration (50–300 mg/L), effect of contact time, adsorbent dose (0.1–0.5 gm/50 mL), and pH (2–9) were studied at constant temperature. Equilibrium time for the adsorption process was found to be 2 h. Adsorption percentage of dye increased with an increase in the adsorbent dose and amount of adsorption increased with an increase in initial dye concentration. Initial pH in the basic region exhibited better results as compared to acidic pH. Langmuir adsorption isotherm fitted better than Temkin followed by Freundlich and Dubinin-Raduskevich adsorption isotherms. Monolayer adsorption capacity was found to be 105 mg/g which is comparable to other reported adsorbents. Adsorption followed Lagergren pseudo second order kinetics model better than Lagergren pseudo first order and Elovich models. Adsorption studies conducted at different temperatures (301–313 K) indicated rise in adsorption with the increase in temperature. This implied that sorption phenomenon was endothermic in this case. Data was fitted to Van't Hoff equation to study thermodynamics. Value of ΔH° was in the range of 23–88 kJ/mol for different concentration which indicated that mechanism of adsorption was complex comprising of both physical and chemical adsorption.

1. Introduction

In special consideration to textile industries the amount of waste water produced by them is increasing proportionally with the increasing demand of textile products. Variety of chemicals which are used in textile industry produces environmental problems. Among them dyes are considered important pollutants [1]. Around 30 percent of reactive dyes are discarded into industrial outlet. Therefore removal of such effluents is a point of ecological concern. In order to achieve the aforementioned, one need to reduce the dye concentration to safer levels [2].

The chemical structure of dye molecules is designed to resist the action of light, chemical attack and further prove resistant toward action of microorganisms. Therefore efficient techniques for removal of such impurities from waste water have drawn significant interest. Among various possible methods for water treatment, adsorption method is one of the significant techniques for dye removal from industrial outlet. Adsorption has advantages over the rest of the techniques because of its simple design and low investment in terms of initial cost and land. In recent years search for low cost and high pollutant binding affinity adsorbents has intensified.

Various categories of adsorbents have been explored and reported in literature like active carbon [3], alginic acid [4], nZVI Immobilized on Cellulose [5], silica gel, activated alumina, zeolites, porous clay hetero-structured, clay minerals [6], Inorganic nanomaterials [7], Oxides of transition metals [8] etc. Moreover Nanomaterials in water treatment are also being used [9]. Several magnetic materials have been utilized for the elimination of contaminants (especially dyes) from waste water [10]. Multiwall carbon nanotube composite was used as adsorbent for the treatment of cationic dyes in coloured effluents [11]. Exclusion and reclamation of acridine orange from solution was carried out by usage of magnetic nanomaterials [12]. Magnetic nanocrystalline barium hexaferrite was used for the purpose of dye removal and arsenic removal from aqueous solvent [13]. Iron oxide doped onto carbon nanocomposite is able to adsorb congo red dye following

* Corresponding author.
E-mail addresses: harminder_env@yahoo.com, harminder.singh@lpu.co.in (H. Singh).

http://dx.doi.org/10.1016/j.jwpe.2016.05.006
2214-7144/

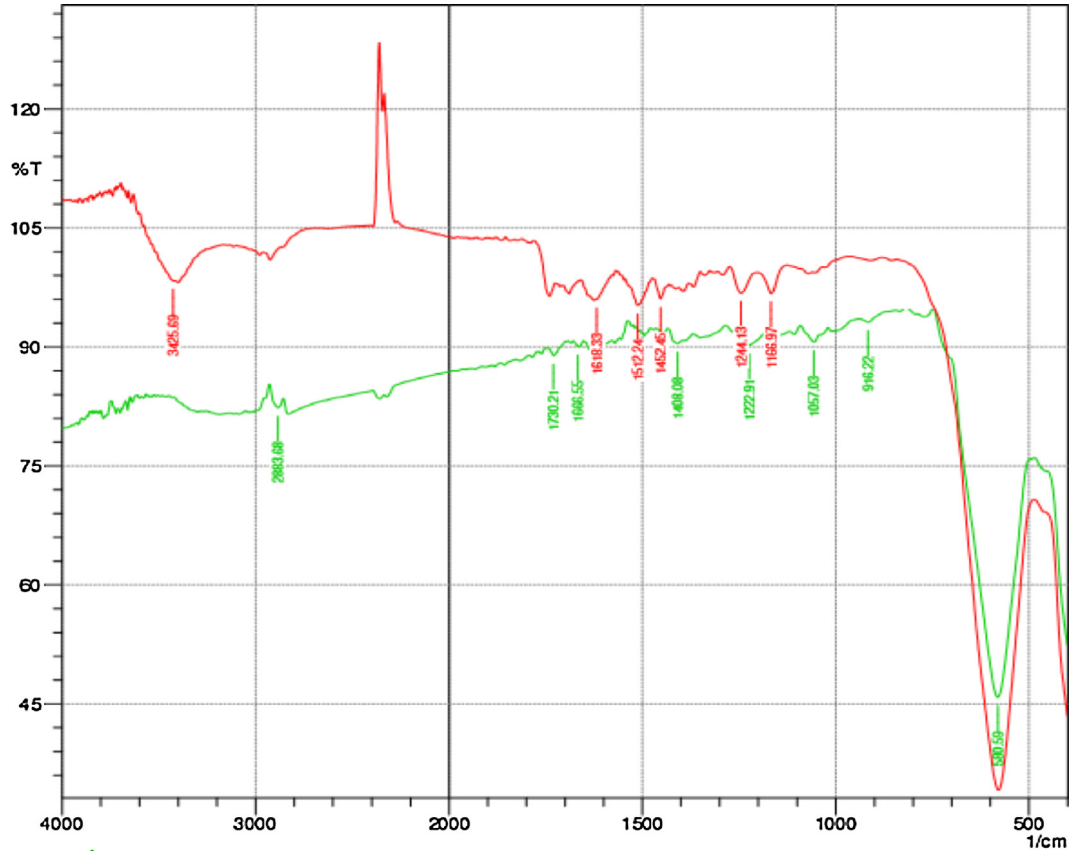

Fig. 1. FTIR image overlay of cobalt ferrite nanoparticles (in red color) and SDS modified cobalt ferrite nanoparticles (in green color).

pseudo second order kinetics [14]. Similarly nanostructured manganese is used for removal of brilliant red dye from water [15].

Though the nanoparticles have various applications in removal of pollutants from water but still there are many challenges in this regard. The main disadvantage of some magnetic nanomaterials is that their pollutant removal potential is low. Thus, they should be modified. To overcome this shortcoming, the surface of magnetic nanomaterials can be modified by the use of surfactant. Zinc ferrites were modified by coating them with Cetyl Trimethyl Ammonium Bromide (CTAB) which increases its efficiency for the removal of anionic dyes [16]. Nickel ferrite nanoparticles coated with SDS were found to adsorb basic blue, basic red and basic Green dye from water following pseudo second order kinetics [17]. Similarly Copper ferrites were modified by coating with Cetyl Trimethyl Ammonium Bromide (CTAB) which increases its dye removal capability [18].

In present study an attempt is made to prepare cobalt ferrite particles by combustion method and their surface modification through SDS surfactant. Surface modification of cobalt ferrite particle prepared by combustion method is not reported in literature. Objectives of this study includes preparation of cobalt ferrites, their surface modification, characterisation and exploring its adsorption potential.

2. Material and methods

2.1. Synthesis of $CoFe_2O_4$ nanoparticles by combustion method

In recent years, synthesis of nanoparticles of desired size and magnetic properties have been the subject of investigation by many researchers. Various methods are used for the preparation of nanoparticles like sol-gel method, precipitation method, combustion method and ceramic method. Out of these combustion method is the most promising method. Redox chemical reaction between metal salts and oxalyldihydrazide results into the formation of ferrites (AB_2O_4). In combustion method, powder obtained is pure, crystalline and of well-defined stoichiometry, size and surface area. All such properties make combustion method useful for the synthesis of nanosized particles because of cost reliability as compared to other techniques [19].

$CoFe_2O_4$ particles were prepared using combustion method. In the combustion method stoichiometric aqueous solutions of respective metal salts were mixed with oxalyl dihydrazide. The obtained mixture was concentrated on water bath and finally combusted in muffle furnace at 600 °C to get ferrite powder.

2.2. Preparation of SDS- modified $CoFe_2O_4$ nanoparticles

An aqueous SDS solution (0.07 M) was added to a 12% aqueous suspension of cobalt ferrite nanoparticles. The mixture was stirred using mechanical stirrer for approximately 3 h at 200 rpm. The surfactant modified cobalt ferrite nanoparticles were separated from the suspension by filtration.

Characterization of $CoFe_2O_4$ particles and surface modified $CoFe_2O_4$ particles was carried out by using FTIR, XRD and SEM techniques.

2.3. Batch adsorption studies

For batch adsorption study aqueous solution of known concentration (50–300 mg/L) of crystal violet (CV) and known mass of adsorbent (0.1 g) were kept in 250 mL conical flasks. Then these flasks were placed in the thermostatic shaker at 125 rpm and at 301 K temperature. The effect of various parameters like contact time, effect of adsorbent dosage, effect of pH and effect of concen-