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Catalytic reduction of Cr(VI) using recovered Silicon from end-of-life photovoltaic panels as a catalyst

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Abstract As installed photovoltaic panels (PVP) approach their end of life, the need for a sustainable recovery plan becomes imperative. This work aims to reuse Silicon from End-of-Life PVP as a potential catalyst/photocatalyst for wastewater treatment. PVPs were pretreated thermally (550°C for 30 min). The resulting mixture of glass, silicon, electrodes, and ash was separated into different fractions in a trommel. Recovered Silicon flakes were washed with water, acetone, HNO_3, and HF in order to obtain pure Si. Then Si was etched through a single stage Ag-assisted Chemical etching process and doped with copper. Doping was performed in aqueous HF solutions containing $CuSO_4$. Photocatalytic reduction of Cr(VI) in the presence of 5mM citric acid was carried out in a 600 mL batch reactor irradiated by a Xenon 150W arc lamp as well as under dark conditions. It was found that in the presence of 1.2 g/L of the Si catalyst, Cr(VI) at an initial concentration of 15 mg/L can be reduced below detection limit (>99%),under dark conditions in 90-240 min, depending on the pH of the solution. Irradiation, however, was shown to inhibit the process, contrary to previous reports that had not examined catalysis in the dark.

Keywords: Hexavalent Chromium reduction; Photocatalyst; Photovoltaic panel; Silicon Recovery; Wastewater treatment

1. Introduction

Due to the rapid development of photovoltaic panels (PVP's), the recycling and reuse of PVP waste is becoming a highly critical and global challenge. Photovoltaic companies and researchers have begun addressing this issue, looking for ways to recover valuable materials from end-of-life PVPs. First generation panels use Silicon as semi-conductor and contain metals like Ag and Cu in the form of electrodes. Silicon's ability to absorb solar light alongside other properties of its nanostructures renders it a potential catalyst for solar driven applications (Liu et al., 2017).

Previous reports (Fellahi et al., 2016) indicate that photocatalytic reduction of Cr(VI) in the presence of citric acid can be achieved by Cu doped Si NWs. However, the performance of the catalyst under dark conditions was not examined. The purpose of the present work was to investigate the potential of elaborating Si nanostructures using Si recovered from end-of-life, first generation PVPsto be used as a catalyst in wastewater treatment and in particular for the reduction of hexavalent chromium. Metals already existing in PVPs (Ag, Cu) in small amounts are retained in the Si structure, in order to develop an economically meaningful utilization procedure.

2. Materials and methods

2.1. Materials

Polycrystalline Si end-of-life PVPs were provided by POLYECO S.A., Copper (II) sulfate 5-hydrate (99%), hydrogen fluoride (48%), oxygen peroxide (30%), nitrates of silver (99.8%), acetone (99.5%) were obtained from Panreac – AppliChem. Nitric acid (65%) was obtained from Honeywell - Fluka. Citric acid monohydrate (99%) and $K_2Cr_2O_7$ crystals were obtained by Sigma-Aldrich.

2.2. Silicon recovery

The PVP was cut into pieces and placed in a furnace in porcelain crucibles at 550 °C for 30 min to remove polymer sheets, ethylene vinyl acetate (EVA). The resulting mixture of Si flakes, glass, electrodes and ash was separated into fractions using a trommel screen. The fraction containing Si flakes was washed with deionized water and acetone to remove ash and residues, followed by 4N HNO_3 treatment, shaken at 200 rpm for 24h. The samples were also treated with 10% w/w HF aquatic solution for 3h to remove the Anti-Reflective Coating, Al coating and oxides from their surface. Both acid treatments were performed at a 5% w/v solution: 5g of Si flakes. Finally, the flakes were dried and ground.

2.3. Silicon modifications

The first process is a single step Ag-assisted chemical etching, which aims to create high surface area Nano Wire structures on Si, schematically described in Figure 1. Si powder was immersed into a 4.6 M HF aquatic solution containing 0.035M $AgNO_3$30 min at 55°C. After etching, Si oxides were removed from the sample's surface using 10% w/w HF aqueous solution for 1 min. Finally, the samples were rinsed with deionized water and dried at 105 °C for 24h(Fellahi et al, 2016).

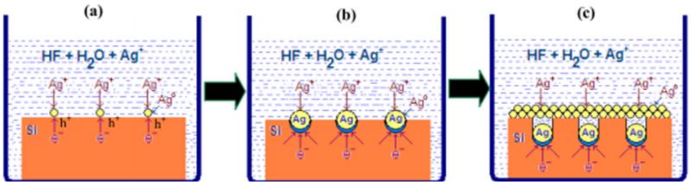

Figure 1. Single step Ag assisted chemical etching (Srivastava et al., 2014)

The second process employed is a simple deposition of Cu on the etched Si surface that aims to create a Schottky barrier that acts as an electron trap. This barrier inhibits the recombination of photo-generated electron-hole pairs assisting the photocatalytic mechanism. It was carried out in 1.4M HF aquatic solution for 2 min at room temperature containing 0.035M $CuSO_4 \cdot 5H_2O$.

2.4. Photocatalytic experiments

A hexavalent chromium solution with initial concentration of 15 mg/L was prepared by dissolving $K_2Cr_2O_7$ powder in deionized water. The photocatalytic degradation was carried out by dispersing the catalyst's powder into a 600mL of the aqueous solution of $K_2Cr_2O_7$ under stirring, in the presence of 5mM citric acid, which acts as an electron donor. The solution was then irradiated with simulated solar light from a 150W Xenon arc lamp immersed in the reactor (Figure 2) using an immersion tube for 240 min. The concentration of hexavalent chromium was measured by1,5-Diphenylcarbazide method as described in "Standard Methods for Examination of Water & Wastewater". Catalytic experiments were carried out in the same conditions without using the Xenon arc lamp.

Figure2. Photoreactor set up by Peschl Ultraviolet GmbH, Mainz -Germany

3. Results and discussion

3.1. Catalytic behavior

The ratio of the concentration (C) to initial concentration (C_0)of hexavalent chromium for 240 min under dark conditions and in the absence of catalyst is presented in Figure 3. There is no significant hexavalent chromium reduction. The catalyst itself does not exhibit any Cr(VI) reduction in the absence of irradiation and citric acid as well (data not shown).

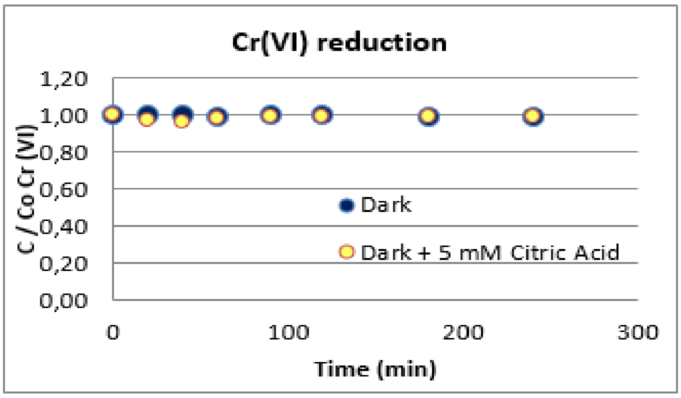

Figure 3. Reduction of Cr(VI) under dark conditions without catalyst after 240 min with and without citric acid.

The performance of three experiments using citric acid along with1.2 g/L of the prepared catalyst under dark conditions is displayed in Figure 4. In two cases, the concentration of Cr(VI) was reduced below the detection limit in 90 and 180 min respectively. In one of the experiments, the reduction was not complete even after 240 min. The only difference in the experiments was the initial pH of the solution, this occurrence is caused by daily fluctuations in the DI system at the time of the experiments. The final pH measured after completion of the experiments had an insignificant drop (~1%). It is seen that the performance increases with decreasing pH and complete reduction is achieved for a pH below 2.7.

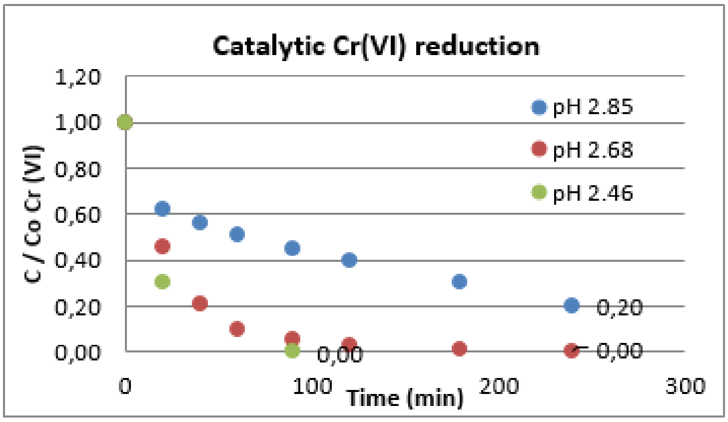

Figure 4. Solution of 15mg/L Cr(VI), 5mM citric acid and 3 samples of 1.2 gcat/L, under dark conditions, at3 different pH values.

3.2. Photocatalytic behavior

The ratio of the concentration (C) to initial concentration (C_0) for 240 min under simulated solar light irradiation in the presence of 5mM citric acid or 1.2 g/L of prepared catalyst is presented in Figure 5. Similarly, to the behavior under dark conditions, the catalyst or the citric acid alone do not have a reduction effect on the concentration of Cr(VI).

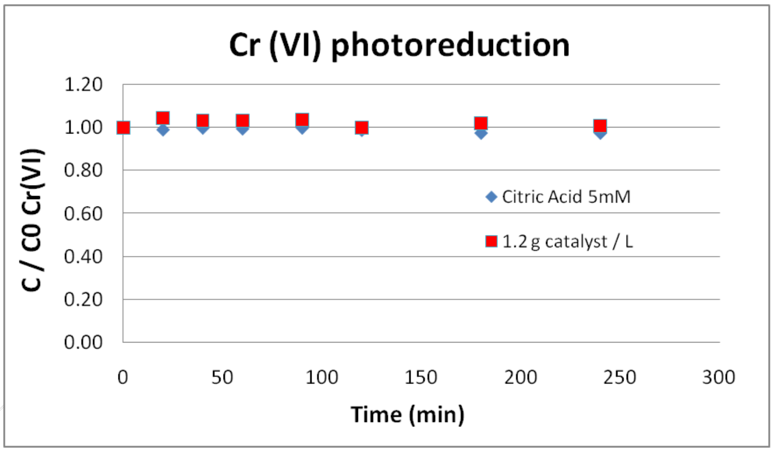

Figure 5. Ratio of concentration (C) to initial concentration (C_0) under simulated solar light irradiation in the presence of 5mM citric acid or 1.2 gcat/L

In the presence of irradiation, 1.2 g/L of catalyst and 5mM citric acid, the reduction of Cr(VI) seems to be inhibited and slower reduction rates are observed in comparison with the performance observed under dark conditions. A reduction of 77-85%was achieved after 240 min of irradiation(Figure 6).

These results indicate that the catalytic process is not photoinduced contrary to previously reported findings(Fellahi et al., 2016). In fact, the irradiation of the solution seems to have an adverse effect to the reduction of hexavalent chromium. This behavior can be explained by the irreversible oxidation of the organic acid that occurs due to the OH radicals developed by the electron/hole separation on the catalyst's surface under irradiation (Hongbo et al, 2020), which reduces the available concentration of citric acid for the reduction of the hexavalent chromium, as described in equation 1, where R = $C_6H_8O_7$.

$$RCOO^- + h^+ / HO^\bullet \rightarrow R^\bullet + CO_2 \qquad \text{(Eq. 1)}$$

As noted earlier (in section 3.1), a good reduction of hexavalent chromium can be obtained with simultaneous presence of the organic acid and the Cu decorated Si NWs, without irradiation. This means that citric acid consumption as a sacrificial agent in the case of photocatalyst might be limiting the reduction phenomenon, as its concentration decreases. The exact nature and mechanism of the interaction among the Cu decorated Si NWs, citric acid and hexavalent chromium is obscured even further by another phenomenon. As Cr(III) precipitate is formed, it deposits on the surface of the catalyst, occupying active sites (Ngo et al., 2018), thus inhibiting the reduction reaction both under dark and solar conditions.Citric acid though is able to form soluble complexes with Cr(III) (Montesinos et al., 2016), preventing or delaying this way the deposition on the catalyst's surface.

Summarizing the aforementioned citric acid:

a. Has anactiverole in the reduction process
b. Forms a soluble complex with Cr(III)
c. Under irradiation acts as a sacrificial agent

In photocatalytic experiments, even though the citric acidacts as a hole scavenger to prevent recombination of electron/hole pairs to increase the rate of the reduction, its own oxidation leads to faster deposition of Cr(III) on the catalyst surface and a slower reaction rate, since its concentration is reduced. Further experiments to clarifythe exact role of citric acid as a function of operating conditions are required.

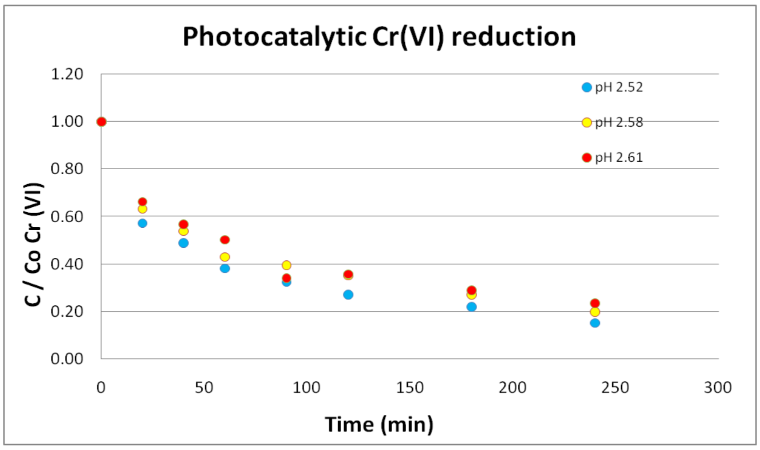

Figure 6: Solution of 15mg/L Cr(VI), 5mM citric acid and 3 samples of 1.2 gcat/L, under simulated solar irradiation in triplicate

4. Conclusion

Si was recovered from end-of-life Si PVPs, etched and Cu doped through simple, electroless, chemical methods for the preparation of a catalyst. The resulting material was tested in heterogeneous catalysis of Cr(VI) reduction under simulated solar light irradiation and dark conditions in the presence of citric acid. Irradiation seems to inhibit the process, whereas under dark conditions,15 g/L of $K_2Cr_2O_7$ are completely reduced even in 90 min depending on the pH of the solution in contrast with simulated solar irradiation, where a total of 77-85% reduction is achievedafter240 min of irradiation. These results indicate that, contrary to what was previously reported, the observed reduction might not be attributed to photocatalytic activity.

Acknowledgements
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