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Effect of Nitrate and Ionic Strength on Hexavalent Chromium (VI) Removal from Aqueous Solution using CMC modified nZVI - Optimisation through Response Surface Methodology

Prathima B[1], G L Sivakumar Babu[2], Ramkumar N[3]

[1]*Research Scholar, Centre for Sustainable Technologies, Indian Institute of Science, Bengaluru, prathimab@iisc.ac.in*

[2]*Professor, Department of Civil Engineering and Centre for Sustainable Technologies, Indian Institute of Science, Bengaluru, gls@iisc.ac.in*

[3]*M Tech Student, Department of Civil Engineering, B M S College of Engineering, Bengaluru*.

ABSTRACT

In this study, Carboxyl Methyl Cellulose stabilized nano Zero Valent Iron (CMC nZVI) was used to remediate Hexavalent Chromium(Cr(VI)) contaminated aqueous solution in the presence of nitrates and ionic concentrations for insitu applications of groundwater remediation. The surface characteristics of the synthesized CMC nZVI were analyzed via Scanning Electron Microscope, X-Ray Diffraction, Fourier Transform Infrared, and Brunauer-Emmett-Teller surface area analysis. The interaction effect of pH (2-10), nitrate (0-300 mg/L), and ionic strength (0-1000 mg/L) was studied using response surface methodology by adopting Box-Behnken Design. The effect of pH, nitrate, and ionic strength under the constant initial concentration of Cr(VI) and CMC nZVI dosage was optimized through the quadratic model. Results showed that the maximum Cr(VI) removal efficiency of 99% was achievable under nitrate concentration up to 147 mg/L and ionic strength up to 875 mg/L operated at pH 2. Under acidic pH, the presence of nitrate and ionic strength showed the least influence on Cr(VI) removal efficiency. The maximized Cr(VI) removal efficiency of 99% predicted from the model was in good agreement with the result obtained experimentally under optimum conditions. Overall, the study revealed that CMC nZVI has greater potential for removal of Cr(VI) in presence of nitrates and ionic strength.

Keywords: CMC nZVI, Hexavalent chromium, Response surface methodology, Nitrates.

1 INTRODUCTION

Due to its widespread use in metalworking, pigment production, leather tanning, and wood preservation, chromium is commonly detected in contaminated groundwater (Wu et al., 2021; Zhao, Zhao, Yang, & Teng, 2019). The pollution of groundwater by nitrate (NO_3), a highly soluble form of nitrogen (N), is frequent in agricultural contexts. Population growth over the past few decades has led to an increase in the use of nitrogen fertilizer on fields globally (Choe, Liljestrand, & Khim, 2004) Thus, it is not unusual to find both nitrate (NO_3) and hexavalent chromium (Cr(VI)) in the ground water. In aqueous environments, trivalent (Cr(III)) and hexavalent (Cr(VI)) forms of chromium are common. It commonly precipitates as oxyhydroxides, hydroxides, or oxides. Yet, because of its negative charges, the cancer-causing form of chromium, Cr(VI), is highly mobile in groundwater (Zhu, Liu, Zhang, & Liang, 2021). Reducing Cr(VI) to Cr(III) is one of the principal strategies for cleaning up Cr(VI)-contaminated groundwater. The majority of reductive remediation strategies are chemical and biological processes (Yu et al., 2020a).

Nano zero-valent iron (nZVI) has been explored and used extensively because it is non-toxic, abundant, affordable, and simple to make, and its reduction process requires no maintenance. Use of zero-valent iron (ZVI) particles in environmental remediation, including soil and groundwater treatment, is made possible by their low cost and simplicity of use. However, because of their chemical and physical characteristics, such as large particle size, low specific surface area, and short lifetime, they have frequently been used exclusively in the treatment of shallow groundwater plumes. Yet in the last two decades, scientists have been focusing on the utilization of nanoscale zero-valent iron (nZVI) particles as a more adaptable approach for cleaning up polluted sites. However, research has shown that non-

stabilized nZVI has low stability and that the nanoparticles were poorly dispersed, resulting in ineffective surface coverage of nZVI particles. Many organic compounds, including microemulsions based on oil, surfactants, ionic and non-ionic polymers, have been explored as stabilizers. Carboxymethyl Cellulose (CMC) is selected due to implications that extend beyond the basic engineering requirement for nZVI stability. CMC compounds have been found to promote particle stability due to the presence of carboxyl functional and hydroxyl groups in cellulose networks (Li, Bhattacharjee, & Ghoshal, 2015; Saberinasr, Rezaei, Nakhaei, & Hosseini, 2016). As reported in the literature, the nZVI is a promising material for the removal of various organic and inorganic contaminants. The organic contaminants such as chlorinated solvents, pesticides, and various other organic compounds are effectively removed by nZVI. The performance of nZVI shown to be promising in the removal of nitrates, heavy metals, and various metalloids present in aqueous solution

Chemical reduction of Cr(VI) to Cr(III) and subsequent precipitation of chromium or chromium-iron oxides/hydroxides/oxyhydroxides on the surface of nZVI are the two main steps in the removal of Cr(VI) in nZVI treatment systems. Evidence suggests that a number of factors, including pH, dissolved oxygen (DO), background ionic strength, and other dissolved contaminants such as nitrates , all these factors influence the performance of nZVI in the removal of Cr(VI) (Yu et al., 2020a). Nitrate (NO_3) is an oxidizing species and competitive oxyanion that may have an impact on chromate remediation. The addition of a NO_3 in a batch experiment increased the apparent specific rate at the lower concentration for the reduction of Cr(VI) by nZVI , but had a significant effect on the Cr(VI) removal efficiency at high nitrate concentration (Choe et al., 2004; Su et al., 2018; Vilardi, Verdone, & Di Palma, 2017). A limited number of studies were carried out in assessing the impact of competitive ion like NO_3 on the removal of Cr(VI) using CMC nZVI. Hence, the major objective of this study is to investigate the influence of nitrates and ionic strength on the performance of CMC nZVI in immobilizing the Cr(VI) from the aqueous solutions.

2 MATERIALS AND METHODS {BIBLIOGRAPHY}

2.1 Synthesis of CMC-modified nZVI

The CMC-modified nZVI was synthesized using ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), sodium borohydride ($NaBH_4$), and carboxyl methyl cellulose (CMC). All chemicals used for synthesis were analytical grade and Sigma Aldrich Make. The synthesis was performed under the nitrogen atmosphere by adding 0.498 gm of $FeSO_4.7H_2O$ and 5% CMC solution. The mixture was purged with nitrogen gas for 30 minutes time period. Further, 0.135 gm of sodium borohydride was dissolved in 20 ml of milli q water and added slowly to the three-neck flask reactor. The resulted CMC nZVI was separated using a strong deuodynm magnet. The CMC nZVI was washed with ethanol and milli q water. The desired concentration of nZVI suspension was prepared using nitrogen purged milli q water for further experiments. The CMC nZVI was synthesized freshly on the day of the experiment and immediately used on the same day.

2.2 Characterisation of CMC nZVI

The synthesized CMC-modified nZVI was dried in a vacuum drying oven at 60° C for 8 hours, and characterization was performed. The high-resolution image of CMC nZVI was captured using a scanning electron microscope (ZEISS, Ultra 55). The crystal structure and surface area of CMC nZVI was determined by powder/thin film X-ray diffractometer system (XRD, Rigaku) and Brunauer-Emmett-Teller (BET) analysis respectively. The functional groups present on the surface of CMC nZVI was determined by KBr method using Fourier transform infrared analysis (FTIR, Perkin Elmer).

2.3 Batch Experiments

The Box Behnken method was adopted to assess the effect of pH, Nitrate, and Ionic Strength on Cr(VI) removal. The amount of Cr(VI) to be removed from the solution served as the dependent response, while the independent factors were pH (A), Ionic Strength (B), and Nitrate (C). The relationship between dependent and independent variables can be represented as shown in equation (1). The constant dosage of 250 mg/L CMC stabilized nZVI was used for the study in all 17 experiments, including five central replicates. A design expert (Version 9.0) was used to analyze the results. The three levels of each independent variable were investigated and assigned the following numeric codes: -1, 0, and + 1. Table 1 depicts independent variables and levels of each variable considered for the present study.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum\sum b_{ij} X_i X_j \quad (1)$$

Where b_o, b_i, b_{ii} and b_{ij} were coefficients was estimated from the model equation. In equation (1), Y was the response variable (Cr(VI) removal efficiency), and the independent variables were Xi and Xj.

The potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr(VI) in an aqueous solution. The potassium nitrate (KNO_3) and calcium Chloride ($CaCl_2$) salts were used as the source of nitrate and to induce ionic strength respectively. The Cr(VI) was analyzed by adopting the Diphenyl Carbazide method using a UV VIS spectrophotometer (Thermo Fisher) at a wavelength of 540 nm (APHA & AWWA). The experiments were conducted using 25 ml of 20 mg/L of Cr(VI) solution at a constant dosage of CMC nZVI of 250 mg/L. Prior to the addition of CMC nZVI the pH of the solution was adjusted according to Table 1 using hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution of known strength. The varying concentration of nitrates and ionic strength was induced as per the levels mentioned in Table 1. The mixture was kept in a rotary flask shaker at 150 rpm for 120 minutes contact time. After the reaction time, the aqueous solution was filtered using 0.45 µm syringe filters, and further analysis was carried out to determine Cr(VI). All experiments were carried out in triplicates, and average values were recorded as results. The percentage removal of Cr(VI) was determined using equation (2).

$$Cr(VI)\%\ removal = \frac{(Ci - Co)}{Ci} * 100 \quad (2)$$

***Table 1**. Parameters and its levels used in the study*

Independent Variables	Coding	Level		
		-1	0	1
pH	A	2	6	10
Ionic Strength	B	0	500	1000
Nitrate	C	0	150	300

3 RESULTS AND DISCUSSIONS

The SEM images of bare nZVI and CMC nZVI are shown in Figure 1. The bare nZVI showed non-spherical particles and arranged in chain like structure whereas the perfect spherical particles with a size ranging from 28 nm to 230 nm (Figure 1) is observed in CMC nZVI. The CMC nZVI particles didn't show any chain-like structures or aggregates of nanoparticles. The specific surface area of CMC nZVI particles was measured through BET isotherm and was found to be 16.12 m^2/gm. The specific surface area of CMC nZVI shown to be nearly 1.6 times the surface of bare nZVI. The CMC coating was clearly visible on the surface of nZVI particles. The presence of nZVI can be deduced from the fact that there was a peak at 2θ of 44.8° during XRD analysis, and the wider diffraction peak provides evidence that the particles of CMC-nZVI are crystallites of a relatively tiny size. The table 2 shows FTIR major absorption bands of CMC and CMC nZVI along with the functional group.

***Table 2**. FTIR major absorption bands for CMC and CMC-Stabilized nZVI*

peak position (cm^{-1})		
CMC Alone	**CMC coated iron nanoparticles**	**Functional groups**
3447	3419	O-H stretch
2899	2899	asymmetric CH_2
1631	1631	COO-(asymmetric)
1061	1061	C-O strectch (RCH_2OH)

Box-Behnken analysis for the synthetic solution:

According to BBD totally 17 experiments were conducted under different experimental conditions. The results of all 17 experiments were shown in Table 3. The Stat Ease Design Expert software version 9 is

used to analyse the data. The coded empirical relation between response variable Cr(VI) removal efficiency and 3 independent factors pH (A), Ionic Strength (B) and Nitrates (C) is given in equation:

Final Equation in Terms of Coded Factors:

Cr(VI) Removal Efficiency = 68.91 – 21.62 *A-1.93*B -1.988*C -2.86 *AB -2.71*AC+3.258*BC +10.68 * A^2-3.03 * B^2-1.63 * C^2. (3)

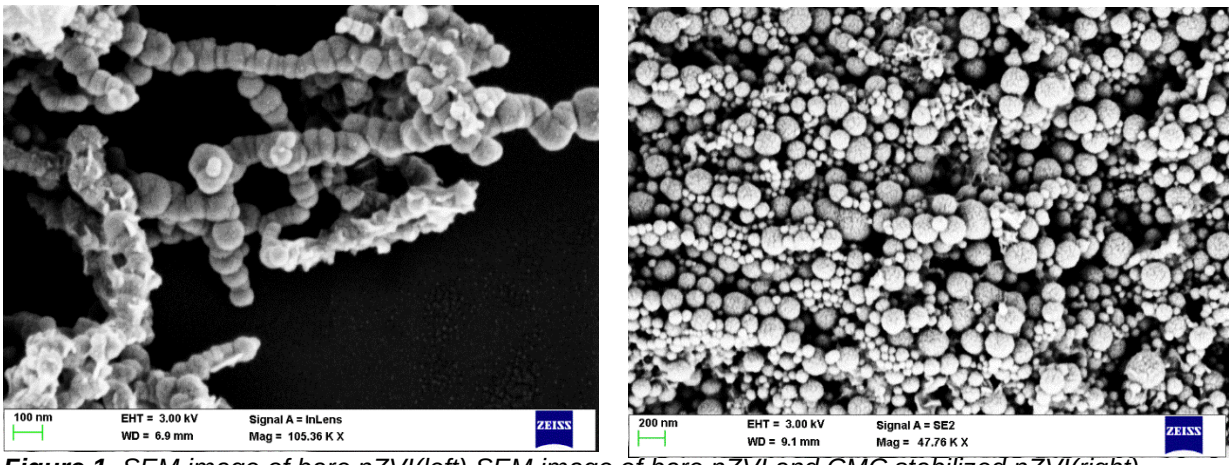

Figure 1. *SEM image of bare nZVI(left).SEM image of bare nZVI and CMC stabilized nZVI(right)*

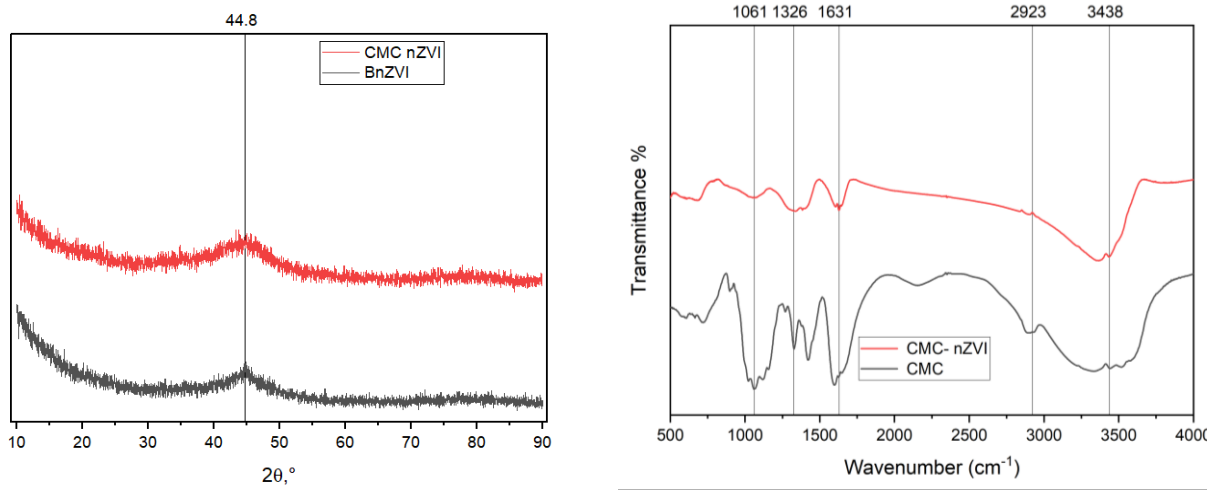

Figure 2*. XRD analysis of CMC stabilized nZVI(left). FTIR analysis of CMC stabilized nZVI(right)*

Table 3*. BBD and its results*

`A:pH	B: Ionic Strength, mg/L	C: Nitrate, mg/L	Cr(VI) Removal Efficiency
6	1000	0	67.5
6	0	0	63.5
10	1000	150	48.9
2	500	0	99
6	1000	300	58.5
6	500	150	69.17
10	0	150	59.83
2	500	300	99
2	1000	150	99
6	500	150	70.5
10	500	300	51.5
6	500	150	69.5
6	0	300	67.5

6	500	150	68.4
2	0	150	98.5
10	500	0	62.33
6	500	150	67

To calculate the response variable (Cr(VI) removal efficiency), pH, ionic strength, and nitrate concentrations in the aqueous solution were used in equation (3). A Model F-value of 197.03, as shown in Table 4, indicates the presence of statistical significance. Significant model terms are those with "Prob > F" values below 0.0500. Important model terms in this scenario are A, B, C, AB, AC, BC, A^2, and B^2. If the value of a model term is greater than 0.1000, it is not important in the model. Compared to the pure error, the "Lack of Fit F-value" of 2.06 indicates that the Lack of Fit is not significant.

As shown in Figure 3, the Cr(VI) removal efficiency was found to be nearly 99% even at a nitrate concentration of 300 mg/L at an acidic pH level (pH 2). This directly implies that, at pH 2 and with a sufficient dosage of CMC stabilized nZVI (250 mg/L) the Cr(VI) removal efficiency was not affected by the presence of nitrates at different levels. Whereas an increase in pH from 2 to 10, decreases the Cr(VI) removal efficiency to nearly 58% from 99% in the absence of Nitrates and the same was further reduced to nearly 49% as nitrate concentration increased from 0 to 300 mg/L.

The impact of initial pH has dual role in this reaction viz., existence of Cr(VI) species and surface charge of CMC nZVI. The pH Eh diagram for Cr(VI) shows that the Cr(VI) in acidic pH present predominantly in the form of $HCrO_4^-$ whereas in neutral to alkaline pH condition CrO_4^{2-} was dominant form. $HCrO_4^-$ has more affinity towards CMC nZVI compared to CrO_4^{2-} and also acidic speeds up the corrosion of CMC nZVI which releases the electrons instantly leading to maximum removal efficiency in the acidic pH. The decrease in removal efficiency can be attributed to formation of hydroxide passivation layer due to formation of ferrous hydroxide on the surface of nZVI (Wang et al., 2010; Yu et al., 2020b).From the interaction plot of pH and nitrate, it can be inferred that to pH plays a significant role in the performance of CMC-stabilized nZVI in removing Cr(VI) from an aqueous solution having nitrates as a co-contaminant.

The effect of other ions on the performance of CMC nZVI was assessed by varying the ionic strength of the aqueous solution from 0 to 1000 mg/L. A similar trend is observed here as similar to the presence of nitrates. The maximum Cr(VI) removal efficiency recorded is 99% again at acidic pH 2 condition. The increase of ionic strength from 0 to 1000 mg/L did not show any inhibitory action on Cr(VI) removal efficiency at pH 2 and CMC nZVI dosage of 250 mg/L. Figures 3 and 4 it can be inferred that at acidic pH, the presence of other ions and competitive ions like nitrate has the least effect on Cr(VI) removal efficiency under sufficient dosage of CMC stabilized nZVI.

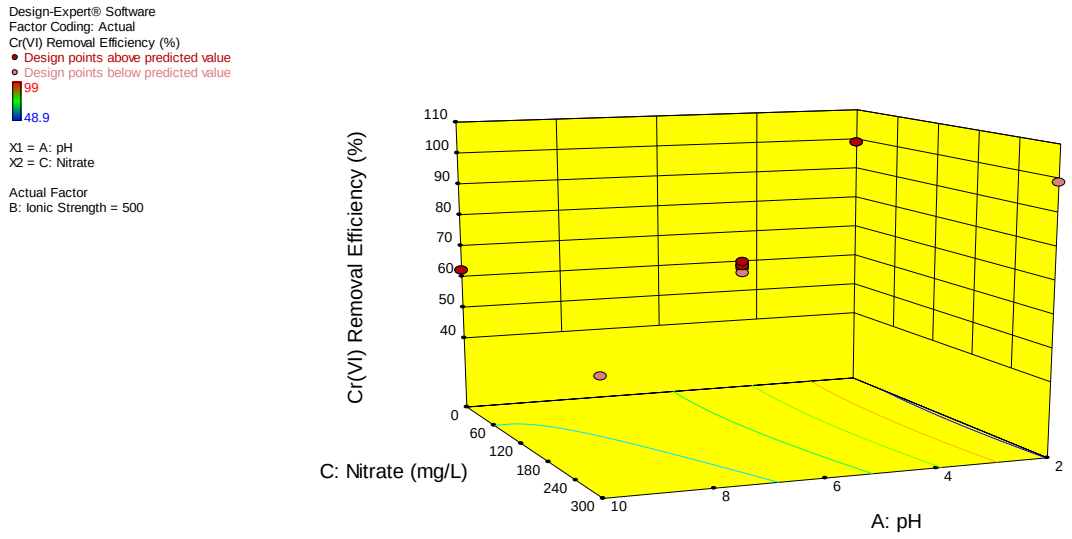

Figure 3. *Effect of Nitrate and pH on Cr(VI) removal at CMC stabilized nZVI dosage of 250 mg/L*

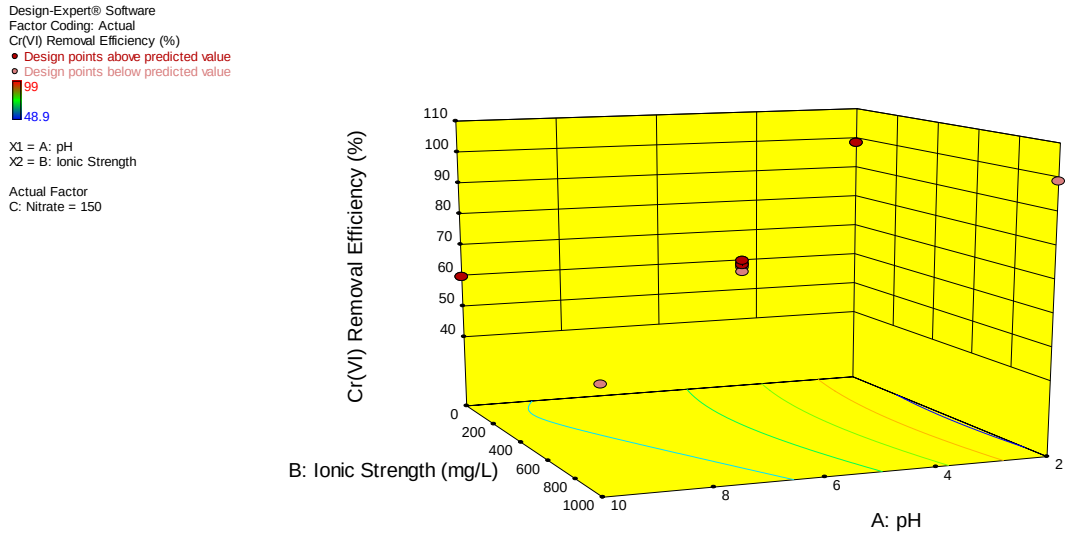

***Figure 4**. Effect of Ionic Strength and pH on Cr(VI) removal at CMC stabilized nZVI dosage of 250 mg/L*

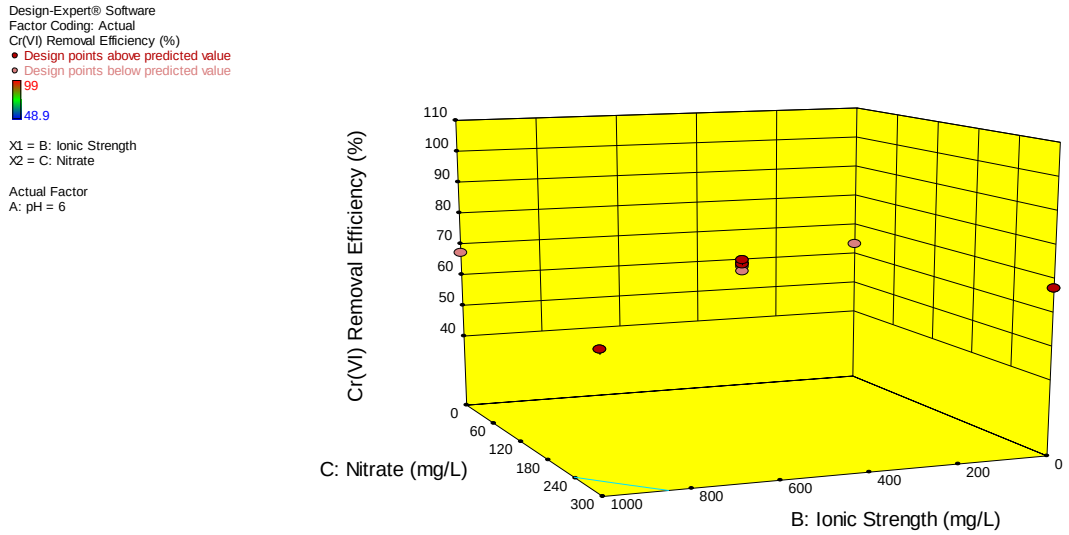

***Figure 5**. Effect of Ionic Strength and Nitrate on Cr(VI) removal at CMC stabilized nZVI dosage of 250 mg/L*

From the nitrate and ionic strength interaction plot (Figure 5) it is observed that at pH 6, the Cr(VI) efficiency decreases as there is an increase in nitrate and ionic strength. The Cr(VI) removal efficiency is decreased from 68% to 60% as the nitrates and ionic strength concentration increased. The most likely explanation for this phenomenon is that an increase in the concentration of Ca^{2+} in the solution caused Na^{+} ions to be replaced by divalent cations, which led to the formation of CMC-metal precipitates, which in turn prevented the reduction of Cr(VI) (Wang et al., 2010). At pH 2 the influence of nitrates and ionic strength is observed to be minimal on Cr(VI) removal. The Cr(VI) removal efficiency is further decreased from 60% to 45% at alkaline pH (pH = 10) at a CMC nZVI dosage of 250 mg/L.

The outcome of the study helps in choosing CMC nZVI as a promising material for the removal of Cr(VI) in presence of competitive ions such as nitrates at a significant ionic concentration in the aqueous solution. However, detailed studies need to be performed by varying dosage of CMC nZVI concentration and contact time.

Table 4. *Analysis of variance of obtained results*

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	4415.64	9	490.63	197.03	< 0.0001	significant
A-pH	3738.53	1	3738.53	1501.32	< 0.0001	
B-Ionic Strength	29.76	1	29.76	11.95	0.0106	
C-Nitrate	31.32	1	31.32	12.58	0.0094	
AB	32.66	1	32.66	13.12	0.0085	
AC	29.32	1	29.32	11.78	0.0110	
BC	42.25	1	42.25	16.97	0.0045	
A^2	479.86	1	479.86	192.70	< 0.0001	
B^2	38.71	1	38.71	15.54	0.0056	
C^2	11.21	1	11.21	4.50	0.0715	
Residual	17.43	7	2.49			
Lack of Fit	10.58	3	3.53	2.06	0.2484	not significant
Pure Error	6.85	4	1.71			
Cor Total	4433.07	16				
Std. Dev.	1.58		R-Squared		0.9961	
Mean	71.74		Adj R-Squared		0.9910	
C.V. %	2.20		Pred R-Squared		0.9594	
PRESS	179.97		Adeq Precision		41.436	

4. CONCLUSIONS

This study investigated the efficacy of nZVI particles as reducing agents for dichromate, nitrate, and both species. When comparing the stoichiometric amounts of reducing agents in both situations, the employment of nZVI in the reduction of Cr(VI) resulted in a remarkable efficiency that exceeded 99% after 120 minutes of treatment, whereas the reduction of Cr(VI) reached nearly 49% after 120 minutes as pH is increased from 2 to 10. The investigation allows for the assertion of nZVI's selectivity for the reduction of dichromate, which exhibits astounding efficacy even in the presence of the higher initial concentration of another active oxidizing species such as NO_3.

The results show that CMC-stabilised nZVI particles are a quick and effective way to reduce hexavalent chromium, but their efficiency is highly dependent on the properties of the external medium, the properties of the nanoparticles, and the presence of other oxidising species.

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