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Exploration of optimum conditions for reduction of nitrobenzene by Fe (II)/Iron Mud System

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ABSTRACT

In this paper, nitrobenzene was taken as target object under research, and iron mud generated in production of nitrobenzene compound by iron powder reduction method was used as carrier to discuss the possibility that Fe (II)/iron oxide surface-bound iron system generated by iron mud load Fe (II) reduces nitrobenzene, and research effects of pH, reaction temperature, reactant concentration and iron mud use level etc on nitrobenzene reduction degree, and explore optimum conditions for reduction of nitrobenzene by Fe (II)/iron oxide surface-bound iron system.

Keywords: Iron mud, Fe(II)/iron oxide surface-bound iron system, nitrobenzene reduction

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INTRODUCTION

Currently, methods for reducing nitrobenzene to phenylamine mainly include iron powder reduction method, electrochemical reduction method and catalytic hydrogenation etc[1-2]. Iron powder reduction method is characterized by low requirement for purity of raw materials, easy control of production, few byproducts and low costs etc; however, iron powder reduction process gives rise to a great deal of iron mud and organic wastewater, while as such mud is discharged, their stockpiling and landfilling, if conducted, entails certain problems[3] and causes severe environmental pollution; main ingredients of iron mud are iron oxide, zero-valent iron and a great quantity of organic impurities[4]; Fe (II)/iron oxide surface-bound iron system generated by iron mud load Fe (II) is adopted to reduce nitrobenzene compound and enable development and utilization of iron mud, which has relatively high possibility.

The author took nitrobenzene as target object under research and used iron mud generated in production of nitrobenzene compound by iron powder reduction method as carrier to research optimum conditions for reduction conservation of nitrobenzene by Fe (II)/iron oxide surface-bound iron system, which is of great significance for comprehensive utilization of energy, energy conservation, emission reduction and environmental protection.

MATERIALS AND METHODS

1.1 Main reagents and instruments

1.1.1 Reagents

Ferrous sulfate heptahydrate, reduced iron powder, nitrobenzene, methanol, sodium hydroxide, sulfuric acid (all of the above reagents are analytically pure)

1.1.2 Instruments

Direct current motor (100w), two-way constant temperature magnetic stirrer (85-2A), high power electric stirrer (JJ-2), high performance liquid chromatograph (LC2000), electronic scale, pH meter (PHSJ-3F)

1.2 Test method
This test was conducted by taking nitrobenzene as target object under research, and successively adding iron mud, ferrous sulfate solution, certain volume of nitrobenzene into flask with four necks, and controlling pH within specified range, using thermostat water bath to control reaction temperature as well as carrying out under stirring and aerobic conditions. After reaction lasted for 30min, high performance liquid chromatograph was adopted to analyze and test unreduced nitrobenzene in reduction product.

1.3 Analytical method
Nitrobenzene and its degradation product were determined by high performance liquid chromatograph (LC200); C_{18}HPLC chromatographic column (column temperature: room temperature; column length: 150nm-200nm; inner diameter: 4mm) and diode array detector were used; mobile phases were methanol and water (volume ratio: 55:45); flow rate was 1.0mL/min; detection wavelength was 256nm; sample size was 20μL; before sample introduction, 0.45μM cellulose filter membrane was used to filter out insoluble matters. Time for peak flowing out was 6.83min.

1.3.1 Plotting of nitrobenzene standard curve:
Preparation of nitrobenzene stock solution: 0.1mL nitrobenzene was transferred by pipette to 100mL volumetric flask; methanol was used to achieve constant volume for preparing 1.2g/L stock solution.

Preparation of nitrobenzene solution standard series: 0.1mL, 0.2 mL, 0.3 mL and 0.4 mL stock solution was transferred to 25mL volumetric flask and constant volume was achieved with water, resulting in nitrobenzene standard solution with mass concentration 4.8mg/L, 9.6 mg/L, 14.4 mg/L and 19.2 mg/L; curve is plotted by peak areas measured by liquid chromatograph and mass concentrations of nitrobenzene; nitrobenzene standard curve is shown below:

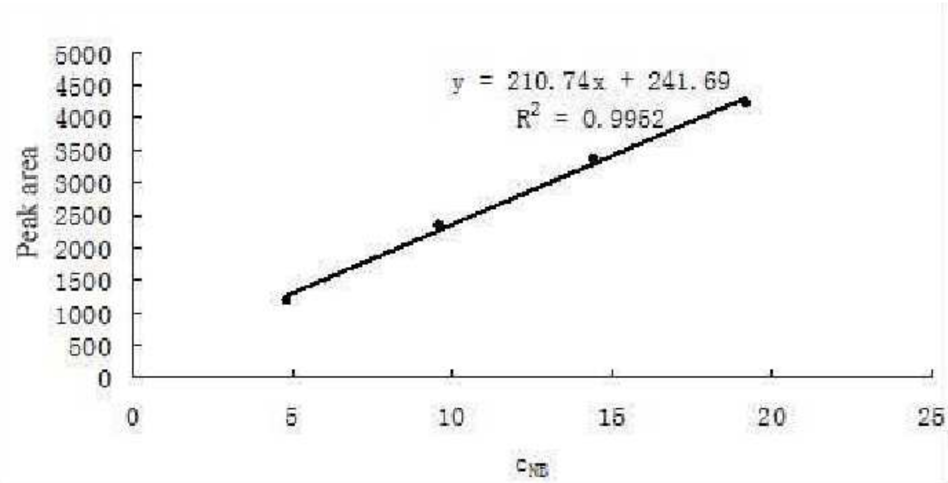

Diagram 1 Nitrobenzene standard curve

1.3.2 Data processing
Reduction degree = (initial mass of nitrobenzene before reaction – mass of nitrobenzene contained in filtrate after reaction) / initial mass of nitrobenzene before reaction

2 Test result and analysis
Iron mud load Fe (II) was used to catalytically reduce nitrobenzene to phenylamine; its reduction degree was affected by many factors. In this paper, effects of nitrobenzene concentration, pH, reaction temperature and iron mud use level etc on nitrobenzene reduction degree were researched; optimum conditions for reduction of nitrobenzene by Fe (II)/iron oxide surface-bound iron system, and possibility of application of iron mud in practical production were discussed.

2.1 Effect of nitrobenzene concentration on test
In this test, temperature=55℃, PH=7, iron mud/Fe (II) amount-of-substance ratio was 1:1, and Fe (II)/nitrobenzene amount-of-substance ratio was 2:1; initial concentration of nitrobenzene was changed; result is shown below:

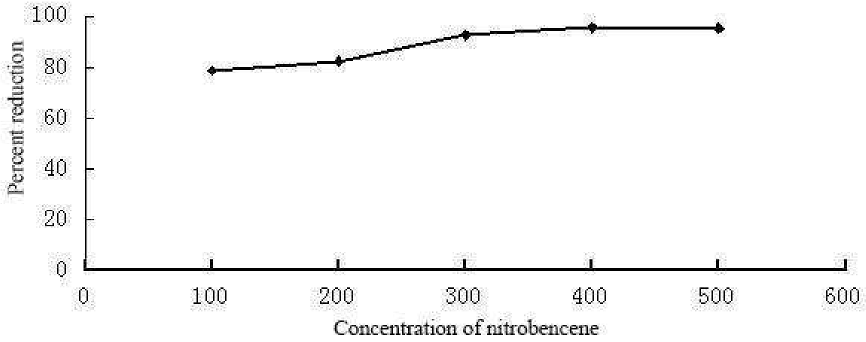

Diagram 2 Effect of nitrobenzene concentration on reduction degree

As shown in Diagram 2, there was relatively great effect of initial concentration of nitrobenzene on reaction; when dosage of nitrobenzene was 400 ppm, nitrobenzene reduction degree reached maximum 95.66%; when concentration was higher than 400 ppm, reduction degree was not significantly increased. Therefore, test was conducted by choosing nitrobenzene concentration as 400 ppm.

2.2 Effect of pH on test

Subject to other fixed testing conditions, pH=4-9 was chosen as research scope and effects of different pHs on reduction of nitrobenzene by Fe (II)/iron mud surface-bound iron system were researched; the result is shown below:

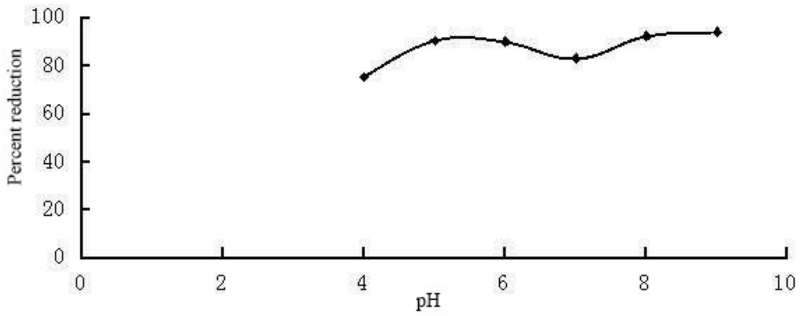

Diagram 3 Effect of pH on nitrobenzene reduction degree

According to research, pH had great effect on reducing capacity of Fe (II)/iron mud surface-bound iron system. As shown in Diagram 3, in Fe (II)/iron oxide surface-bound iron system, nitrobenzene reduction conversion rate increased with rising pH in solution. When pH=4, reducing capacity of the system was relatively low; when pH=7, reduction degree decreased possibly because iron oxide surface adsorption became saturated and surface sites were reduced along with reaction; when pH was higher than 8, Fe(II) would exist in the form of $Fe(OH)_2$ [5], further enhancing reducing capacity of the system and increasing nitrobenzene reduction conversion rate. Though reduction degree was higher when pH was 9, given that concentrated alkaline was extremely corrosive to equipment, pH=8 (reduction degree reached 96.1%) was chosen as optimum reaction condition for this test.

2.3 Effect of temperature on test

Effect of reaction temperature was examined in this test; result was shown in Diagram 4.

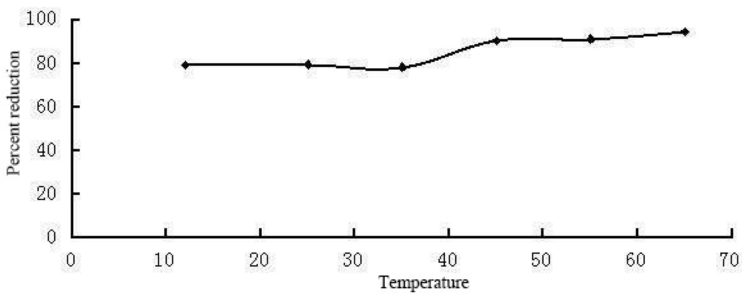

Diagram 4 Effect of temperature on nitrobenzene reduction degree

As shown in Diagram 4, nitrobenzene reduction degree increased with rising reaction temperature; however, nitrobenzene reduction degree did not greatly go up in the case of exceeding 65℃. Higher temperature does not necessarily result in better effect in practical industrial production. We chose 65℃ as optimum temperature by considering bearing capacity of equipment, funding and energy utilization etc.

2.4 Effect of iron mud use level on test

Effect of iron mud use level on reaction was researched in this test; result is shown below:

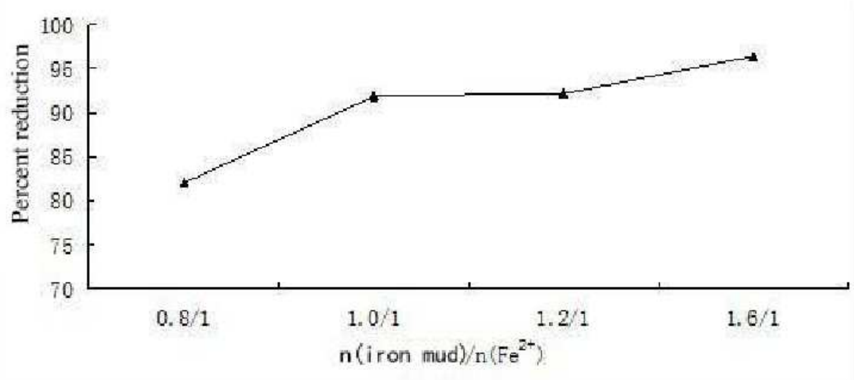

Diagram 5 Effect of iron mud use level on nitrobenzene reduction degree

As shown in Diagram 5, when iron mud/Fe (II) amount-of-substance ratio was 1.6:1, maximum degree of nitrobenzene reduction was achieved; as iron mud use level increased, nitrobenzene reduction degree decreased. Therefore, 1.6:1 was chosen as iron mud/Fe (II) amount-of-substance ratio. Nitrobenzene reduction degree reached 96.43%.

2.5 Effect of Fe (II) use level on test

In this test, 1:1～3.5:1 was chosen as Fe (II)/nitrobenzene amount-of-substance ratio, and effect of n(Fe^{2+})/n(NB) on nitrobenzene reduction degree was researched; result is shown below:

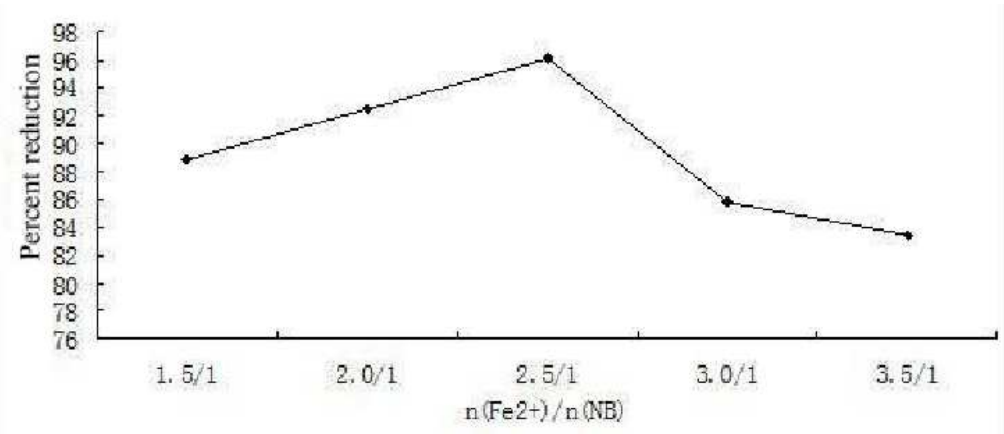

Diagram 6 Effect of ferrous sulfate heptahydrate use level on nitrobenzene reduction degree

As shown in Diagram 6, n(Fe^{2+})/n(NB) had certain effect on nitrobenzene reduction. When n(Fe^{2+})/n(NB)=2.5:1, nitrobenzene reduction degree reached maximum 96.08%, thus 2.5:1 was chosen as Fe (II)/nitrobenzene amount-of-substance ratio.

2.6 Effect of reaction time on test

In order to increase nitrobenzene reduction degree, reaction time was examined in this test in which nitrobenzene reduction degrees at different times were measured, as indicated below:

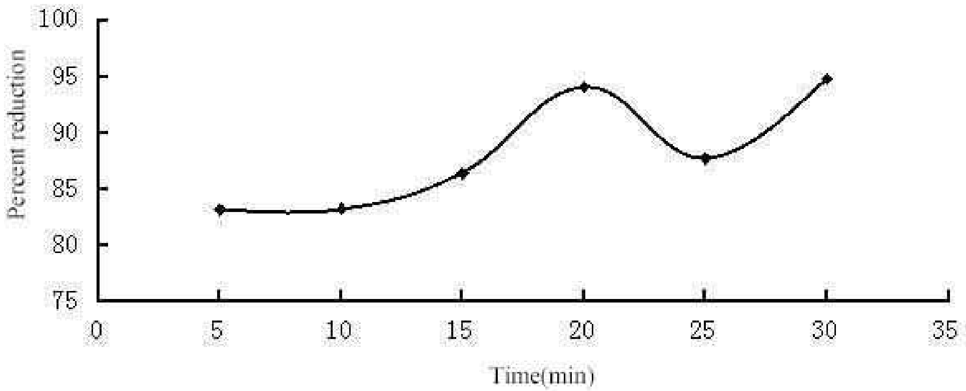

Diagram 7 Effect of reaction time on nitrobenzene reduction degree

As shown in Diagram 7, when reaction time was 25min and 30min, reduction degree was higher than 94%. Thus 20min was chosen as reaction time in this test.

2.7 Parallel test

In order to validate nitrobenzene reduction degree under optimum condition, we conducted five parallel tests; test result is shown below:

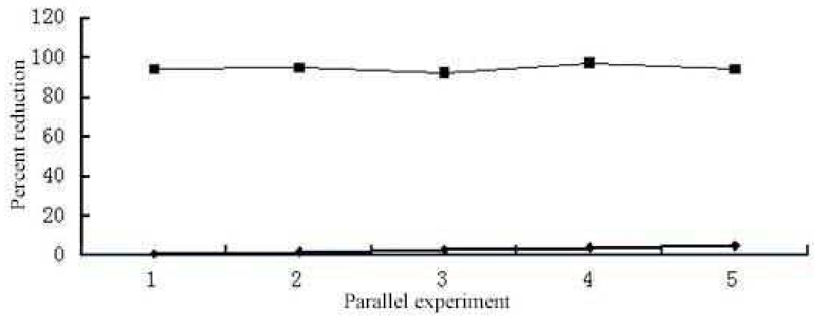

Diagram 8 Nitrobenzene reduction degree under optimum condition

As shown in Diagram 8, with five parallel tests, this curve was basically one straight line, and nitrobenzene reduction degree exceeded 90%. With small test and scale-up, experimental data were highly repeatable and stable, providing experimental basis for industrial clean synthesis of aromatic amine compounds.

CONCLUSION

We explored nitrobenzene concentration, pH, temperature, iron mud use level, Fe (II) quantity and reaction time, and found the following optimum reaction conditions: pH=8, T=65℃, nitrobenzene concentration was 400ppm, iron mud/Fe (II) amount-of-substance ratio was 1.6:1, Fe (II)/nitrobenzene amount-of-substance ratio was 2.5:1, reaction time was 20min, and nitrobenzene reduction degree exceeded 90% in five parallel tests.

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