Magnetite nanoparticles for reduction of hexavalent chrome in soil of an industrial park, Cerro Colorado - Arequipa

[Nanopartículas de magnetita para reducción de cromo hexavalente en suelo de un parque industrial, Cerro Colorado – Arequipa]

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Resumen

Uno de los problemas de contaminación más importantes en cuerpos receptores producto de actividades industriales es la presencia de cromo (VI). Una manera de reducir la agresividad de dicho contaminante es su reducción a la forma de cromo (III). En la investigación se determinó la eficiencia de nanopartículas de magnetita en el tratamiento de suelo contaminado con cromo (VI) del Parque Industrial de Rio Seco del distrito de Cerro Colorado, provincia y departamento de Arequipa, para reducirlo a cromo (III).

Se tomaron 22 muestras de 1 kg de suelo, luego se homogenizaron según las distancias de extracción, considerándose al final solo 3 muestras denominadas “Orilla”, “6 Metros” y “9 Metros”, cuyas concentraciones fueron: 146 mg/kg, 126 mg/kg y 67 mg/kg de Cr (VI) respectivamente. Estas muestras fueron sometidas a 3 tratamientos (T1, T2 y T3) con 3 repeticiones cada uno utilizando para ello dosis de 15, 30 y 45 gramos de nanopartículas de Magnetita por tres semanas. Al final del tratamiento usando el método EPA 3060 se realizó el análisis de Cromo (VI). Los 3 tratamientos “T1”, “T2” y “T3”, tuvieron diferencia significativa para las concentraciones finales del Cromo Hexavalente en el suelo; pero fue en el Tratamiento 3 en las muestras de suelo “Orilla”, “6 Metros” y “9 Metros”, donde se alcanzó mayor efecto en la reducción del Cr (VI) a Cromo (III) con una eficiencia del 99.96%, 99.93% y 99.93% respectivamente, para este tratamiento se usó 45 gramos de nanopartículas de magnetita.

Palabras clave: Tratamiento de suelo, nanopartículas de magnetita, reducción, cromo hexavalente.

Abstract

One of the most important contamination problems in receiving bodies due to industrial activities is the presence of chromium (VI). One way to reduce the aggressiveness of said contaminant is its reduction to the form of chromium (III). The investigation determined the efficiency of magnetite nanoparticles in the treatment of soil contaminating with chromium (VI), to reduce it to chromium (III) of an Industrial Park at the district Cerro Colorado, province and department of Arequipa. 22 samples of 1 kg of soil were taken, then homogenized according to the extraction distances, considering at the end only 3 samples called “Shore”, “6 Meters” and “9 Meters”, whose concentrations were: 146 mg / kg, 126 mg / kg and 67 mg / kg of Cr (VI) respectively. These samples were subjected to 3 treatments (T1, T2 and T3) with 3 repetitions each using 15,
30 and 45 grams doses of Magnetite nanoparticles for three weeks. At the end of the treatment using the EPA 3060 method, the Chrome (VI) analysis was performed. The 3 treatments “T1”, “T2” and “T3”, had significant differences for the final concentrations of Hexavalent Chromium in the soil; but it was in Treatment 3 in the soil samples "Shore", "6 Meters" and "9 Meters", where a greater effect was achieved in the reduction of Cr (VI) to Chromium (III) with an efficiency of 99.96%, 99.93% and 99.93% respectively. 45 grams of magnetite nanoparticles were used for this treatment.

Keywords: Soil treatment, magnetite nanoparticles, reduction, hexavalent chromium.

1. Introduction

At present there are different methods to decontaminate soils and one of them is the use of nanotechnology with advantages in decontaminating the environment more quickly and efficiently, including the soil as a receiving body generally contaminated with heavy metals as in research. de Pérez et. al (2018) that reduced Zn and Cu or like Sierra et al., (2014) that performed washing of soil contaminated with heavy metals using magnetite nanoparticles reducing them by approximately 60%. In the district of Cerro Colorado in the jurisdiction of Arequipa is the Industrial Park of Rio Seco that presents a contaminated soil for several years, by companies installed there who have poured polluting waste, leaving a great focus of pollution for the people who live there , as well as generating negative environmental impacts on the fauna and flora of the place; therefore this contamination causes the soils to lose their quality and sustainability (García, et al., 2002). The contamination of soils by heavy metals causes toxicity, infertility and people who have contact with it even to death, according to the specifications made by the Agency for the Registry of Toxic Substances and Diseases (ATSDR). In the Industrial Park of Rio Seco, more than 30 companies are operating, including tannery industries with spills to the ground with contents of up to 184 mg / kg of hexavalent chromium, which exceed the permitted standards for residential, agricultural and even industrial soils. Therefore, nanotechnology combined with conventional methods arise as another promising way for the remediation of soils contaminated with heavy metals, achieving their removal or stabilization (Carrillo and Gonzales, 2009) and organic pollutants (Fernandez, 2013). The investigation was aimed at determining the efficiency of reducing the concentration of hexavalent chromium found in the soils of the Industrial Park of Rio Seco through the use of magnetite nanoparticles, the physicochemical properties were also evaluated: pH, conductivity (following the guide EC monitoring by Doerge et al, 2015) and redox potential after treatment with nanoparticles.

2. Materials and methods

The method consisted of the following stages:
Stage 1: Collect soil samples from the Industrial Park of Rio Seco
Stage 2: Add magnetite nanoparticles to the soil samples in three doses (5%, 10% and 15%) equivalent to 15, 30 and 45 g respectively.
Stage 3: Evaluation and analysis of the concentration of Chromium (VI) in the soil and physicochemical properties (pH, electrical conductivity and redox potential), following the corresponding methods and protocols

3. Results

A. Physicochemical characteristics: The main physicochemical characteristics of the soil of the Industrial Park of Rio Seco, Cerro Colorado-Arequipa, after having been treated with magnetite nanoparticles that were evaluated were the hydrogen potential (pH) (Table 1), to the variation of the electrical conductivity (see Table 2) and the Redox Potential (see table 3).
### Hydrogen potential (pH):

Table 1. Variations in Hydrogen Potential (pH) with Magnetite Nanoparticle Treatments

| Repetition | Sample          | Initial pH | D1: 5% (15g) | D2: 10% (30 g) | D3: 15% (45 g) |
|------------|-----------------|------------|--------------|----------------|----------------|
| 1st        | En orilla       | 8.06       | 6.32         | 6.20           | 6.10           |
|            | A 6 metros      | 7.54       | 6.2          | 6.16           | 6.08           |
|            | A 9 metros      | 7.6        | 6.9          | 6.53           | 6.25           |
| 2nd        | En orilla       | 8.06       | 6.5          | 6.36           | 5.89           |
|            | A 6 metros      | 7.54       | 6.1          | 6.2            | 5.75           |
|            | A 9 metros      | 7.6        | 6.5          | 6.3            | 6.26           |
| 3rd        | En orilla       | 8.06       | 6.4          | 6.35           | 6.28           |
|            | A 6 metros      | 7.54       | 6.32         | 6.28           | 6.23           |
|            | A 9 metros      | 7.6        | 6.32         | 6.3            | 6.1            |

### Electrical Conductivity (CE):

Table 2. Variation of Electrical Conductivity (EC) with Magnetite Nanoparticle treatments

| Repetition | Sample          | Initial EC | D1: 5% (15g) | D2: 10% (30 g) | D3: 15% (45 g) |
|------------|-----------------|------------|--------------|----------------|----------------|
| 1st        | On shore        | 4.53       | 330          | 340            | 368            |
|            | 6 meters away   | 4.55       | 1700         | 1719           | 1853           |
|            | 9 meters away   | 676        | 673          | 605            | 672            |
| 2nd        | On shore        | 4.53       | 357          | 352            | 345            |
|            | 6 meters away   | 4.55       | 1832         | 1804           | 1758           |
|            | 9 meters away   | 676        | 633          | 663            | 613            |
| 3rd        | On shore        | 4.53       | 356          | 360            | 330            |
|            | 6 meters away   | 4.55       | 1703         | 1750           | 1794           |
|            | 9 meters away   | 676        | 503          | 544            | 564            |

### Redox Potential (Eh):

Table 3. Variation of Redox Potential (Eh) with Magnetite Nanoparticle Treatments

| Repetition | Sample          | Initial Eh | D1: 5% (15g) | D2: 10% (30 g) | D3: 15% (45 g) |
|------------|-----------------|------------|--------------|----------------|----------------|
| 1st        | On shore        | -26.3      | 47           | 54             | 73             |
|            | 6 meters away   | -22.1      | 63           | 65             | 73             |
|            | 9 meters away   | -22.3      | 45           | 62             | 62             |
| 2nd        | On shore        | -26.3      | 56           | 85             | 78             |
|            | 6 meters away   | -22.1      | 72           | 78             | 92             |
|            | 9 meters away   | -22.3      | 59           | 65             | 77             |
B. Efficiency of magnetite nanoparticles for chromium reduction (VI)

Table 4. Efficiency of magnetite nanoparticles in the soil sample M1 on shore

| Treatment | Initial Cr(VI) (mg/kg) | Final average Cr(VI) (mg/kg) | % Treatment Efficiency |
|-----------|------------------------|-------------------------------|------------------------|
| T1: 15g   | 146                    | 0.28                          | 99.81                  |
| T2: 30g   | 146                    | 0.16                          | 99.89                  |
| T3: 45g   | 146                    | 0.06                          | 99.96                  |

Table 5. Efficiency of magnetite nanoparticles M2 soil sample at 6 meters from the shore

| Treatment | Initial Cr(VI) (mg/kg) | Final average Cr(VI) (mg/kg) | % Treatment Efficiency |
|-----------|------------------------|-------------------------------|------------------------|
| D1: 15g   | 67                     | 0.25                          | 99.63                  |
| D2: 30g   | 126                    | 0.19                          | 99.71                  |
| D3: 45g   | 126                    | 0.05                          | 99.93                  |

Table 6. Efficiency of magnetite nanoparticles M3 soil sample at 9 meters from the shore

| Treatment | Initial Cr(VI) (mg/kg) | Final average Cr(VI) (mg/kg) | % Treatment Efficiency |
|-----------|------------------------|-------------------------------|------------------------|
| D1: 15g   | 55                     | 0.35                          | 99.72                  |
| D2: 30g   | 55                     | 0.28                          | 99.74                  |
| D3: 45g   | 55                     | 0.09                          | 99.93                  |

4. Conclusions

- The use of magnetite nanoparticles for the reduction of hexavalent chromium is that the dose D3 with 45 grams of magnetite, has an efficiency of 99.96% in the sample M1: shore, while in the dose D1 with 15 grams of magnetite, presents 99.81%. The amount of magnetite that was added to the soil does not define the greatest efficiency, since other environmental or anthropic factors of the same place intervene. At the time of using the magnetite nanoparticles, no acid or other chemical was applied, in this respect Robles and Rodriguez (2017) imply that acetic acid was used to favor the formation, this could be a factor of lower efficiency.

- Regarding the pH reduction, the dose was reduced to 6.09 in the “D3” dose with 45 grams of magnetite and with the “D1” dose with 15 grams of magnetite the pH is 6.5, which not too low, these results show that the more magnetite is added the pH becomes more acidic. This result was demonstrated by Sotelo (2012), which indicates that if more magnetite is added the pH will continue to reduce less than 5.5 and chromium (VI) to chromium (III).
With regard to the electrical conductivity (CE) of the soil according to the results found, the EC increased but not because it has a direct relationship with the amount of magnetite used to treat the soil, but because of a high cation exchange capacity that it exists on the ground and because Cr VI undergoes a reaction converting it to Cr (III). The result is confirmed by Doerge et al. (2015), indicating that soils with high levels of clay have the much higher capacity to catch cations.

The efficiency of magnetite nanoparticles was determined, where it was carried out by doses "D1, D2 and D3", with quantities of 15 gr, 30 gr and 45 gr, in three soil samples, which with the results it was observed that the The highest percentage of efficiency was the "D3" dose with 45 grams of magnetite with an efficiency percentage of 99.96% in the shore sample, 99.93% in the 6 meter sample and 99.93% in the 9 meter sample.

It was shown that magnetite nanoparticles reduce hexavalent chromium and soil pH decreased with dose D3. The pH was shown to decrease in the three samples M1, M2 and M3 of 6.09, 6.02 and 6.2 respectively. Therefore, the more the addition of nanoparticles the pH decreases, being positive for reduction of Hexavalent Chromium to Trivalent Chromium.

It was shown that the electrical conductivity in the soil increased. This is because magnetite is made up of Fe (II and III), and iron is an element that is already present in the earth's crust and is an essential nutrient in the soil, increasing the amount of salts in the soil.

It was shown that the redox potential (Eh) before treating the soil, its results were mostly negative (-), treating the soil with magnetite in its different doses the final results of the Eh were positive (+), this means that the soil went from being alkaline to acid and where the reduction of hexavalent chromium to trivalent chromium is seen.

The concentration of Cr VI was reduced in the M1 sample from 146 ppm to 0.28 ppm with 15 grams of magnetite, to 0.16 ppm with 30 grams of magnetite and 0.06 with 45 grams of magnetite. The concentration of Cr VI was reduced in the M2 sample from 126 ppm to 0.32 ppm with 15 grams of magnetite, to 0.24 ppm with 30 grams of magnetite and to 0.09 ppm with 45 grams of magnetite. The concentration of Cr VI was reduced in the M3 sample from 67 ppm to 0.25 ppm with 15 grams of magnetite, to 0.19 ppm with 30 grams of magnetite and to 0.05 ppm with 45 grams of magnetite.

It was shown that in only 3 weeks the hexavalent chromium reacted with the magnetite nanoparticles reducing it by a variance of 99.63% and 99.96% and complying with the ECA soil standard, which in commercial and agricultural soils is 0.4 ppm and in soils 1.4 ppm industrial.

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