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Removal of Nitrogenous Heterocyclic Compounds (NHCs) by Nano Zero Valent Iron

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Abstract: In this study, the low-cost composite, nano-zerovalent iron (nZVI) immobilised on granular activated carbon (GAC) was prepared by using the NaBH₄ reduction method at ethanol atmosphere. The morphology, structure, and composition of nZVI-GAC are studied by scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and BET surface area. The presence of support material apparently decreased the extent of aggregation and the size of the nanoparticles thus increases removal efficiency. Batch experiments revealed that nZVI -GAC exhibited an efficient removal of NHCs and by-products could be completely adsorbed onto the composite. Accordingly, it is believed that nZVI -GAC developed in the present study is practically applicable for the NHCs contaminated wastewater.

Keywords: Nitrogenous Heterocyclic Compounds; Nano Zero Valent Iron.

1. Introduction

Nitrogen heterocyclic compounds are common species found in wastewater effluent, typically from pharmaceutical, coal tar, oil shale, petroleum refinery, and it serves as raw material and solvent in manufacture of dyes, pharmaceuticals, paints, fungicides, and wood treatment chemicals. These NHCs includes pyridine, picoline, lutidine, quinoline, etc. and have paid more attention recently, because of its persistence in the environment and their toxic and carcinogenic potential^{1,2}. The Nitrogen atom has incorporated in the ring system which distinctly enhanced the solubility of water. Thereby, the bio-availability is increased with a hasten risk to the environment. Earlier studies show that the traditional technologies (i.e., Biological, physical, and chemical methods) are used for the treatment of NHCs effluents^{3,4} and limited success has been achieved because, these processes are less effective for very stable refractory and toxic compounds. Hence, there is an urgent need for the development of a technology which shall be effective in degradation of NHCs to innocuous end products at a reasonable and acceptable cost.

In current years, Environmental Nanotechnology based treatments are receiving much attention due to their high selectivity, reactivity, low cost and environmentally benign nature. Numerous nano materials have been applied in abatement of contaminants, among that nano zero valent iron (Fe⁰) has been progressively used in the last decade for degradation of chlorinated organic compounds⁵, Nitro compounds⁶, herbicides⁷, pharmaceuticals⁸ and explosives⁹. Furthermore, Fe⁰ has been proven to be effective in eliminating a broad range of pollutants. There are still technical challenges associated with this application. For example, nZVI is rapidly oxidized with exposed to air loses its high reactivity. Besides, nZVI particles tend to agglomerate into particles due to the

high surface energy and intrinsic magnetic interaction which results in the decrease of surface area, mobility and reactivity. To conquer these issues support materials are used in literature. GAC (Granular Activated Carbon) is the most viable option due to its high sorption capacity, high surface area, porous structure and relatively low cost.

In this paper, a novel composite nZVI/GAC composite was synthesized using waste coal based granular activated carbon by chemical reduction method. The synthesized composite (nZVI/GAC) was characterized and employed for the removal of NHCs in aqueous solution.

2. Materials and Methods

3.1 Materials

Ferrous sulfate heptahydrate (SD fine chemicals India), sodium borohydride (Sigma Aldrich), ethanol (SD fine chemicals India), granular activated carbon Calgon Filtrasorb 400 (F400) and Quinoline (99% purity) was purchased from Lobial Chemie and Millipore water were used in this study.

3.2 Synthesis of nZVI/GAC

From the supported literature, the synthesis of nZVI-GAC is based on borohydride reduction of Fe (II) at ethanol atmosphere¹⁰. The synthesis of nZVI /GAC follows successive steps. First, GAC was cleaned with deionized (DI) water and heated, then washed with deionised water and dried overnight at 120°C. Thereafter, FeSO₄.7H₂O was dissolved in a 4/1 (v/v) ethanol/water mixture. Second, the GAC was added to the Fe (III) solution sonificated for 15 minutes to disperse the GAC grains. Third, to reduce Fe (III) to zero valent iron, NaBH₄ was prepared and added slowly to mixture. The mixture was left for another 10 minutes after the addition of the entire borohydride solution. The solution obtained was separated by centrifugation, filtration and washed with copious amount of ethanol. Finally, oven dried at 50°C over night. Then solid materials were stored for further use. The reduction of iron ions by borohydride ions can be represented by the below reaction:

$$\operatorname{Fe}_{(aq)}^{+2} \operatorname{or} \operatorname{Fe}_{(s)}^{+2} / \operatorname{GAC} + 2\operatorname{BH}_{(aq)}^{-4} + 6\operatorname{H}_{2}\operatorname{O}_{(1)(aq)} \rightarrow \operatorname{Fe}_{(s)}^{0} + \operatorname{Fe}_{(s)}^{0} / \operatorname{GAC} + 2\operatorname{B}(\operatorname{OH})_{3(aq)} + 7\operatorname{H}_{2(g)}^{+} \uparrow - (1)$$

In the reaction, $Fe_{(s)}^{+2}/GAC$ indicate iron ions attached to a GAC surface, $Fe_{(s)}^0/GAC$ refers to nZVI dispersed on GAC, $Fe_{(s)}^0$ denotes for nZVI retaining its chain-like structure.

3.3 Batch Experiments

The requisite amount of nZVI-GAC was added to the quinoline aqueous solution in Conical Flasks. During the treatment, the flasks were stirred within the orbital shaker (Remi Instruments, Mumbai). The flasks were withdrawn at constant time (7h) and supernatant solution was analysed. The analysis was carried out in a UV/VIS spectrophotometer (DR500, USA). The amount of quinoline removal was calculated as:

% Removal = $\frac{C_{o} - C_{f}}{C_{o}} \times 100 - -(2)$

3.4 Characterization of nZVI-GAC

The crystal structure of the composite were determined by Powder X-ray diffraction (XRD) using Cu-K radiation (= 0.154 nm). The scanning angle (2) range was 10 to 90° and Goniometer speed was kept at 2° min⁻¹.

The BET surface area was obtained from nitrogen adsorption isotherms at 77.15 K using an ASAP 2020 analyzer (Micromeritics, USA).

The morphology of composite was observed with aid of Scanning Electron Microscopy (SEM).

4. Results and discussions

4.1 Characterization

The XRD pattern of nZVI-GAC was shown in Figure 1. The characteristic peak of 2 = 44.57 was assigned to (1 1 0) reflections of the ZVI with a body centered cubic (bcc) structure¹¹. In addition to that a weak bands around $2 = 26.9^{\circ}$ which was deviation of the baseline indicated to the amorphous carbonaceous structure of organic matrix¹².

The morphology of GAC and nZVI-GAC were depicted in Figure 2. It is clearly indicated that chain like agglomerates are formed on the surface of GAC attributed to the high surface energy and intrinsic magnetic interaction of nZVI¹³. The introduction of granular activated carbon material increased the dispersity on the surface.

The BET surface area of GAC, and nZVI-GAC were 273.02 m^2/g , 240.55 m^2/g respectively can be seen in Table1. The decreases in surface area of nZVI-GAC likely to ensured the entry of Fe⁺² within the pores, that can be reduced by NaBH₄ solution to generate nZVI⁵.

4.2 Effect of Dose

The effect of nZVI-GAC on the removal efficiency was investigated at pH= 5, $C_0=100$ mg/l and T= 303K. The degradation pattern was increased for all samples with different amounts such as 1, 2.5, 5, 7.5 and 10 g/l the removal efficiencies were found to be 14.1, 55.6, 82.2, 92.8, and 98.4 % shown in the Figure 3. When the dose of nZVI-GAC was increased, the total surface areas and the active sites were increased respectively for fixed quinoline molecules in aqueous solution. As a result, higher removal efficiency can be obtained. For the first 5 *h* of reaction, the degradation of quinoline was hasty. As the reaction progresses, the gradual oxidation on the surface of nZVI formed a passivated layer, which covered some reaction sites⁸. This may possibly decrease the removal efficiency of quinoline with respect to time. The respective dose was employed in further studies.

4.3 Effect of Initial Concentration

Initial concentrations of quinoline 50, 100, 300 and 500 mg/l were studied the removal efficiency for each concentration is shown in Figure 4. The removal efficiency were decreased attributed to fact that the fixed dosage of nZVI, increasing concentration of quinoline may lead to pack onto the nZVI surface thus blocked the surface for further contact and preventing the release of the continuously generated hydrogen⁸. It can be found that 100 mg/l was higher removal efficiencies compare to the other concentrations. The same concentration was used in subsequent studies.

4.4 Effect of Temperature

The influence of temperature in the range of 293-323 K on the removal efficiencies of quinoline is shown in <u>Figure 4</u>. It may be seen that increase in temperature accelerates the percentage removal of Quinoline. The Quinoline removal was 88.4% at 293K and increased to 99.0% at 323K. This may be attributed to an increase in temperature, the mobility of quinoline molecules increases, thus increase the removal efficiency of quinoline bearing wastewater.

5.Conclusion

The low cost waste coal based granular activated carbon was utilized in synthesizing nano zero valent iron at ethanol atmosphere. The S_{BET} of GAC and nZVI-GAC were 273.02 m^2/g and 240.55 m^2/g , respectively. The removal of quinoline by nZVI-GAC may contain two processes namely; degradation process and adsorption process. Batch experiments showed that the synthesized composite is practically applicable for removal of NHCs contaminated water.





Figure 1: a) Granular Activated Carbon (GAC)





Figure 2: Wide angle powder X-ray Diffraction patterns of nZVI-GAC

Surface Area (m^2/g)			Pore volume (cm^3/g)			Pore size Å		composite
S _{BET}	Micro	BJH	Total	Micro	BJH	Avg	BJH	
273.02	165.78	109.4	0.162	0.0865	0.0788	23.28	28.3	GAC
240.55	149.77	91.77	0.140	0.0076	0.0644	23.98	28.5	nZVI-GAC

Table 1. BET surface area and pore volume of the GAC and nZVI- GAC.





Figure 3: Effect of dose (g/l) on % Removal of quinoline at C_o=100 *mg/l*, pH=5, Time= 8*h* and T=303K.

Figure 4 : Effect of Initial concentration on % Removal of quinoline at pH=6, Dose =7.5 g/l, Time= 8h and T=303K



Figure 5: Effect of Temperature on % Removal of quinoline at pH=6, $C_0=100 \text{ mg/l}$, m =7.5 g/l and Time=8h.

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