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Analogy of iron-copper and iron-silver bimetals during the corrosion process

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Abstract: *Because of their strong magnetic properties, the Fe based nanomaterials have successfully been used in order to remediate environmental contamination. The synthesis of the bimetallic nanoparticles was done following chemical reduction of ferric chloride with sodium borohydride then deposition of the respective bimetal. This study was conducted to determine the concentration influence on the dissolution of iron in the presence of the bimetallic nanoparticles along with determining the role of FeCu and FeAg bimetals during iron corrosion. The results showed that the higher the dosage, the higher the iron dissolution due to increased surface area hence reactivity. Also, the bimetals improved the reactivity of iron.*

Keywords: Nanoscale Zero Valent Iron (NZVI); Bimetal; Dissolution; Oxidation.

1. INTRODUCTION

The quality of air, soil and water has currently been depleted by human development activities such as industrialization which exposes contaminants to the environment [1]. Because of their strong magnetic properties, the Fe based nanomaterials have successfully been used in order to remediate environmental contamination [2]. Particularly, Nanoscale Zero-Valent Iron (NZVI) has proven to be the most effective and increasingly used nanomaterial due to adsorptiveness, high reactivity as a result of surface area exposure, eco-friendliness as well as cost-effectiveness [1, 3]. NZVI has a capability of contaminant removal through sorption, precipitation, complexation and surface reduction [4, 5, 6, 7]. However, the performance of NZVI has been limited by the nanoparticles' agglomeration influenced by high surface energy charges, as a result, metal-doped nanoparticles have successfully been used in order to solve this problem. The properties of metal-doped nanoparticles include enhanced reactivity owing to minimized oxidation and improved reduction due to physical properties' alteration [3, 8]. In terms of characterization, Scanning Electron Microscopy (SEM) is used to analyze the size and structure of the nanoparticles whereas the elemental composition and crystal structure are analyzed using the Transmission Electron Microscopy with Energy Dispersive X-ray (TEM-EDX) and X-ray diffraction (XRD) respectively [9]. The method of chemical reduction of ferric chloride using sodium borohydride was used to synthesize NZVI, FeCu and FeAg nanoparticles in this study and the effect of concentration on the nanoparticles' reactivity as well as the role of the bimetals during reactivity were studied.

2. MATERIALS AND METHODS

2.1 Materials

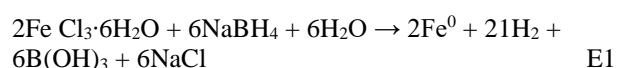
The NZVI nanoparticles were synthesized using Ferric chloride (FeCl₃), Sodium borohydride (NaBH₄) whereas the bimetals were correspondingly synthesized using silver nitrate and copper (II) chloride. FerroVer and Ferrous reagents were used for total iron and ferrous ions analysis respectively. Nitrogen gas (N₂) was purged in

the Deionized (DI) water to maintain anoxic conditions and the pH was adjusted using 0.1M HCl, 5M NaOH.

2.2 Synthesis procedure

2.2.1 NZVI nanoparticles synthesis

Two solutions of 200ml and 100ml deoxygenated (10 minutes N₂ purging) DI water that was respectively mixed with 5g ferric chloride (FeCl₃) and 2.2g sodium borohydride (NaBH₄) were prepared. Inside a 500ml round bottom flask with 4 holes which was immersed in a 30°C water bath, the sodium borohydride solution was added dropwise (pump speed 10 RPM – 16 ml/min) to the ferric chloride solution and the continuous N₂ purging as well as vigorous overhead stirring (400 RPM) conditions were maintained. The reaction was given 5 minutes aging time after which the synthesized nanoparticles were filtered, washed with 250ml deoxygenated DI water then vacuum dried for about 20 minutes. The reaction involved in the synthesis of NZVI is according to E1 [10]:



2.2.2 NZVI bimetallic nanoparticles synthesis

With respect to the aforementioned NZVI synthesis procedure, the respective FeCu and FeAg bimetallic nanoparticles were synthesized through the addition of 1% (wt/wt) CuCl₂, and AgNO₃ into reactor immediately after 5 minutes aging time and the reaction was allowed to further proceed for the following 30 minutes. The synthesized nanoparticles were therefore filtered, washed with 250ml deoxygenated DI water then vacuum dried for about 20 minutes and stored in a N₂ rich atmosphere to avoid oxidation. The main process involved in the formation of bimetallic nanoparticles is reduction then deposition and E2-E3 represent the overall equations involved [10, 11]:



2.3 Batch experiments

The 300ml Erlenmeyer flasks with three-hole, valve controlled stoppers were used as the batch experiments reactors. The activity of the bimetallic nanoparticles concentrations of 1g/L, 2g/L, 3g/L was studied. The initial conditions of the batch experiments were: pH 7, 200ml DI water, anoxic condition (10 minutes N₂ purging), 25°C temperature and the system was kept closed throughout. The sampling time was during the first 3 hours where the first sample was taken within the first 10 minutes of the reaction whereas the rest of samples were taken within the at the 30 minutes' interval since the commencement of the experiment. After 3 hours, the samples were taken daily for a duration of 7 days.

2.4 Analysis

The 5ml samples were withdrawn by the 10ml syringe pump after which they were filtered by 0.45µm syringe filters. The total iron and ferrous iron content were analyzed using UV-visible spectrophotometer (DR 3900, Hach Co., USA). Before analysis, the samples were diluted and their pH was adjusted in accordance with the spectrophotometer requirements. FerroVer and ferrous ion reagents were used to analyze the total iron and ferrous ions respectively.

3. RESULTS AND DISCUSSION

3.1 Nanoparticles' concentration

The results of three concentration ranges (1g/L, 2g/L and 3g/L) are shown in Fig. 1. It can be noted from the results that the total iron concentration was recorded during the first 3 hours at 30 minutes' interval with the exception of the first sample that was take within the 10 minutes' period of the reaction then the rest of the results were recorded for the overall period of 7 days (168 hours) at the 1 day (24 hours) interval. Fig. 1a shows the results of FeCu bimetal where the 3g/L dosage resulted in the highest iron concentration with the maximum concentration of 32.08mg/L during the first 10 minutes of the reaction followed by the rapid decrease up to an equilibrium state at around 1 hour. The total iron concentrations of 2g/L and 1g/L followed a similar trend to that 3g/L with respective maximum values of 8.05g/L and 7.67g/L during 10 minutes' interval. After 24 hours, all the total iron concentrations increased to 6.74mg/L, 12.46mg/L and 9.04mg/L in respective dosages of 1g/L, 2g/L, 3g/L, however, the concentration of 2g/L surpassed that of 3g/L after 24 hours due to rapid precipitation and aggregation of nanoparticles. Regarding FeAg nanoparticles (Fig. 1b), the maximum total iron concentration was still attained at 10 minutes' period in all the dosages of 3g/L, 2g/L and 3g/L respectively after which equilibrium were reached around 1 hour. Similarly, the concentrations in all the dosages increased at 24 hours' period before the second equilibrium state was attained.

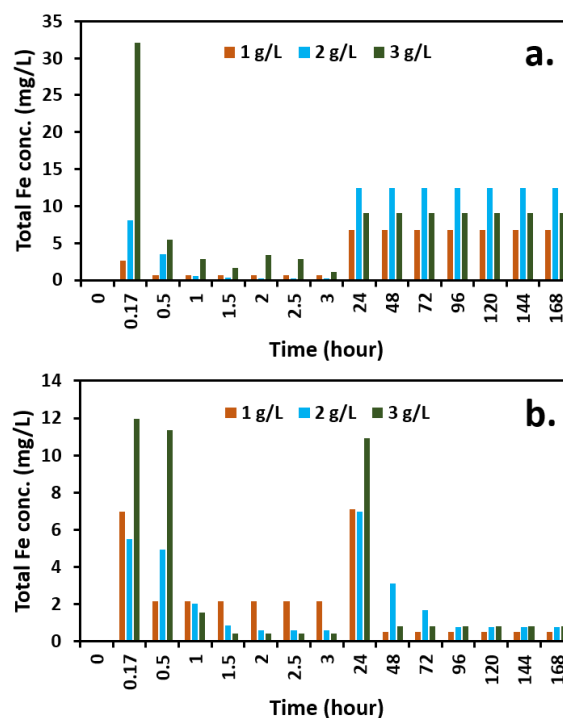


Fig. 1: FeCu (a) and FeAg (b) dosage for 168 hours (7 days) [Conditions: dosage = (1, 2, 3) g/L, anoxic condition, temperature = 25°C, pH = 7]

The NZVI alone during the period of 3 hours (Fig. 2) also showed a similar trend where the concentration of 3g/L attained the greatest dissolution of iron followed respectively by 2g/L and 1g/L. In overall, it can be noted from all the nanoparticles' results that the highest concentration of total iron was generally attained in the 3g/L dosage because of the increased number on nanoparticles that avail the surface area hence the active sites for reaction thus increasing the iron concentration [12]. The governing equations involved during the dissolution of iron are E4-E7 whereas those attributed to precipitation process are with respect to E8-E9 [5, 10, 13].

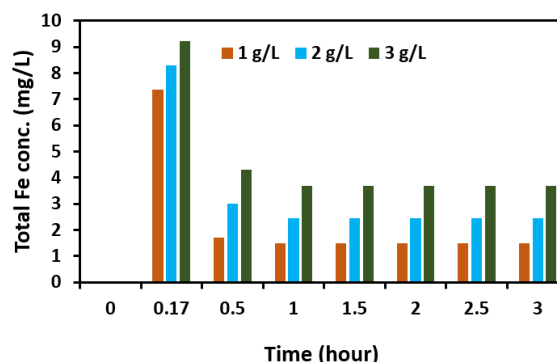
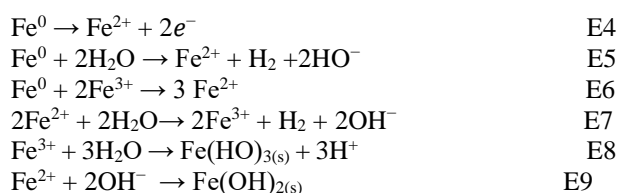


Fig. 2: NZVI dosage for 168 hours (7 days) [Conditions: dosage = (1, 2, 3) g/L, anoxic condition, temperature = 25°C, pH = 7]

3.2 The role of bimetal

Although all the results revealed that the respective trend of iron dissolution from highest to lowest under similar conditions was according to 3g/L, 2g/L and 1g/L for all the nanoparticles, it is evident that the highest dissolution was attained by the bimetallic nanoparticles (Fig. 1a and b) whereas the least was attained by NZVI alone (Fig. 2). Therefore, taking 3g/L for instance, the highest total iron concentrations of 9.22mg/L, 11.98mg/L and 32.08mg/L were correspondingly accomplished by NZVI, FeAg and FeCu particularly within the first 10 minutes of the reaction. Thus it is clear that the dissolution of iron was increased in the presence of the bimetallic nanoparticles where FeCu showed the best performance. According to the corresponding explanation, the bimetallic nanoparticles play a role in increasing the surface area thus reactivity as well as immobilizing the nanoparticles through the creation of a discontinuous layer that disconnects the nanoparticles [14]. As a result, the bimetallic nanoparticles act as reaction catalysts that increase the reduction process [3, 8].

4. CONCLUSIONS AND RECOMMENDATIONS

The higher the dosage of the bimetallic nanoparticles, the higher the iron dissolution. Furthermore, bimetallic nanoparticles increase the reaction process due to their catalytic nature. In comparison, FeCu bimetallic nanoparticles attained the highest iron dissolution as opposed to FeAg bimetallic nanoparticles and NZVI. Generally, the reactivity is improved in the presence of the bimetal. It must be noted however that although the highest dosage of the nanoparticles leads to increase reactivity, too much of it in the real-life application might result in environmental toxicity hence its application must be with respect to the water standard limits.

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