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NANOPARTICLES ASSISTED REMEDIATION FOR MOLASSES BASED DISTILLERY WASTE CONTAMINATED GROUNDWATER

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Abstract

Remediation of contaminated groundwater of any molasses based distillery using nanomaterials may prove to be one of the effective treatment methods. For this purpose magnetite (Fe_3O_4) nanoparticles were synthesized by the reduction of anhydrous ferric chloride ($FeCl_3$) in natural environment. These nanoparticles were characterized using field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) techniques. Due to their infinitesimally small size, the particles were employed for the remediation of contaminated groundwater sample of a distillery. Remarkable decline in the values of color, TOC and TDS were observed in four days upon treatment of 100 mL sample with 0.22 g of freshly synthesized magnetite nanoparticles.

Keywords: Groundwater, Distillery, Magnetite, Nanoparticles, Remediation

Introduction

The cane sugar molasses-based distillery industry, which manufactures rectified spirit for use both as industrial alcohol and for human consumption, is considered to be one of the most polluting industries. Today there are about 295 distilleries in India with an installed capacity of 3198 million liters (L) of alcohol production per annum. About 15 L of wastewater is produced per L of alcohol production. It is one of the most complex, troublesome and strongest organic industrial effluents, having extremely high color, total organic carbon (TOC), total dissolved solids (TDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values. Raw spent wash (wastewater), generated from distillation of fermented wash, is deep brown in color, acidic in nature (low pH) with high concentrations of organic material and suspended solid. It cannot be directly discharged into rivers or on land without treatment due to its deleterious effect on human health and the environment. Cost-effective management has not hitherto been possible.

Due to the high TOC and BOD values of raw spent wash, application of anaerobic treatment technology (involving biogas recovery) has been reported to be highly effective[1-5]. In recent years, a great deal of attentions has been focused onto the application of nanostructured materials as adsorbents or catalysts to remove toxic and harmful substances from wastewater and air[6-7]. The application of nanotechnology is showing promising results for the remediation of contaminants. Reactive nanoparticles appear to be useful in remediating groundwater[8]. Iron nanoparticles are increasingly being applied in site remediation and hazardous waste treatment. Over the last few years, nano zero valent iron (nZVI) has been extensively used in the degradation of toxic and hazardous organic pollutants. These include the degradation of lindane and astrazine[9] and pentachlorophenol[10]. Efforts to study the reductive capacity of nano zero valent metals have focused not only on halogenated hydrocarbons (specifically chlorinated e.g. DDT, DDD, DDE)[11], but also on contamination of water due to nitrate[12] and arsenic[13-14].

In this research communication the synthesis, characterization and application of magnetite (Fe_3O_4) nanoparticles for providing remediation to the contaminated groundwater of a distillery has been reported.

Methodology

The synthesis of nanoscale Fe_3O_4 was carried out using sodium borohydride ($NaBH_4$) as the reductant. 100 mL (0.25 M) of sodium borohydride ($NaBH_4$) aqueous solution was added drop wise with constant vigorous stirring to 100 mL (0.045 M) of ferric chloride ($FeCl_3$) aqueous solution in natural environment. After constant vigorous stirring for about 20 minutes, jet-black precipitates were obtained. These precipitates were separated from the solution by centrifuging the product on a centrifuge machine at 1200 rpm for 10 min. The particles were then washed 3 to 4 times using 150 mL of anhydrous methanol and instantaneously after washing the jet-black particles were dried under vacuum at 80ºC for 4 h. Soon after drying the particles

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were finely grinded using agate mortar and pestle and were stored in an airtight bottle.

The surface morphology of the synthesized Fe_3O_4 nanoparticles was studied by making a thin film of particles over a thin transparent glass slide of 1x1 cm, sputter-coating with gold and observing with a field emission scanning electron microscope (FESEM, Quanta 200 FEG, FEI Netherlands) operated at 20 KV connected with electron dispersive X-ray (EDX). EDX was used to quantify percent Fe in the nano Fe_3O_4. X-ray diffraction (XRD) analysis of mineralogical characteristics of the nanoscale particles was carried out using XRD diffractometer (Bruker AXS D8 Advance) at 30 kV and 30 mA with iron K_α radiation (λ = 1.93604) and a scan rate 2θ of 0.5˚ per min.

Five sets each of 100 mL contaminated groundwater sample collected from the hand pump located at the premises of the distillery was reacted with the freshly synthesized Fe_3O_4 nanoparticles at room temperature with constant manual stirring at regular intervals of time. These reacted samples were then measured for TOC (using Shimadzu TOC-V CSN analyzer), total dissolved solids (TDS), color, electrical conductivity (EC) and pH (using Hach portable kit), values after every 24 h for 4 days.

Figures 1a and b shows the FESEM image and EDAX plot of Fe_3O_4 nanoparticles. From the FESEM image it is clear that the average diameter of the nanoparticles is of the order of 20-30 nm. The EDAX plot of the nanoparticles confirms the presence of iron (Fe). Moreover the presence of oxygen (O), silicon (Si) and gold (Au) is also indicated in the plot. The presence of silicon and oxygen is due to the fact that the sample preparation was done over a thin glass film which mainly composes silicates (compounds of Si and O). High percentage of oxygen also indicates the formation of an oxide of iron. Furthermore, since the gold polish was used to prevent the overcharging of the sample hence the presence of gold in the sample is also indicated in the EDAX plot. The histogram shown in figure 1c indicates that the average diameter of the nanoparticles is of the order of 20-30 nm.

The XRD pattern of the synthesized Fe_3O_4 nanoparticles is shown in figure 2(a). The diffractogram obtained from the XRD data analysis of Fe_3O_4 was matched with the standard database (JCPDS International Centre for Diffraction Data, 1998) using software PCPDFWIN Version 2.00. The various peaks were found to match with the standard database as shown in figure 2(b).

Results and Discussions

Fig. 1. FESEM image [x100000] (a), EDAX analysis [intensity (y-axis) and KeV (x-axis)] (b) and histogram plot of magnetite (Fe_3O_4) nanoparticles

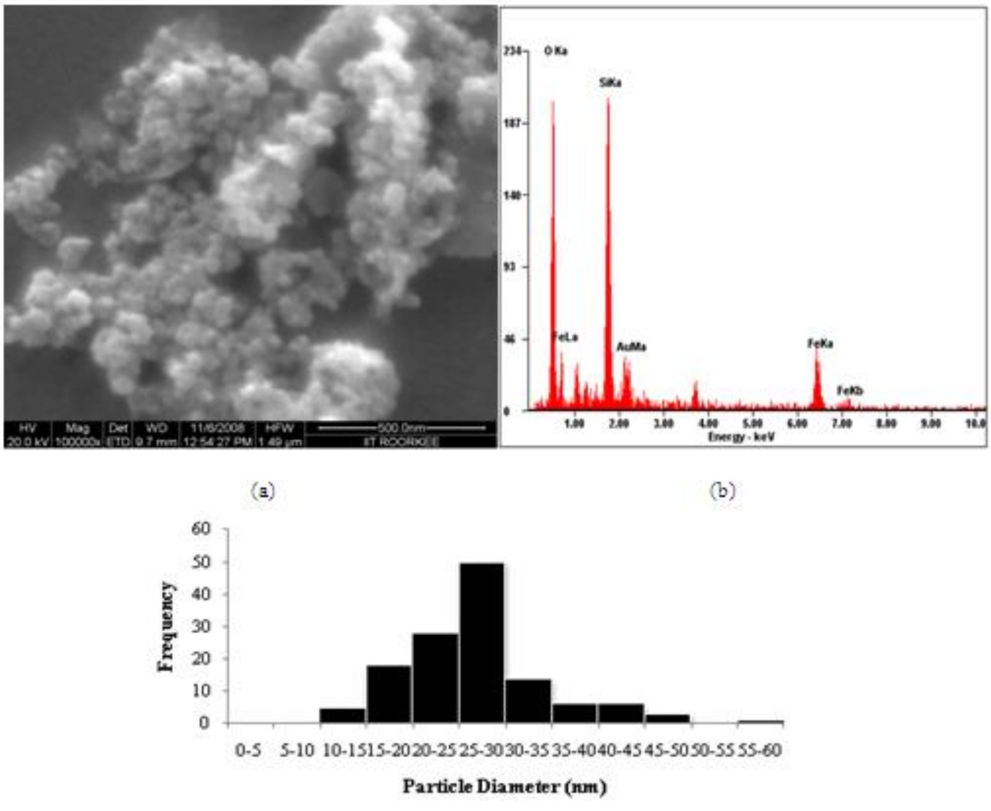
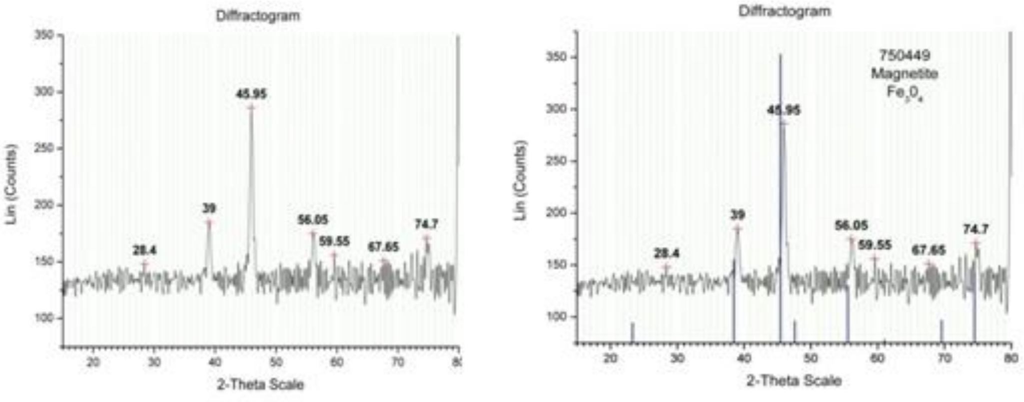


Fig. 2. Original (a) and matched (b) XRD pattern of Fe_3O_4 nanoparticles with standard data base

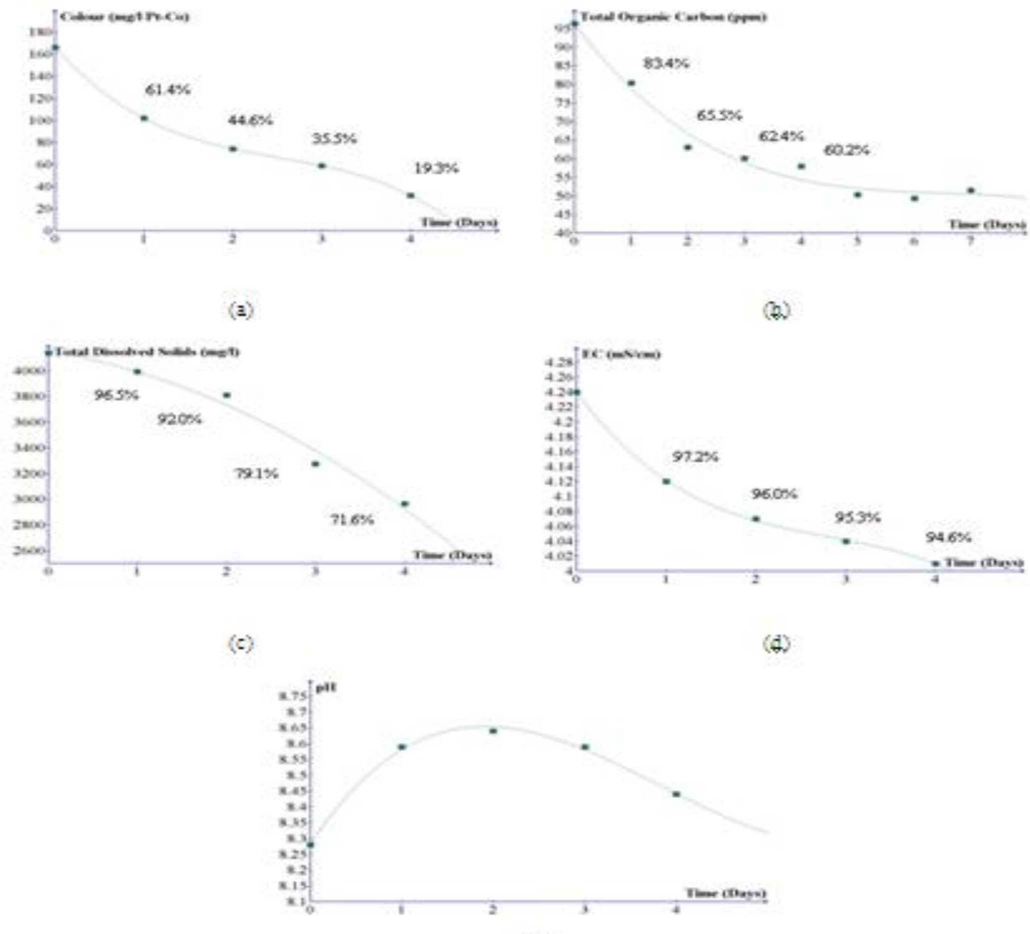


(a) (b)

The blue color lines in figure 2(b) show the peak positions and intensities as per the existing JCPDS, 1998 database. The diffractogram figure 2(a) matches completely with the JCPDF database number 750449 confirms the formation of cubic Fe_3O_4 (magnetite) nanoparticles. In this figure each peak position was found to be shifted by a constant 2-Theta value of 5 degree which may be due to some instrumental zero error. The mean crystallite size as evaluated using Scherrer's formula was found to be 18.10 nm. Further the unit cell edge and volume of cubic Fe_3O_4 nanoparticles were found to be 5.01875 Å and 126.41 Å^3 respectively.

The temporal variations in the values of color, TOC, TDS, EC and pH as obtained by the treatment of 100 mL of contaminated groundwater sample of the distillery with 0.22 g of freshly synthesized nanoparticles is graphically represented in figures 3a, b, c, d & e.

Fig. 3. Temporal variation in color (a), total organic carbon (TOC) (b), total dissolved solids (TDS) (c), electrical conductivity (EC) (d), pH (e), upon treatment of 100 mL of groundwater sample of the distillery with 0.22 g of freshly synthesized Fe_3O_4 nanoparticles



(a) (b) (c) (d) (e)

Among all the five parameters monitored during the course of the reaction, a large falloff in color was observed. Figure 3a shows that the value of color decreased to ~ 20% in four days. A sharp drop in color from 166 to 32 mg/l Pt-Co units was observed. Even remarkable decline in the TOC as well as the TDS values were also observed during the period as shown in figure 3b & c. The TOC values dropped down to 60% in four days. The EC values reduced from 4.24 to 4.01 mS/cm as shown in figure 3d, which is not to a significant extent. On the other hand the variation in pH values is not astonishing still a small maxima was obtained during the reaction track. Negligible variation in pH values indicates that the adsorption phenomenon was dominant during the course of the treatment.

The high values of color, TOC and TDS in the groundwater sample of the distillery is due to the presence of organic hydrocarbons generated during the fermentation of molasses into ethyl alcohol. The decline in the values of color, TOC, TDS and EC upon addition of freshly synthesized Fe_3O_4 nanoparticles to the sample is due to the adsorption of organic compounds on their large surface area. This fact has been proved by the above finds which shows the decline in the values of color, TOC and TDS to a remarkable extent. Thus, on the basis of exploratory experiments, it can be concluded that Fe_3O_4 nanoparticles may be used effectively for remediation of the contaminated groundwater of such distillery. Comparative performance evaluation with conventional adsorbents along with study of adsorption kinetics is, however, continuing to validate the findings further.

Conclusions

The ability of nanotechnology to abate pollution production is just beginning to be explored and could potentially catalyze the most revolutionary changes in the environmental field. There is no doubt in saying that the quality of groundwater is decreasing day by day and there is an immense need for adopting a new and advanced technique for the remediation of groundwater as a whole. Hence the search for new and advanced materials as stated in this paper is an important task of contemporary research in the field of environmental protection. The application of Fe_3O_4 nanoparticles for remediation of distillery contaminated groundwater may provide a new direction. New technologies may be implemented making use of such nanomaterials which are easy to synthesize and handle.

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