International Journal of Recent Engineering Research and Development (IJRERD)
ISSN: 2455-8761
www.ijrerd.com || Volume 02 – Issue 12 || December 2017 || PP. 66-68

Role of nanoscale zerovalent iron against contaminated lake water sample as remediation agent

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Abstract: Hexavalent chromium is a heavy metal used in a variety of industrial applications which is highly toxic to humans, animals, plants and microorganisms. Moreover, it is a well-established human Carcinogen by the inhalation route of exposure and by the oral route of exposure. Therefore, it should be removed from contaminated waters. Its reduction to trivalent chromium can be beneficial because a more mobile and more toxic chromium species is converted to a less mobile and less toxic form. The reduction of hexavalent chromium [Cr(VI)] by nanoscale zerovalent iron (nZVI) has received considerable attention in recent years because of large surface to volume ratio. A considerable volume of research has been carried out in order to investigate the mechanism of Cr (VI) reduction with nZVI, as well as the influence of various parameters controlling the reduction efficiency. This study was performed to carry out a remediation test in a water sample collected from saturated zone of a historically Cr (VI)-contaminated site known as Puliyanthangal lake (Tamilnadu) using nanoscale zero-valent iron (nZVI). The water samples were examined before and after the nZVI application.The present experimental results revealed that Cr (VI) is considerably adsorbed on nZVI nanoparticles and it could be a cost effective method for the in situ remediation of Cr (VI).

Keywords: Nanoscale zero-valent iron: nZVI, Iron nanoparticles, Ground water remediation,

Introduction

Chromium is one of the most abundant heavy metals, causing pollution of groundwater and soil due to its frequent industrial application. Chromium occurs naturally mainly in the trivalent Cr (III) and hexavalent Cr (VI) forms. The majority of its adverse effects is caused by Cr (VI) because of its solubility, mobility and high oxidizing potential leading to generally higher toxicity causing health problems such as liver damage, pulmonary congestion, vomiting and severe diarrhoea (Nriagu and Nieboer, 1988). On the other hand, Cr (III) is less reactive and toxic and can be readily precipitated out of solution. Therefore, the majority of in situ treatment methods employed at the present time utilizesgeofixation of Cr (VI) by its reduction to Cr (III) and formation of insoluble Cr (III) compounds (Jardine et al., 1999). A number of articles have been published to date describing various applications of individual biological or chemical approaches to precipitate chromium into its insoluble Cr(III) form. One of the most promising methods is reduction using iron-based materials such as zero-valent iron and dissolved Fe (II) and solids containing Fe(II) (Barrera-Diaza et al., 2012). Interest has increased over the past few years in using zero-valent iron (Fe0) and its respective nano-scale form to reduce chromium (VI) contamination.

Zero-valent iron (ZVI) is a readily available and low-cost reducing agent that is also used extensively to remove a number of other kinds of contaminants, such as chlorinated compounds, pesticides and heavy metals e.g. As(V). Although the efficiency of ZVI and especially nano-scale ZVI (nZVI) in reducing the concentrations of Cr(VI) and other pollutants is well documented, only a few works have focused on its ecotoxicty for native organisms in the soil (Ahamed et al., 2016 and Ahamed et al., 2017).

This study was performed to carry out a remediation assessment in the saturated zone of a historically Cr (VI)-contaminated site known as PuliyanthangalLake (Tamilnadu) using nZVI. The water samples were examined before and after the nZVI application by means of various physic-chemical characterization studies and tests.

Materials and Methods

Chemicals

Diphenyl carbazide(Analytical grade) was procured from SD Fine Chemicals Ltd (India). All other reagents used were of analytical grade.

Synthesis of nano zerovalent iron particles

For the synthesis of nZVI; 0.5406 g $FeCl_3.6H_2O$ was dissolved in a 4/1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water) and stirred well followed by the addition of 10 ml of plant extract. Then the sample was incubated in dark for 24 hours. After 24 hours, the sample was measured for its maximum absorbance using UV-Visible spectrophotometry. The sample was then heat dried to obtain the synthesized nano zerovalent iron particles for characterization (Ahamed et al., 2016).

Characterization of the synthesized nano zerovalent iron particles

Prepared nanoparticles were characterized by means of various physico-chemical studies includes; UV-Visible spectroscopy analysis, Fourier transform infrared spectroscopy (FTIR) analysis, scanning electron microscopy (SEM) analysis, transmission electron microscopy (TEM) analysis and Dynamic Light Scattering (DLS) analysis (details in our previous report, Ahamed et al., 2016).

Chromium remediation Test

Water samples were collected from Puliyanthangal Lake (leather industrial site and study area). The initial and final water characterization including determination of pH, temperature, DO, TDS etc., was carried out using water quality analyser (ELICO-PE 138). Metals concentration was determined after acid digestion according to the EPA (US-Environmental Protection Agency) method followed by atomic absorption spectrophotometry (AAS) analysis. The concentration of Cr (VI) was determined by the colorimetric method using diphenyl carbazide after alkaline digestion.

Results and Discussion

The water samples were collected from Puliyanthangal Lake wascharacterized using various physio-chemical characterization studies (Table-1& 2). nZVI treatment was significantly reduced the heavy metals present in the lake water sample. The total and hexavalent chromium concentration was found to be 1mg/L and 0.06mg/L respectively in the untreated lake water sample. By the results of the nZVI treatment leads to the reduction of both total and hexavalent chromium concentrations in the same sample, which may be due to the reduction property of nZVI. Similar trend was absorbed in the case of dissolved oxygen, total hardness, calcium, magnesium, nitrite, phosphate and chloride concentrations. In the other hand opposite results was observed after the addition of nZVI, for example the concentrations of sodium, potassium, iron, ammonia, nitrate, fluoride and sulphate were slightly increased. In addition the physical parameters like pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) was not affected by the addition of nZVI.

Table-1

Physical parameters	Before nZVI Treatment	After nZVI treatment
Atmospheric temperature (°C)	21	21
Water temperature (°C)	24	25
Total Dissolved Solids (TDS)	6909	7121
Electrical Conductivity (EC)	9870	9837

Table-2

Chemical parameters	Before nZVI Treatment(ppm)	After nZVI treatment (ppm)
PH	7.31	7.8
Total Alkalinity	740	800
Total Hardness	2814	2712
Calcium (Ca)	579	570
Magnesium (Mg)	328	317
Sodium (Na)	664	814
Potassium (K)	62	69
Iron (Fe)	0.08	0.34

Free Ammonia (NH_3)	0.73	0.77
Nitrite (NO_2)	0.03	0.02
Nitrate (NO_3)	258	287
Phosphate (PO_4)	0.07	0.1
Chloride (Cl)	1812	1718
Fluoride (Fl)	0.4	0.6
Sulphate (SO_4)	828	837
Total chromium	1	0.05
Hexavalent Chromium (Cr^{6+})	0.6	Bdl
Dissolved Oxygen (O_2 mg/ l)	1.68	1.22

Conclusions

The present study explores the mechanistic aspects of remediation test in the saturated zone of a historically Cr (VI)-contaminated site known as Puliyanthangal Lake (Tamilnadu) using nZVIat low exposure conditions. In this context understanding the underlying fundamental chemistry of the nZVI–lake water contaminant will be helpful for future studies.

Acknowledgement

Authors thank the Science and Engineering Research Board (SERB), Govt. of India for the financial support to carry out this project and alsothank the Secretary and Principal of Sacred Heart College (Autonomous), Tirupattur for having provided the necessary facilities.

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