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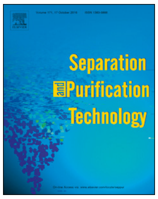

Facile preparation of $PbCrO_4$ and $PbCrO_4/Ag$ nanostructure as an effective photocatalyst for degradation of organic contaminants

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ABSTRACT

Pure monoclinic lead chromate nanoparticles ware prepared via a new simple way with lead nitrate and chrome chloride as Pb and Cr sources. For the first time, nanostructured lead chromate was synthesized with utilizing triethylenepantamine as a new alkaline agent. The citric acid, succinic acid, maleic acid and benzene tricarboxylic acid as stabilization agent and capping agent in presence of ethylene glycol and propylene glycol as connecting agent were employed to prepare of the lead chromate. The as-prepared nanostructured $PbCrO_4$ and $PbCrO_4/Ag$ was analyzed by UV–Vis diffuse reflectance spectroscopy (DRS), energy dispersive X-ray microanalysis (EDX), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). To examining the influence of various stabilization agents, connecting agent and alkaline agents on the morphology, grain size and photocatalytic performance of $PbCrO_4$, different experiments were performed. The effects of various factors including kind of contamination, grain size of $PbCrO_4$ nanostructures and pH on photocatalytic behavior of products was evaluated. Rhodamine B, methylene blue, methyl orange and murexide were used as pollutant model. It was observed that by using of $PbCrO_4/Ag$ nanostructure instead $PbCrO_4$ nanoparticles the photocatalytic activity from 53 to 67 increased. Also by decreasing of pH from 7 to 5 destruction percentage of rhodamine B from 67 to 55 decreased.

1. Introduction

In the last decades, nanoscale inorganic materials created great interest because of their unique properties such as; optical, electronic and magnetic properties and potential application in nanodevices [1–5]. Lead chromate ($PbCrO_4$) crystallized in two crystal structures such as stable monoclinic and the unstable orthorhombic [6]. The Lead chromate is an important solid material that is applied as a photosensitizer with a stable monoclinic structure and yellow pigment because of their thermal stability and electrical properties [7]. $PbCrO_4$ is an important photoelectricity solid functional material that has been widely applied in decorative and protective systems, and mass coloration of fibers, plastics and elastomers [8,9]. Also, lead chromate was applied as a host material for humidity-sensing resistor, photosensitizer and so forth [10].

Many routes to prepare of lead chromate with various morphologies have been reported. Spherical $PbCrO_4$ nanoparticles were obtained by the microemulsion method [11]. $PbCrO_4$ nanorods were prepared by the hydrothermal route [12–14], microwave assisted ionic liquid method [15]. $PbCrO_4$ nanotubes were obtained by microemulsion treating a mixture of $Pb(Ac)_2$ and Na_2CrO_4 [16]. $PbCrO_4$ nanowires were synthesized by a reaction of $Pb(NO_3)_2$, K_2CrO_4, and, poly(vinylpyrrolidone) in aqueous solution at room temperature [8].

In recent years, with development of nanotechnology, much effort has been done to prepare nanostructured $PbCrO_4$ with different morphologies. It is well known that the morphology, dimensions and size of nanomaterial have important influence on their physical and chemical properties [17,18]. Hence, the synthesis of nanomaterial with controlled morphology remains a great challenge. Now, the many routes to the synthesis with desirable shape and size, such as nanorods, nanowires, nanotubes, and specific morphologies, have been reported [19–25].

Among of different routes of the preparation nanoscale materials, Pechini way is well-known as a useful, cost-effective and simple process for grain size and shape controlling of the nanoscale materials. This work reports a modified Pechini way to prepare of nanostructured lead chromate with the aid of lead nitrate and chrome nitrate and benzene tricarboxylic acid as new stabilization agent and capping agent in presence of propylene glycol as connecting agent. It is the first time that benzene tricarboxylic acid as stabilization agent in presence of

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propylene glycol as connecting agent are used for the preparation of nanostructured lead chromate and the effect of factors such as the kind of capping agent and alkaline agent on the grain size, purity and morphology of the nanostructured lead chromate by a new simple route are studied. As a novel alkaline agent, triethylenetetramin was applied in the presence of lead nitrate and chrome nitrate to prepare lead chromate.

This paper has several distinctions with other work such as: synthesize of this nanostructure via modified Pechini way for the first time, using of new capping agent, connecting agent and alkaline agent, and improvement photocatalytic performance of this nanoparticles with added silver particles to structure.

Today, water refinery is known as one of the most important fields in scientific research and organic dyes are the major contaminant kinds of wastewater. Using of photocatalysts is known as one of the best and promising routes for omission organic contaminants from water [26–28].

Also many articles water refinery reported by using photo catalyst process [29–31]. The $PbCrO_4$ nanostructures rarely in the photocatalytic process were used. Abou-gamra et al. reports synthesis of $PbCrO_4/TiO_2$ nanostructure for photodegradation of rhodamine B in aqueous solution by visible light [32]. The photocatalytic demolition of methylene blue, rhodamine b, methyl orange and murexide pollutants have been performed to compare the photocatalytic efficiencies of lead chromate nanoparticles under ultraviolet irradiation. The effect of various factors including kind of pollutant, grain size of lead chromate nanostructures and pH on photocatalytic behavior of products were evaluated.

2. Experimental

2.1. Preparation of lead chromate nanostructures

Lead chromate nanoparticles were prepared via modified Pechini route by using of the reaction of lead nitrate with chrome chloride and deionized water as solvent. In a typical route, 0.5 g of lead nitrate and 1.21 g of chromium chloride were dissolved in distilled water. Then 2 mmol of citric acid were added to the mixed solution and the pH of the above solution was adjusted to 9 by adding TEPA drop-wise, and the next step 2 mmol of ethylene glycol as esterification agent was added the resultant solution. With increasing temperature and evaporation of the gel-like solution leads to the preparation of porous solid mass. Now the prepared powders were calcinated at 700 °C for 3 h. Table 1 the production conditions of $PbCrO_4$ structures were summarized. The effects of stabilization agent, alkaline agent and esterification agent on the shape and size of $PbCrO_4$ was investigated. Schematic diagram of the synthesis of the $PbCrO_4$ and $PbCrO_4/Ag$ is demonstrated in Scheme 1.

2.2. Synthesis of $PbCrO_4/Ag$ nanocomposite

$PbCrO_4/Ag$ nanocomposite (sample 10) was prepared by using of photodeposition method. First 0.016 g (sample 8), 0.048 g (sample 9) and 0.08 g (sample 10) of $Ag(NO)_3$ dissolved in 50 ml deionized water and then 0.2 g as-prepared $PbCrO_4$ nanostructures (sample 6) were added to resultant solutions. The mixtures stirred for 30 min in ultrasound bath to dispersion magnetic nanoparticles in the solvent. Then the solution was shifted to quartz tube and stirred under UV irradiation for 2 h. Final solid separated, washed with ethanol and water three times and dried at 70 °C.

2.3. Materials and characterization

The materials applied in the present work for synthesis of $PbCrO_4$ were lead nitrate ($Pb(NO_3)_2$), Merck, 99.9%), $CrCl_3$ (Merck, 99.9%), $AgNO_3$, ethylene glycol, propylene glycol, citric acid, tetraethylenepentamine, succinic acid, maleic acid, benzene tricarboxylic acid and liquor ammonia solution containing 25% ammonia. All chemicals were used without further purification. Also de-ionized water was used as solvent. Powder X-ray diffraction (XRD) patterns of the as-synthesized $PbCrO_4$ nanostructures were recorded by applying a diffractometer of Philips Company with X'PertPromonochromatized Cu Kα radiation ($\lambda = 1.54$ Å). FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a Nicolet-Impact 400D spectrophotometer. SEM images were taken using an LEO instrument model 1455VP. Prior to taking images, the samples were coated by a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) to make the sample surface conductor, to prevent charge accumulation, and to obtain a better contrast. The EDS analysis of the as-produced lead chromate nanostructure was carried out by employing a Philips XL30 microscope. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer. The UV–vis diffuse reflectance spectrum of the as-produced lead chromate nanostructures was obtained on a UV–vis spectrophotometer (Shimadzu, UV-2550, Japan). GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.4. Photocatalytic measurements

The photocatalytic activities of as-synthesized $PbCrO_4$ and $PbCrO_4/Ag$ samples was done by monitoring the demolition of methylene blue, murexide, methyl orange and rhodamine B in aqueous solution, under irradiation with UV light. The maximum absorbance wavelength for rhodamine B, methylene blue, methyl orange and murexide are 543, 668, 510 and 506 nm respectively. The reaction mixture comprising of the 40 ml of the organic pollutants solutions and 40 mg of $PbCrO_4$ and $PbCrO_4/Ag$ in the glass reactor was employed to determine the photocatalytic activity. The mixture of dye and nanocomposite was placed

Table 1
The optimization steps for synthesis of $PbCrO_4$ and $PbCrO_4/Ag$ via a Pechini method.

Sample number	Esterification agents	Chelating agents	Alkaline agents	Figure of SEM image	Temperature calcination	Ag-doped
1	EG	Citric acid	NH_3	4a and b	–	–
2	PG	Citric acid	NH_3	4c and d	700	–
3	PG	Maleic acid	NH_3	5a and b	700	–
4	PG	Succinic acid	NH_3	5c and d	700	–
5	PG	Benzene tricarboxylic acid	NH_3	5e and f	700	–
6	PG	Benzene tricarboxylic acid	TEPA	6a and b	700	–
7	PG	Benzene tricarboxylic acid	NaOH	6c and d	700	–
8	PG	Benzene tricarboxylic acid	TEPA	–	700	1%
9	PG	Benzene tricarboxylic acid	TEPA	7a and b	700	3%
10	PG	Benzene tricarboxylic acid	TEPA	–	700	5%