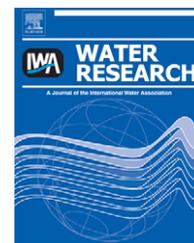


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Photocatalytic magnetic separable beads for chromium (VI) reduction

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ABSTRACT

Magnetically separable photocatalyst beads containing nano-sized iron oxide in alginate polymer were prepared. This magnetic photocatalyst beads are used in slurry-type reactors. The magnetism of the catalyst arises from the nanostructured particles γ -Fe₂O₃, by which the catalyst can be easily recovered by the application of an external magnetic field. These synthesized beads are sunlight-driven photocatalyst. In the system without magnetic photocatalyst beads, no chromium reduction was observed under sunlight irradiation due to the stability of the chromium (VI). Upon the addition of magnetic photocatalyst beads, the photo-reduction of Cr(VI) was completed in just after only 50 min under sunlight irradiation due to the photocatalytic activity of the beads. However when placed away from sunlight, the reduction rate of the chromium is just about 10%. These observations were explained in terms of absorption occurrence of chromium (VI) onto the catalyst surface which took place in this reaction. In addition, photo-reduction rate of chromium (VI) was more significant at lower pH. The results suggest that the use of magnetic separable photocatalyst beads is a feasible strategy for eliminating Cr(VI).

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1. Introduction

The elimination of toxic and hazardous chemical substances such as lead, mercury, cadmium and chromium from waste effluents is a major concern world wide. Conventionally, industrial waste treatments for metal removal include techniques such as biological treatment, ion exchange, liquid–liquid extraction, precipitation, reverse osmosis, activated

carbon adsorption and reduction to elemental form. These techniques often utilized potentially hazardous or polluting materials and most are non-destructive. Therefore, the development of an effective treatment process that can convert pollutants into non-toxic or less harmful forms would be attractive.

Semiconductor-based photocatalysis is a developing technology for the reduction of toxic metals. The method

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has the advantage of destroying pollutants or transforming them into less toxic forms. This is an essential characteristic of photocatalytic technology for water treatment because the toxicity of inorganic substances depends on their oxidation states. For example, photocatalysis can reduce Cr(VI), which is harmful, to Cr(III) which is significantly less toxic. Moreover, as photocatalysis can reduce metals to their elemental form, the metals can be readily recovered using conventional techniques.

Numerous researches have been devoted to fundamental studies and applications of photocatalysis. Many of these studies have focused on air purification and wastewater treatment (Fujishima et al., 2000). The oxidation of a wide range of organic pollutants using the photocatalytic process has been extensively investigated. Organic pollutants are often accompanied by metal ions, and only recently the application of photocatalysis for decontamination and recovery of metals from waste water has received much attention (Howe, 1998; Litter, 1999).

Hu et al. (2005) have focused on the maghemite adsorption property for the removal and recovery of Cr(VI) from wastewater. Ngomsik et al. (2006, 2009) have used the magnetic alginate beads containing Cyanex272 for the removal of cobalt and nickel ions from effluents. These current treatment methods for this contaminant merely concentrate the chemicals present, by transferring them to the adsorbent but they do not convert them into non-toxic wastes. Thus, one of the major advantages of the photocatalytic process over existing technologies is that there is no further requirement for secondary disposal methods.

Titania-based photocatalysts have been extensively studied for the oxidative photodestruction of organic and inorganic pollutants in wastewaters (Khalil et al., 1998). However, commercial exploitation of this new technology is limited by the fact that titania is only active with UV light or radiation with wavelength below about 387 nm, which makes it impossible to wider application. Moreover, TiO₂ particles cannot be used as the photocatalyst in a commercial suspension reactor system due to the high costs required for separating and recovering these particles from the treated water. Thus, there is an urgent need to develop a particular photocatalyst sensitive to sunlight and easy to separate for wastewater treatment.

Several studies on photocatalytic activities of titania-coated magnetite (Beydoun and Amal, 2000) and titania coated nickel ferrite (Chung et al., 2004) were reported but most of them involved organic and dye degradation. To the best of our knowledge no studies were reported on the use of magnetic alginate beads containing maghemite as photocatalyst for Cr(VI) reduction.

In this paper, magnetic separable photocatalyst beads were prepared by combining the magnetic property and photocatalytic activity of nano-sized γ -Fe₂O₃ encapsulated in sodium alginate matrix. Photocatalytic property was investigated based on chromium (VI) as reduction substance. In addition, the effect of pH on Cr(VI) photo-reduction by magnetic catalyst beads was further investigated.

2. Material and methods

2.1. Synthesis and characterization of magnetic nanoparticles

The magnetic material used is a ferrofluid composed of maghemite nanoparticles (γ -Fe₂O₃) dispersed in an aqueous solution. They were synthesized according to the process described by Massart (1981) and improved by Bee et al. (1995). This method allows controlling the size and the superficial charge of particles. Particles were synthesized by alkaline coprecipitation of a stoichiometric mixture of ferrous and ferric chloride in an ammonium hydroxide solution. The magnetite (Fe₃O₄) precipitate obtained was acidified by nitric acid (to provoke a reversion of the surface charges) and oxidized into maghemite (γ -Fe₂O₃) in a solution of ferric nitrate at 100 °C. The last steps stabilized the nanoparticles and make them suitable for our purposes. At this stage, nanoparticles of γ -Fe₂O₃ are polydispersed in size (5 nm < *d* < 20 nm) and exists as a 2 phase solution. The supernatant is composed of smaller sized particles which were removed by suction. The fraction with the larger particles was carefully washed several times, in order to decrease the ionic strength of the acidic anionic ferrofluid (pH = 2) (Lefebure et al., 1998). This suspension is the ferrofluid. Its stability is due to the presence of surface charges which induces screened electro-static repulsions between the particles.

The surface charge comes from the ionization of surface hydroxyl groups, the charge being positive below the point of zero charge (PZC is equal to about 7.3 for maghemite) and negative above PZC. The ferrofluid flocculates in neutral medium for pH values close to the PZC (Bee et al., 1995) before being dispersed into water.

The synthesized nanoparticles were then characterized before use. Their size, shape and distribution and polydispersity were examined by transmission electron microscopy (TEM) (JEOL-JSM 6390LV). The elemental information and structure of synthesized materials were determined by an X-ray diffractometer (XRD) (Siemens D-5000). Their size, shape and distribution and polydispersity were verified by the magnetization curve measured by a vibrating sample magnetometer (VSM).

2.2. Preparation and characterization of magnetic photocatalyst beads

The magnetic photocatalyst beads were prepared by entrapping γ -Fe₂O₃ particles in the matrix of sodium alginate, which was formed by ionic polymerization. About 300 mL of the precursor solution was prepared by mixing 8.0 g of sodium alginate powder and 50.0 mL of ferrofluid in distilled water. The mixture was vigorously stirred with a mechanical stirrer for 1 h. The resulting suspension was added dropwise in a calcium chloride solution (400 mL, 0.5 mol L⁻¹). A magnet set under the calcium chloride solution drew the beads out of the dropping zone without having to stir the bath. The beads were cured in the calcium chloride solution overnight, so that the gelation reaction has sufficient time to take place in the whole

volume of the bead. The instantaneous crosslinking of the interfacial alginate chains by calcium ions leads to a protective membrane which prevents magnetic nanoparticles from going out of the beads. After the curing period, the beads were washed several times with distilled water and kept in a distilled water bath to remove the maximum amount of unbound calcium. Unless specifically noted, no drying was done and the beads were kept wet to avoid the collapse of the internal structure. The iron content of the beads was determined by ICP-MS (Perkin Elmer Elan-6100). The diameter of the beads was measured at 10X magnification using the toolmakers microscope (Nikon).

2.3. Photocatalysis experiment

The photocatalytic activity of magnetic photocatalyst beads was evaluated by photoreduction of chromium (VI) aqueous solution. All photocatalytic reactions were performed under sunlight irradiation. 100 ml of chromium (VI) solution (50 mg/l) was contacted with 10.0 g (wet weight) magnetic photocatalyst beads in a beaker. Samples were taken periodically from the mixture and analyzed for the residual Cr(VI) concentration. The concentrations of Cr (VI) solution were determined by UV-vis spectrophotometer (UV-1240, SHIMADZU and adsorption at $\lambda_{\max} = 540$ nm). The solution pH was adjusted to the desired values including 1–4, 6, 8 and 10 by using HCl and NaOH solutions to evaluate the effect of pH on photo-reduction of Cr(VI). In addition, control experiments were conducted under 3 other different conditions: (i) under sunlight illumination in absence of photocatalyst beads, (ii) with alginate beads without maghemite under sunlight irradiation (iii) away from the sunlight irradiation with magnetic photocatalyst beads.

2.4. Analytical method

The reduction of chromium (VI) was determined colorimetrically at 540 nm using the diphenylcarbazide (DPC) method with a detection limit of $5 \mu\text{g L}^{-1}$ (Zainul Akmar et al., 2007). In a 10 mL volumetric flask, 1 mL of sample was mixed with 9 mL of 0.2 M H_2SO_4 . Then 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added to the volumetric flask. The mixture was then vortexed for about 15–30 s and let to stand between 10 and 15 min for full colour development. The red-violet to purple colour formed was then measured at OD_{540} using distilled water as reference.

3. Results and discussion

3.1. Characterization of nano-sized $\gamma\text{-Fe}_2\text{O}_3$

The TEM image of the particles as shown in Fig. 1 revealed that the maghemite nanoparticles synthesized in this study were multidispersed with an average diameter of around 10 nm. The electron diffraction pattern indicated that the maghemite nanoparticles were highly crystalline. The identity and purity of the maghemite nanoparticles were verified by XRD (Fig. 2), with the XRD peaks of the nanocrystallite matching well with standard $\gamma\text{-Fe}_2\text{O}_3$ and without other crystalline phases

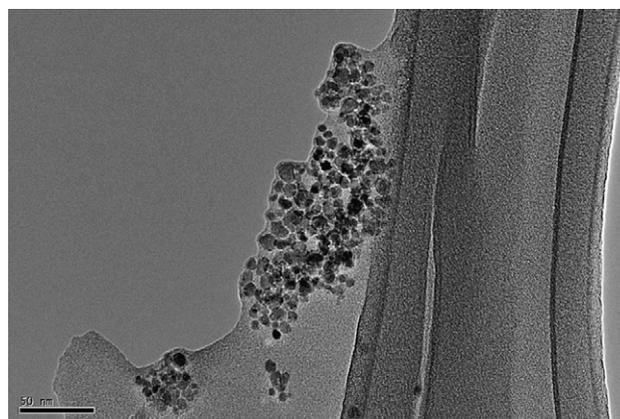


Fig. 1 – TEM image of maghemite particles.

detected. It is known that magnetic particles of less than 30 nm will exhibit paramagnetism (Watson and Cressey, 2000). The paramagnetic properties of the magnetic particles were verified by the magnetization curve measured by VSM (Fig. 3). The saturation magnetization of synthesized particles from the hysteresis loop measured from VSM was found to be 49.8 emu/g. Therefore, the prepared maghemite nanoparticles are expected to respond well to magnetic fields without any permanent magnetization, therefore making the solid and liquid phases separate easily.

3.2. Characterization of the magnetic photocatalyst beads

The beads are found to be spherical and dark brown due to the presence of maghemite nanoparticles. Fig. 4 shows that beads can be easily removed from the aqueous solution with a magnet. Fig. 5 illustrates the size distribution curve fitted with a Gaussian distribution. The mean diameter of the beads is 2.5 mm and the polydispersity factor is 0.41. The results obtained for different syntheses show good reproducibility. The iron content of the beads is 0.119 mmol/g (wet beads).

3.3. Photocatalytic activity

Fig. 6 illustrates the percentage reduction of chromium (VI) as a function of illumination time at pH 1. As can be observed, without photocatalyst beads, no appreciable photo-reduction was observed during the 100 min of irradiation as chromium (VI) is stable and cannot yet be decomposed. In the system with plain alginate beads without maghemite under sunlight irradiation, the rate of chromium (VI) reduction is only about 2–5%. The percentage reduction in the chromium (VI) is due to the adsorption by the alginate polymer as the alginate beads were protonated at low pH and the dichromate species would be electrostatically bonded to the alginate beads surface. However, upon the addition of magnetic photocatalyst beads, the photo-reduction of Cr(VI) was completed in just after only 50 min sunlight irradiation with reduction of almost 100%.

Fig. 7 shows that Cr(VI) reduction rate was just 10% when the system was not exposed to sunlight indicating the occurrence of Cr(VI) removal. These observations were

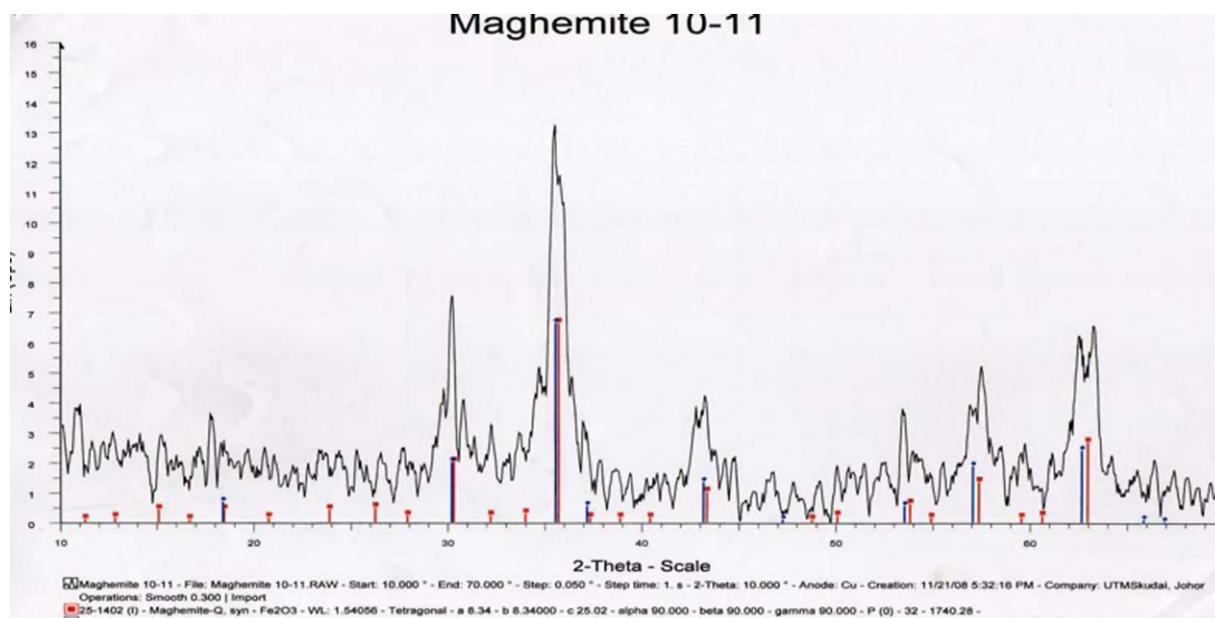
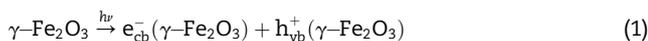


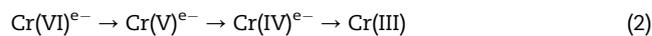
Fig. 2 – XRD patterns of maghemite particles.

explained in terms of chromium (VI) adsorption onto catalyst surface which took place in this reaction. Conversely, when the system was exposed to sunlight, more rapid decrease in Cr(VI) concentration was observed. The results show that light energy is of crucial importance in Cr(VI) reduction and suggest that the photocatalytic process for the removal of heavy metals may occur via direct reduction by the photogenerated electrons. Photocatalysis over a semiconductor oxide such as γ -Fe₂O₃ is initiated by the absorption of a photon, producing electron-hole pairs, as written in the equation (1)



where cb is the conduction band and vb is the valence band. Consequently, following irradiation, the γ -Fe₂O₃ particle can act as either an electron donor or acceptor for molecules in the surrounding medium. In the direct pathway of metal reduction by the photocatalytic process, metal ions are reduced to their metallic form by the photogenerated electrons (Chen and Ray, 2001). In this case the γ -Fe₂O₃ which produces electron-hole pair is responsible for the Cr(VI) reduction to Cr(III). Under sunlight irradiation, electron (e⁻) and hole (h⁺) pairs

were produced and the three-electron reaction of Cr(VI) reduced to Cr(III), while the conjugate anodic reaction was the oxidation of water to oxygen demonstrated by equations (2)–(4). Cr(VI) reduction probably occurred via three subsequent one-electron transfer processes, ending in Cr(III) which is the stable final product.



The overall reaction at extreme acidic conditions (pH 1 and 2) are as follows:

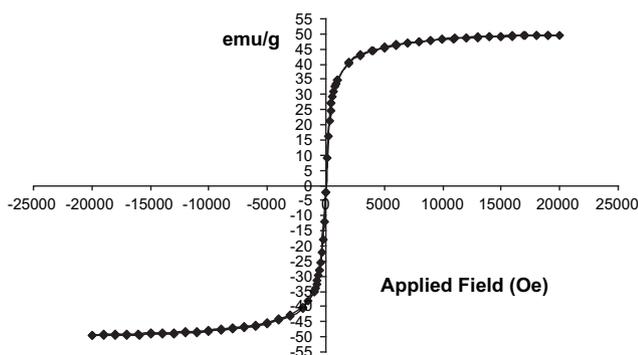
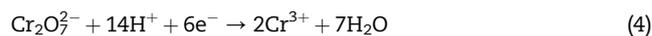


Fig. 3 – Magnetization curve.



Fig. 4 – Photograph of magnetic photocatalyst alginate beads attracted by a magnet.

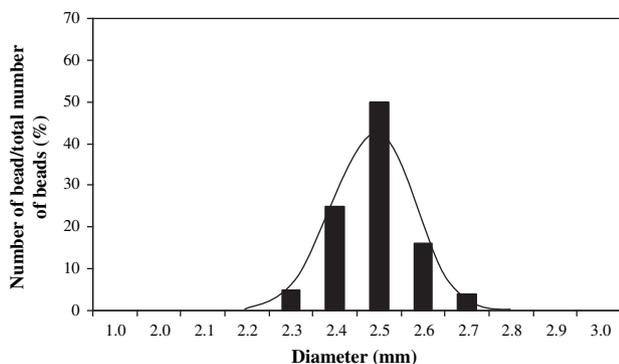


Fig. 5 – The size distribution of wet beads; the full line represents a Gaussian distribution ($d_0 = 2.5$ mm and $\sigma = 0.07$).

The photocatalytic mechanism suggests that both catalyst light source are necessary for the photo-reduction reaction to occur (Tang et al., 1997). The reduction of Cr(VI) to Cr(III) can be observed and detected clearly by the distinct colour change as illustrated in Fig. 8.

3.4. Effect of pH on Cr(VI) photo-reduction

Fig. 9 exhibits the influence of pH on the photocatalytic process. It is observed that the reduction of chromium (VI) is favored in the extreme acidic pH range (pH 1-2) for the successful only photocatalyst. When the photocatalytic process was performed under acidic conditions the Cr(VI) was removed in less than 50 min. The surface of γ -Fe₂O₃, has a point of zero charge (PZC) value around pH 7 as reported by a number of authors (Ngomsik et al., 2006; Hu et al., 2005).

Below this pH, the γ -Fe₂O₃ surface has a net positive charge and above this pH, it has a negative charge. Therefore, the anionic species of Cr(VI) will be deposited well in the acidic pH on the catalyst surface. In addition, the pH also determines the speciation of the metal ions to be transformed, hence their capability to adsorb on the surface of the catalyst, and subsequently affecting their reduction (Litter, 1999).

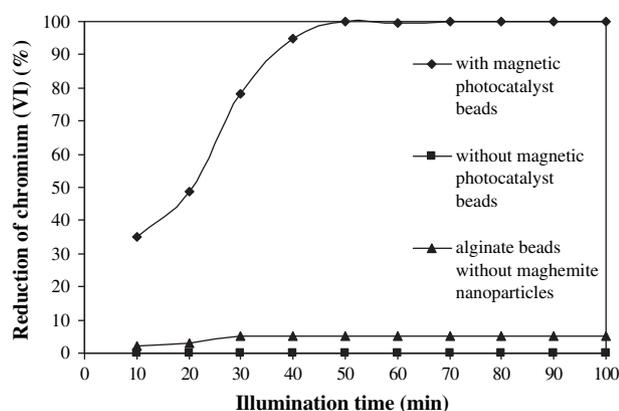


Fig. 6 – The photocatalytic activity of magnetic photocatalyst beads and alginate beads under sunlight irradiation.

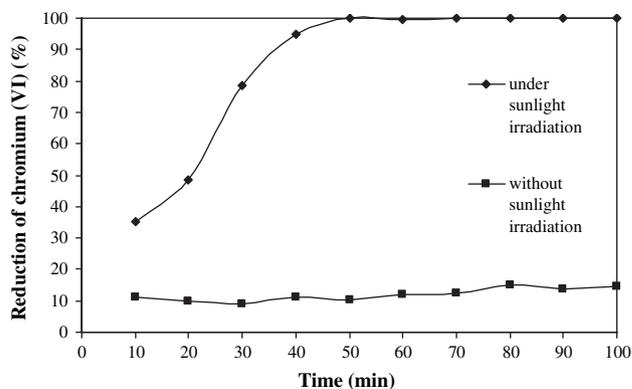


Fig. 7 – The photocatalytic activity of magnetic photocatalysts beads in the presence of sunlight irradiation and without sunlight irradiation.

The findings are in line with recent researches on photocatalytic which revealed that the reduction rate of metal ions was intimately related with the pH in solution (Iwata et al., 2003). In this study, it was reasoned that maghemite nanoparticles has a positive charge at pH lower than the point zero charge (PZC), and contains abundant functional groups on the surface, such as $-OH_2$, which participates in the sorption of metal ions. The solution pH affects the ionization state of these functional groups. For example, $-OH_2$ groups were protonated into OH_2^+ , that could easily interact with the negative ions, such as $Cr_2O_7^{2-}$. Meanwhile, pH influenced not only the functional group chemistry but also the Cr(VI) chemistry and speciation. Cr(VI) generally occurred in the forms of oxy anions as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} , CrO_3 , etc. The predominant form of Cr(VI) was the acid chromate ion species, $HCrO_4^-$ at lower pH solution and subsequently $HCrO_4^-$ was shifted to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$ with increasing pH (Tewari et al., 2005). In this investigation, the maximum adsorption occurred at pH 1 and 2. The main forms of Cr(VI) should be $HCrO_4^-$ and CrO_4^{2-} . Therefore, the ionic forms of Cr(VI) in solution and the charge of maghemite depend on the pH of solution. The lower pH would cause the surface of the sorbent to be protonated to a higher extent. This resulted in



Fig. 8 – Samples (a) before and (b) after treatment with photocatalytic beads.

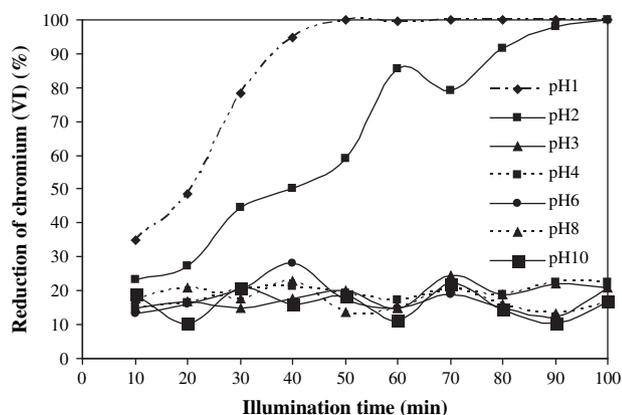


Fig. 9 – Influence of pH on the chromium (VI) photo-reduction.

a stronger attraction for negatively charged Cr(VI) complex ions in the solution. As pH increases, the protonated surface becomes weaker and this led to the photocatalytic reaction to decrease as depicted in Fig. 9.

4. Conclusion

The procedures for successfully fabricating magnetic photocatalyst beads through the immobilization of magnetic nanoparticles with alginate were illustrated. The photocatalyst beads prepared exhibited super paramagnetic properties and can be separated easily by an external magnetic field. Its photocatalytic property was systemically investigated. Chromium (VI), as a considerable stable inorganic pollutant, was almost entirely reduced within 50 min under sunlight irradiation in acidic solution. In short, the present work illustrated the use of magnetic photocatalytic beads in treating effluents contaminated with Cr(VI).

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