Removal of Hexavalent Chromium using Iron Nanoparticles Prepared using Date Seed Extract

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Abstract. Removal of hexavalent chromium from contaminated water systems is critical due to their high toxicity to aquatic and human health. Iron based nanoparticles (FeNPs) have emerged as promising materials for chromium removal. However, greener alternatives to the chemical synthesis routes of FeNPs are highly desirable while retaining their remediation ability. In this study we evaluate the removal efficiency of chromium using iron nanoparticles synthesized using aqueous extracts of date tree seeds (ds-FeNPs). Characterization of ds-FeNPs reveal the presence of 20-100 nm spherical nanoparticles containing Fe, C, O and S elements. Batch experiments demonstrated that the removal efficiency increased with increase in nanoparticles dose for a fixed chromium concentration (from 18 to 98% at nanoparticles dose of 166 to 1000 mg/L), whereas an opposite trend was observed for varying chromium concentrations at fixed nanoparticles dose. Removal efficiency was also probed at different initial pH levels and results indicate complete removal of chromium in acidic pH (100% at pH 3) whereas basic pH hindered chromium removal.

1. Introduction
Chromium is a heavy metal discharged into water streams from industries such as electroplating, glass, steelworks manufacturing, ceramics, leather tanning, and synthesis of pigments [1-4]. Chromium can be found in the environment in varying oxidation states; however, the most stable states are the trivalent Cr (III), and the hexavalent Cr (VI) species, with hexavalent chromium being five hundred times more toxic than trivalent chromium [5]. Chromium can be toxic at concentrations as low as 0.1 mg/g of the total bodyweight and regulatory authorities have set a maximum acceptable limit of 0.05 mg/L for hexavalent chromium and 2 mg/L for total chromium [6]. In fact, for the past 15 years chromium has been identified as one of the top 20 pollutants on the Superfund priority list of hazardous constituents [7].

Due to its high toxicity, wastewater effluent containing chromium should be treated properly [8]. Various techniques have been used for the removal of chromium from the environment such as electrical enrichment, reverse osmosis, ion exchange and adsorption [9]. Finding effective methods for remediation of Cr (VI) from wastewater is being explored. Reduction of hexavalent chromium into its less toxic trivalent form is also desirable [7].

Iron based Nanoparticles (FeNPs) such as iron oxides, nanoscale zerovalent iron and iron sulphides are recognized as excellent ecological restoration materials due to their unique physicochemical properties such as high surface area to volume ratio, high catalytic activity, and magnetism [10]–[13]. They have also shown promise for chromium removal from wastewater [14]. However, their synthesis methods are associated with the use of very strong reducing agents such as sodium borohydride,
potassium borohydride and hydrazine hydrate which are considered toxic to environment and expensive to use [15]. Thus, in recent years researchers have been investigating more eco-friendly approaches for synthesizing FeNPs by using greener reagents [16], microorganisms [17], and natural extracts from plants [18]. Plant mediated synthesis of green iron nanoparticles is the most preferable method for green synthesis as it’s faster than other methods [19]. Moreover, Plants contain natural organic reducing agents such as polyphenols and flavonoids which show high antioxidant activity [20]. Removal of chromium using green synthesized (plant mediated) iron nanoparticles has received significant attention recently. The exact mechanism for removal of Cr (VI) from aqueous solution for green synthesized iron nanoparticles is still not clear due to the existence of complex functional groups of the plants. For instance, Eucalyptus globules leaf extract was used for synthesizing NZVI in single step at room temperature and then utilized for chromium removal. Green NZVI has shown an adsorption efficiency of 98.1% with reaction time of 30 minutes and 0.8 g/L dosage of NZVI [14]. Another study used three plant extracts including Rosa damascene (RD), Thymus vulgaris (TV), and Urtica dioica (UD) for synthesizing NZVI and then applied a batch experiment for the three types of NZVI nanoparticles. The results indicated >90% for the three NPs with dosage of 0.2g/L and contact time of 10 minutes. A contact time of 25 minutes was required for 100% removal for TV-Fe and UD-Fe while 30 minutes was required for RD-Fe [12].

Date palms are a common plant located in the middle east and north Africa region. Date flesh and seeds have been proven to have high antioxidant capacity and can thus also be employed in the preparation of iron nanoparticles. However, studies on synthesis of iron nanoparticles using date seeds have not yet been reported. In this paper, we synthesized iron nanoparticles using aqueous extracts from date seeds and used it for the removal of chromium from aqueous solution in batch studies. Removal efficiencies and effect of nanoparticles dosage and pH were evaluated.

2. Materials and methods

The metal precursor was Iron sulphate heptahydrate (FeSO4.7H2O) (ACS reagent ≥ 99.0%). The source of chromium was Potassium Chromate (K2CrO4) from Sigma Aldrich. Concentrated HCl was used for cleaning all the glass-ware and then washed with deionized water before using them. The chromium reagent ChromaVer 3 (Permachem reagents) was obtained from Hach.

2.1. Green synthesis of iron nanoparticles using date seeds (ds-FeNPs) 
Khallas dates were purchased from commercially available market. The fruits then were de-pitted, and the obtained date pits were washed carefully from any adhering flesh. The date seeds were dried at oven at 50 0C for 24 hours. The dried dates were then crushed by an ultra-centrifugal mill ZM-200 using ring sieve Zm-200 Conidur Holes 10 mm. The obtained fine powder was then stored in the fridge.

Date seed water was prepared by boiling 5 grams of date seed powder in 50 ml of water for 10 minutes. The solution then was filtered using a filter paper of 0.45 µm size. A stock solution of iron (II) sulphate was prepared by dissolving 2 grams of FeSO4 in 50 ml of deionized water. To produce iron nanoparticles, date seed water was introduced to FeSO4 solution at 2:1 ratio. The solution then was heated to 70 0C and stirred continuously thereafter for 30 minutes. The solution changed colour from brownish to black which indicated the formation of iron nanoparticles. The nanoparticles then were centrifuged at 5000 rpm for 5 minutes, saved in 3 ml ethanol at 5 0C. Prior to using the nanoparticles for batch experiments, they were dried using XcelVap evaporator at 55 0C water bath and nitrogen pressure of 15 psi for 45 minutes.

2.2. Characterization

Nanoparticles were characterized using Scanning electron microscopy coupled with EDX. (Tescan VEGA XM variable pressure SEM coupled with Oxford Instruments X-Max 50 EDS detector).

2.3. Batch experiments for chromium removal

Batch experiments were conducted to determine the removal efficiency of chromium by ds-FeNPs. Potassium chromate (K2CrO4) was used as the source of Cr (VI). 50 mg/L stock solution was
prepared by dissolving 10 mg of K2CrO4 in 200 ml of distilled water. All experiments were carried out using 50 ml Erlenmeyer flask with 30 ml of the stock solution and were mixed using magnetic mixer at 300 rpm speed for 6 hours at 25°C. Periodically samples were withdrawn at the required time and filtered using 0.22 µm syringe filters. Influencing factors such as pH (3, 5, 7, 9), dS-FeNP loading (166, 333, 500, 666, 1000) mg/L and the initial K2CrO4 concentration (5, 15, 30, 50, 75) mg/L were studied. All experiments were conducted in duplicates and the average values are presented in the graphs.

2.4. Analysis of residual Cr (VI) concentration
At each desired time point, samples were taken and filtered immediately to prevent any further reaction from occurring. The filtered samples were then diluted at 1:10 ratio prior to analysis. The residual Cr (VI) was determined using ultraviolet-visible (UV-Vis) spectrophotometer (model DR 3900) following the 1,5-Diphenyicarbohydrazide method (USEPA method 8023) and involved adding ChromaVer 3 reagent for program 90 Chromium, Hex.

3. Results and discussion

3.1. Nanoparticle characterization

![SEM image of dS-FeNPs and EDX scan of the nanoparticle surface](image)

**Figure 1.** (a) SEM image of ds-FeNPs (b) EDX scan of the nanoparticle surface

Nanoparticles employed in this study were synthesized using date seed extract. The date seed extract consists of strong antioxidant and reducing phytochemicals that can transform iron salt precursors to nanoparticles [21], [22]. As shown in Figure 1a, b the ds-FeNPs appeared spherical and in the range of 20-40 nm. Some large agglomerates greater than 100 nm were also observed. The EDX analysis revealed the presence of Fe, C, O and S. C and O are likely from the presence of organic coating due to the presence of date seed macromolecules. Interestingly, along with Fe, S is also observed possibly due to reduction of both Fe and sulphate precursors. Al, Mg and K originated from the material of the SEM sample holding stage.

3.2. Effect of dS-FeNP dose on Cr (VI) removal efficiency

The effect of varying the initial dS-FeNP dose on chromium removal efficiency over time is shown in Figure 2 (a,b,c,d,e). We observe that as the contact time between the nanoparticles and chromium is increased, the removal efficiency generally increases, although to different extents. For instance, at lower doses of nanoparticles (less than 500 mg/l), changing the contact time did not show a significant change beyond 50 minutes in the removal efficiency implying that the equilibrium removal extents were reached. However, as the dS-FeNP dose was higher than 500 mg/l, the removal efficiencies increased with increasing contact time, reaching maximum removal around 300 minutes. This can be explained by the increase of concentration of available adsorption sites resulting from the increased dS-FeNP loading [23]. In figure 2f, the dependence of removal efficiencies as a function of dS-FeNP...
The Cr (VI) removal percentage at different time points for various doses of FeNP is shown in the figure. The curves tend towards an S-type behaviour, indicating that at higher doses of nanoparticles (i.e., higher than 500 mg/L), chromium uptake through enhanced surface redox reactions likely provide high removal efficiencies.
Figure 2. (a,b,c,d,e,f) Chromium removal efficiency over time at different ds-FeNP dose (f) Final removal efficiencies at end of reaction, for different ds-FeNP dose

3.3. Effect of initial Cr (VI) concentration on removal efficiency

We also evaluated the effect of varying initial chromium concentrations on the removal efficiency, at a fixed dose of ds-FeNPs. As shown in Figure 3a, the equilibrium removal efficiencies of chromium were achieved in less than 100 minutes for all systems. We observe in figure 3b, that as the initial Cr (VI) concentration increased from 1.72 to 18.98 mg/L, a decrease in the removal efficiency was observed. The highest removal efficiency was obtained at the low initial chromium concentrations (e.g. 98% at 1.72 mg/L), and decreased dramatically to 40% at initial chromium concentration 18.98 mg/L. This can be attributed to the fact that with an increase of initial chromium concentration, the fraction of available adsorption sites does not increase, thus decreasing the removal efficiency [24].

Figure 3. Final removal efficiencies at end of reaction, for different initial Cr (VI) concentrations
3.4. Effect of reaction pH on Cr (VI) removal efficiency

Figure 4. Effect of solution initial pH on chromium removal efficiencies by ds-FeNPs

3.5. Chromium removal mechanism by ds-FeNPs

A possible mechanism for the removal of Cr (VI) by ds-FeNPs is suggested based on previous studies of chemically synthesized FeNPs and Cr (VI). It has been reported that Cr (VI) is reduced to Cr (III) by Fe nanoparticles at the surface as shown in the following equation [28], [29].

$$Fe + Cr^{4+} \rightarrow Fe^{3+} + Cr^{3+}$$

Fe and Fe-oxides present in ds-FeNPs likely undergo redox reaction releasing Fe (II), donating electrons to the contaminant forming less toxic Cr (III). The presence of sulphur in the particle (Figure 1b) may also potentially indicate presence of iron-sulphur composites which are also known to reduce and adsorb Cr(VI) [30].

4. Conclusion

This study demonstrates the potential of employing FeNPs synthesized using date seed extracts for the removal of hexavalent chromium. Batch experiments indicated nanoparticle concentration, chromium concentration and solution pH significantly influenced the chromium removal efficiencies. For a fixed initial Cr (VI) concentration of 13.35 mg/L, 100% removal was obtained only at high ds-FeNP dose of 1000 mg/L. Conversely, at a fixed dS-FeNP dose, increasing concentrations of chromium decreased the removal efficiency. Acidic pH conditions favoured removal of chromium, while basic conditions caused a dramatic decrease in the efficiency of removal. Further studies are needed to elucidate the exact mechanisms of chromium removal and probe approaches to further improve the treatment efficiency.

5. References

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