Powder Technology 246 (2013) 125–136

Contents lists available at SciVerse ScienceDirect

Powder Technology

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

Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution

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ARTICLE INFO

Article history:
Received 22 August 2012
Received in revised form 17 April 2013
Accepted 4 May 2013
Available online 16 May 2013

Keywords:
Adsorption
Chromium
Malachite Green Oxalate
Metal oxides
Regeneration

ABSTRACT

Metal oxide nanoparticles such as ZnO and SnO_2 with specific surface areas of 15.75 and 24.48 m^2/g respectively were successfully synthesized by precipitation method and then employed as adsorbents for removal of Malachite Green Oxalate (MGO) and hexavalent Chromium (Cr) from aqueous solution. The nanoparticles were characterized by XRD, SEM, TEM, SAED, FT-IR and BET surface area analysis. The adsorption of MGO and Cr was achieved under different adsorbate concentration, contact time, adsorbent dosage, pH and temperature conditions. Adsorption equilibrium was studied with Langmuir and Freundlich isotherm models. Equilibrium data were best fitted with the Langmuir and Freundlich isotherm models. Kinetic studies indicated that the adsorption process follows second order kinetics and particle diffusion mechanisms are operative. Thermodynamic parameters were studied in detail to know the nature and mechanism of adsorption. The spent adsorbents were regenerated with CH_3COOH or NaOH solutions and regenerated adsorbents showed very good adsorption efficiencies. All the above results demonstrated that metal oxide nanoparticles could be used as a possible alternative low-cost adsorbent for the efficient removal of dyes and heavy metals from aqueous solution.

1. Introduction

Water is essential to all life on our planet. Surface and ground waters support a variety of human activities including drinking, irrigation of crops and landscape, industrial processes, domestic applications, and recreation [1].

Water pollution is a common environmental problem faced in many places worldwide. With the rapid development of economies and industries [2], wastewater from electroplating industries, mining operations, tanneries, etc contains many heavy metals such as copper(II), nickel(II), chromium (total), zinc(II), cadmium(II), and lead(II) [3,4]. Many industries like dye industries, textile, paper and plastics use dyes for coloring their products, and also consume substantial volumes of water. As a result they generate a considerable amount of colored wastewater [5–7]. Many of these dyes and heavy metal ions were tend to accumulate in the living organisms causing diseases and disorders.

Cr(VI) is the most toxic form, being carcinogenic and mutagenic to living organisms. In addition, it leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation [8–10]. Because of its high toxicity, Cr(VI) must be substantially removed from the wastewater before being discharged into the aquatic system.

MGO selected in this study has been widely used in aquaculture as a parasiticide and in food, health, textile and other industries for one or the other purposes. Several adverse effects from the consumption of the dye due to its carcinogenic, genotoxic, mutagenic and teratogenic properties in animal studies have been reported [11,12].

Physico-chemical methods like coagulation, flocculation, ion exchange, membrane separation, oxidation, etc. are available for the treatment of heavy metals and dyes. Major drawbacks of these methods include high sludge production, handling and disposal problems, high cost, technical constraints, etc. This necessitates cost effective and environmentally sound techniques for treatment of wastewaters containing dyes and metals. This search brought adsorption to the foreground of scientific interest as a potential basis for the design of novel wastewater treatment processes. Adsorption using low-cost adsorbents could be technically feasible and economically viable sustainable technology for the treatment of wastewater streams [13–17].

Nanostructured metal oxides fit these criteria well. Their nanometer sized building blocks provide high surface area, a high surface-to-bulk ratio, and surface functional groups that can interact with heavy metal ions and dyes. As a result they show a remarkable potential for water treatment including the removal of heavy metal ions and dyes [18–22].

This study is novel in a way as nanostructured ZnO and SnO_2 have been used for removing metal ion and dye from aqueous solution. Owing to scarce publications concerning the adsorption of heavy metal ions and dyes by metal oxide nanoparticles, lack of complete characterization of adsorbent as well as adsorption properties of

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http://dx.doi.org/10.1016/j.powtec.2013.05.017

spent metal oxide nanoparticles after regeneration, we developed metal oxide nanoparticles by simple precipitation method and used for the adsorption of heavy metal ion and dye.

2. Methods and materials

2.1. Materials

All the reagents were of analytical grade and used as received without further purification. Zinc nitrate [$Zn(NO_3)_2$], tin chloride ($SnCl_2$), triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$), sodium hydroxide (NaOH), and potassium dichromate ($K_2Cr_2O_7$) were purchased from SD Fine chemicals, Mumbai, India. MGO ($C_{52}H_{54}N_4O_{12}$) and 1,5-Diphenyl carbazide ($C_{13}H_{14}N_4O$) (DPC) were purchased from Fisher Scientific India Pvt. Ltd. Mumbai, India and Loba Chemie. Pvt. Ltd. (Mumbai, India) respectively.

2.2. Preparation of ZnO and SnO_2 nanoparticles and characterization

Fig. S1 shows flow chart for the synthesis of ZnO and SnO_2 nanoparticles by precipitation method. In a typical route, metal oxide nanoparticles were prepared by adding 100 ml of basic precipitant 0.4 M NaOH solution into 100 ml of 0.2 M metal salt under constant stirring. About 50 ml/L triton X-100 was added as capping agent which inhibits the anomalous growth of metal hydroxide crystals during the course of precipitation. Then the resulting solution was kept at room temperature for about 3 h under constant stirring. The obtained slurry was centrifuged at 1000 rpm and precipitate was washed several times with water and alcohol, dried in an oven for a period of 1–2 h at 60 °C. Then powder is further heated in silica crucible for a period of 6 h at 600 °C. Finally, the resulting adsorbent was stored in an air-tight container for further use to adsorption experiments.

X-ray diffraction (XRD) patterns were obtained on a Bruker D2 Phaser XRD system. Surface morphology (SEM) was studied using scanning electron microscope (JEOL JSM 840). Transmission electron microscope (TEM) and selected area diffraction patterns (SAED) were recorded by using Philips CM-200 instrument. Fourier transform infrared (FT-IR) analysis was applied to determine the surface functional groups, using FT-IR spectroscope (Bruker ATR), where the spectra were recorded from 400 to 4000 cm^{-1}. Finally, the BET surface area, total pore volume and average pore size of the metal oxide nanoparticles were measured using ASAP 2010 Micrometrics instrument by Brunauer–Emmett–Teller (BET) method.

2.3. Batch equilibrium studies

To study the effect of parameters such as initial concentration, contact time, adsorbent dose, solution pH and temperature for the removal of MGO and Cr on metal oxide nanoparticles were studied by batch adsorption techniques in a 250 ml stoppered flasks (Erlenmeyer flasks) that contain definite volume (100 ml in each flask) of fixed initial concentrations of adsorbates. The flasks were then subjected to agitation using incubator shaker at 200 rpm until equilibrium is reached. The resultant solutions were centrifuged and the supernatant liquids were analyzed by a UV–vis spectrophotometer (Shimadzu UV-1650, Japan) at 617 nm and 540 nm respectively, for MGO and Cr. The amount of adsorbate adsorbed at equilibrium condition, q_e (mg/g) was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)}{W} V \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) respectively. V is the volume of solution (L) and W is the mass of adsorbent used (g).

2.3.1. Effect of initial concentration and contact time

In order to study the effect of initial concentration of adsorbates and contact time on adsorption uptake, MGO solution with initial concentrations of 10–40 mg/L and Cr solutions with initial concentrations of 1–5 mg/L were used. Adsorbent dose was fixed at 200 mg/L and 2000 mg/L respectively for the adsorption MGO and Cr for all the studies and the solution pH was kept at 5.5 and 2, unless and otherwise mentioned.

2.3.2. Effect of adsorbent dose

To observe the effect of adsorbent dose on MGO, different amounts of adsorbents (200–800 mg/L) were added into 20 mg/L initial concentration of MGO solution. To a 3 mg/L initial concentration Cr solution, adsorbents doses were varied from 2000 to 4000 mg/L. The mixture was shaken at room temperature until the equilibrium time was reached. The initial concentration of MGO and Cr solution was kept 20 mg/L and 3 mg/L respectively for all the studies, unless and otherwise mentioned.

2.3.3. Effect of solution initial pH

To study the effect of pH on MGO adsorption, 20 mg/L of initial concentration at different pH values (2.0–8.0) was agitated with 200 mg/L of adsorbents. The pH was adjusted with 0.1 N NaOH or 0.1 N HCl solution using pH meter. Percentage removal of Cr was not studied at higher pH. The literatures on Cr adsorption showed that in the pH range of 0.5–4, the coexisting Cr^{6+} and Cr^{3+} can be separated, since Cr^{6+} exists mainly in the anionic forms of ($HCrO_4^-$) and (CrO_4^{2-}) or ($Cr_2O_7^{2-}$). So in the determination of Cr(VI), pH was monitored in this range of acidity. It can be seen that when the pH is 2, there is a maximum adsorbed intensity. Thus, this pH is preferred [23–25].

2.3.4. Effect of solution temperature

To observe the effect of temperature on dye and metal ion adsorption characteristics, the experiments were studied at three different temperatures (303 K, 313 K and 323 K) with all other variables such as initial concentration, contact time and adsorbents dose, which were kept as the original, without any adjustment.

2.4. Regeneration of adsorbents

In majority of applications, the disposal of adsorbent as waste is not an economic option, therefore regeneration is carried out. So, dye and heavy metal loaded metal oxide adsorbents were regenerated by treating with 1 N CH_3COOH and 0.1 N NaOH solution respectively for about 1 h in a digitally controlled water bath shaker. Obtained particles were washed several times with water, dried in an oven and reused for adsorption studies.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 shows XRD spectrum of ZnO and SnO_2 nanoparticles prepared by precipitation method. The diffraction peaks in Fig. 1(a) and (b) can be perfectly indexed to the hexagonal and tetragonal structures of ZnO and SnO_2 respectively (JCPDS Card No. 80-0075, 88-027), no characteristic peaks of impurities were detected in the XRD pattern, implying the formation of single phase crystals. The strong and narrow diffraction peaks indicate that the product has good crystallinity. The average crystallite size (D_p in nm) of ZnO, SnO_2 particles can be estimated according to the diffraction reflection by using Debye–Scherrer equation:

$$D_P = \left(\frac{K\lambda}{\beta_{1/2} \cos\theta} \right) \tag{2}$$