

Synthesis of copper coordinated dithiooxamide metal organic framework and its performance assessment in the adsorptive removal of tartrazine from water



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ARTICLE INFO

Article history:

Received 23 September 2016

Received in revised form 5 December 2016

Accepted 8 December 2016

Available online 8 December 2016

Keywords:

Adsorption

Dithiooxamide

Metal organic frameworks

Tartrazine

Kinetics

Regeneration

ABSTRACT

Copper coordinated dithiooxamide metal-organic framework (Cu-DTO MOF) was synthesized and applied for the removal of tartrazine from aqueous solutions. The properties of Cu-DTO MOF were extensively examined through different instrumentation techniques including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), energy dispersive X-ray analysis (EDX), atomic force microscopy (AFM), N₂ adsorption-desorption for surface area analysis, thermo-gravimetric analysis (DTA/TGA/DTG) and zeta potential analysis (pH_{ZPC}). The effects of various process parameters such as pH, temperature, ionic strength, contact time and initial dye concentration were systematically studied. The interpretation of sorption kinetic data suggest that pseudo-second order model represents data more appropriately. Moreover, consideration of intraparticle diffusion model suggested that both film diffusion and pore diffusion phenomenon dictate the adsorption process. The equilibrium isotherm data agrees well with Freundlich model and the highest adsorption capacity of the synthesized MOF for removal of tartrazine was found to be 309.2 mg/g at 323 K. Thermodynamic parameters like change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated and it was observed that the sorption process was spontaneous and endothermic in nature. Desorption study recommended that the regenerated adsorbent can be effectively used without significant loss in adsorption capacity upto five cycles.

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1. Introduction

Metal organic frameworks (MOFs) materials have found great applications in energy storage, heterogeneous catalysis, sensing, and environmental science and technology [1–4] due to their exceptional properties such as high surface area to volume ratio, enhanced physicochemical stability, increased functionality, biocompatibility, and highly tailorable microporous properties [5,6]. During the last 5 years, due to their excellent properties, the MOFs have been successfully applied in the pollutants separation and remediation from both gaseous and liquid phases [7–11].

Continuous discharge of dye bearing industrial effluents from textile industries, pulp and paper factories, wool dyeing, paint and varnish manufacturing, and medicinal products into the near water bodies have become a global concern because of potential health hazards associated with the toxicity and their byproducts into the food chains of humans and aquatic animals [12]. The synthetic aromatic dyes into the aquatic ecosystem alters the aqueous chemistry by changing the solution pH, color, chemical oxygen demand and causes hindrance in the growth of aquatic organisms [13]. Synthetic dye also impedes the penetration of solar-light, thus changes the photosynthetic activity in phytoplanktons. Therefore, there is an urgent need to remove dyes before effluent is discharged into the receiving water bodies. For a couple of decades certain distinctive treatment techniques such as chemical coagulation, photocatalytic degradation, electrochemical degradation, photo-Fenton processes, and adsorption [14–21] have been employed for the treatment of contaminated water. However,

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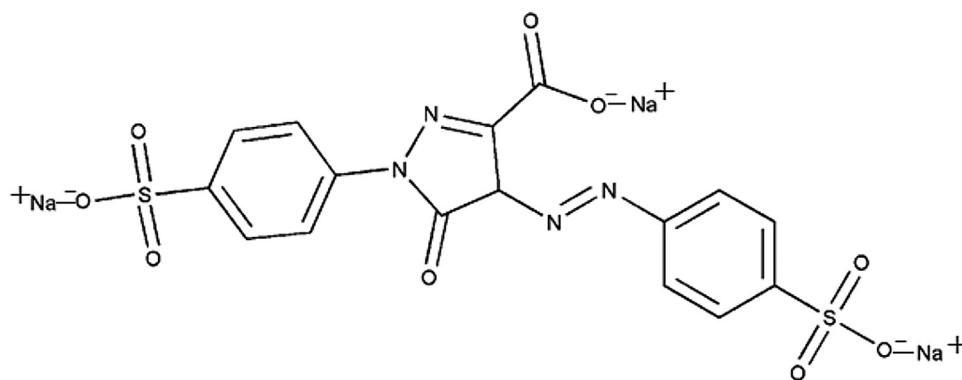


Fig. 1. Chemical structure of tartrazine dye.

among all the available treatment techniques adsorption is acknowledged as the most promising method due to its cost effectiveness, operating conditions, energy requirements, and regeneration of the used materials. So far several adsorbents have been developed and utilized for the abatement of toxic substances from the aqueous solutions. Activated carbon considered as the highly versatile adsorbent material but its high running costs wooed the scientific community to explore certain alternates that exhibit performance comparable to that of activated carbon in terms of high surface area and porosity at the same time the material must demonstrate high capability for regeneration. Very recently, a new class of materials, better known as metal-organic frameworks (MOFs), reportedly demonstrates high efficacy for scavenging of contaminants from wastewater. However, little work has been reported on the use of MOFs to remove toxic dyes from industrial wastewater. Huang et al. [22] applied hierarchically mesostructured MIL-101 MOFs for the adsorptive removal of methylene blue from aqueous media. Recently, Chen et al. [23] synthesized MOF material based on chromium-benzenedicarboxylates (MIL-101) and applied to the adsorption of xylene orange from aqueous solution. Another important study reported by Khanjani et al. [24] where MOF-5 was synthesized on silk fiber through electrostatic layer by layer assembly and the same was investigated in adsorptive removal and recovery of Congo red dye.

In this paper we reported the synthesis of Cu coordinated dithioxamide complex (Cu-DTO) by precipitation method. The use of Cu as the metal in Cu-DTO MOF is due to the formation of highly stable and insoluble complex with dithioxamide [25]. Moreover, according to Irving-Williams series [26], among transition metals Cu considered to form highly stable and irreversible complexes with the ligands. Therefore, keeping this in mind, Cu complexed dithioxamide was synthesized. However, there are very few reports on the Cu-DTO MOFs for the wastewater treatment. Li et al. [27] used Cu-DTO MOFs for the adsorptive removal of basic dye crystal violet from aquatic media. Yet, the potential of Cu-DTO MOF has not been explored for the removal of azo dye laden wastewater from industrial effluents.

In view to filling the paucity of published data on the use of MOFs based adsorbents for removing dye molecules, in the present study; the removal of chemical grade tartrazine was studied using Cu-DTO MOFs. Tartrazine was selected as a model dye because it is widely used in pharmaceuticals, food products, drugs, cosmetics, and for dyeing of textile fibers [13]. Tartrazine is considered to be highly toxic for humans as it acts as hyperactivity and causes asthma, migraines, eczema, thyroid cancer and other behavioral problems [28]. Batch adsorption experiments were conducted using synthetic aqueous solutions of tartrazine and the effects of initial dye concentration, initial solution pH, and temperature were investigated. The kinetics of adsorption has been studied, and

various kinetic models, such as pseudo-first order, pseudo-second order and intra-particle diffusion models were tested with experimental data for their validity. The equilibrium sorption behavior of the Cu-DTO MOFs adsorbents has been studied using the adsorption isotherm techniques. Experimental data have been fitted to the Langmuir and Freundlich isotherm models to determine the best isotherm to correlate the experimental data. Thermodynamics of the adsorption process has also been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

2. Experimental

2.1. Materials

Tartrazine (Trisodium (4*E*)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl)hydrazono]-3-pyrazolecarboxylate; C.I., 19140; molecular formula, $C_{16}H_9N_4Na_3O_9S_2$; molar mass, $534.30 \text{ g mol}^{-1}$) was purchased from British Drug House, Poole, England. Fig. 1 shows the chemical structure of the tartrazine molecule. Tartrazine stock solutions (1000 mg/L) were prepared by dissolving the required amount in double distilled water, and the working solution was prepared daily with the required dilution. Solution pH was measured using a pH/ion meter (pH meter 335, Systronics, Ahmedabad, India) and absorption studies were carried out using UV-visible spectrophotometer (spectrophotometer 2203, Systronics, Ahmedabad, India). The ligand, dithioxamide ($\text{NH}_2\text{—C(S)—C(S)—NH}_2$), abbreviated as DTO, was procured from Hopkin & Williams, England. All chemicals with the highest purity analytical reagent grade available were purchased: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, NaOH, HCl, NH_4OH , KNO_3 , and ethanol absolute (Merck, Mumbai, India) and were used as such without any further purification.

2.2. Synthesis of copper coordination with dithioxamide MOFs

The complex of copper with dithioxamide was prepared according to procedure previously reported in literature [27,29]. The process flowchart for the synthesis of Copper Coordinated Dithioxamide MOFs is illustrated in Fig. 2. The synthesized adsorbent had a percentage yield of 73%.

2.3. Characterization

Fourier transform infrared spectroscopy (FTLA 2000, ABB, Canada) was used for the determination of the functional groups present on the surface of the adsorbent. The spectra were collected in the range of $400\text{--}4000 \text{ cm}^{-1}$ using a resolution of 4 cm^{-1} with 32 scans. Transmission electron microscopy (TEM) images of the magnetic nanoparticles were obtained with a Transmission

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