Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(2):40-42

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Exploration on optimal conditions to reduce 3-nitrobenzene sulfonic acid with iron mud

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ABSTRACT

Based on research on production process of metanilic acid, a new idea of iron mud reducing nitrobenzene compounds was proposed, the optimum conditions to reduce 3-nitrobenzene sulfonic acid with iron mud were explored. In iron mud/Fe(II) reduction system, the main factors affecting the reduction of 3-nitrobenzene sulfonic acid are temperature, pH value, iron mud quantity, mass ratio between ferrous sulfate and the 3-nitrobenzene sulfonic acid, etc. The yield of metanilic acid is over 92% with temperature at 60°C, pH value at 8.0, iron mud quantity at 0.3g, and the mass ratio between ferrous sulfate and 3-nitrobenzene sulfonic acid at 1:1, which are the optimal conditions obtained by orthogonal experiment.

Key words: iron mud; 3-nitrobenzene sulfonic acid; metanilic acid; optimal conditions; yield

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INTROUDUCTION

In many chemical production processes, iron reduction of the nitro aromatic compound to amino compounds were widely used, but this process generated a large number of industrial waste - iron mud [1]. There are also serious problems for sludge treatment of iron mud either by stockpiled or landfilled. In consideration of current situation, chemists have made a lot of research for iron sludge utilization, and have achieved many significant results, such as using iron mud as raw material to prepare ferrous sulfate, iron oxide dyes, PFS and poly ferrotremolite, etc. Jeon et al [2] have proposed an IET's reaction model based on the interface between Fe^{2+} and Fe oxide. Klausen et al found that iron oxides combined with free state Fe(II) can quickly reducing nitro aromatic compounds, and named this reduction system as surface combined iron reduction system [3,4]. For adsorption theory, surface of iron oxide provides an adsorption Fe(II) sites and reaction place, adsorbed Fe (II) and hydroxyl in iron oxide surface form inner ligand [5-8], so that electron density in Fe(II) center is increased [9-11], and reducing capacity of the system is enhanced. Based on iron oxide/Fe(II) bound to the surface reduction mechanism, iron mud instead of zero-valent iron was used to reduce nitrobenzene sulfonic acid, which opened up new areas for iron mud application.

EXPERIMENTAL SECTION

1.1 Reagents
$FeSO_4 \cdot 7H_2O$, Fe, H_2SO_4, CH_3OH, $C_6H_5NO_2$, HCl (all are analytical reagents).
Iron mud (Cangzhou City Jianxin Chemical Co., Ltd.)

1.2 Instrument
pH meter (PHSJ-3F), Shanghai Precision & Scientific Instrument Co., Ltd.
Agilent HPLC (1260 lines), Agilent Science and Technology Ltd.

1.3 Procedure
Accurately weigh an amount of ferrous sulfate into a small dried beaker, add a rust removal nail, then start to stir

using a magnetic heating stirrer (HJ-1), until ferrous sulfate was completely dissolved. Add a certain amount of iron mud into a clean four-necked round-bottomed flask, stir by electric blender, place it to electric heated thermostatic water bath to heat the temperature to the rated value and activation for half an hour, then add 100mL of nitrobenzene sulfonic acid solution, adjust pH to the specified value. Keep the pH constant, and react for 20min. Centrifuge after reaction is finished. Filter the solution with vacuum suction filtration, to 500mL flask and make up the volume for further HPLC testing.

RESULTS AND DISCUSSION

For iron mud reduction nitrobenzene acid reaction, use the major effect reaction conditions-temperature, pH, the amount of iron mud, and mass ratio of ferrous sulfate/nitrobenzene sulfonic acid as study objects, respectively. Set temperature at 40°C, 50°C, and 60°C, iron mud taken 0.1g, 0.2g, 0.3g, pH at 7, 7.5, and 8, mass ratio of ferrous sulfate/nitrobenzene sulfonic acid as 2:1, 1:1, and 1:2. Select $L_9(3^4)$ orthogonal table to design experiment, factors and levels as well as experimental results of specific programs are shown in Table 1 and Table 2.

Table 1 Table of Levels and Factors

Level	Temperature/℃	pH	Iron Mud/g	Mass ratio of ferrous sulfate and 3-nitrobenzenesulfonic acid
1	40	7	0.1	2:1
2	50	7.5	0.2	1:1
3	60	8	0.3	1:2

Table 2 Conditions and Results of Each Experiment

Experiment	Temperature/℃	pH	Ratio	Amount	yield
1	40	7.0	2:1	0.1	62.26
2	50	7.0	1:1	0.2	61.49
3	60	7.0	1:2	0.3	27.71
4	40	7.5	1:2	0.2	25.74
5	50	7.5	2:1	0.3	72.26
6	60	7.5	1:1	0.1	79.48
7	40	8.0	1:1	0.3	80.30
8	50	8.0	1:2	0.1	24.46
9	60	8.0	2:1	0.2	85.70
K1	56.10	50.49	73.41	55.40	
K2	52.74	59.16	73.76	57.64	
K3	64.30	63.49	25.97	60.09	
R	11.56	13.00	47.79	4.69	

The yield of corresponding metanilic acid, was calculated by the corresponding peak area of target product analyzed by HPLC, brought into metanilic acid standard curve to obtain its concentration. Respectively dilute 0.40mL, 0.80mL, 1.20mL, 1.60mL, 2.00mL of metanilic acid standard solution (0.01mol/L) to corresponding concentration of 0.00016mol/L, 0.00032mol/L, 0.00048mol/L, 0.00064mol/L, 0.0008mol/L, use above data to obtain metanilic acid standard curve shown in Figure 1.

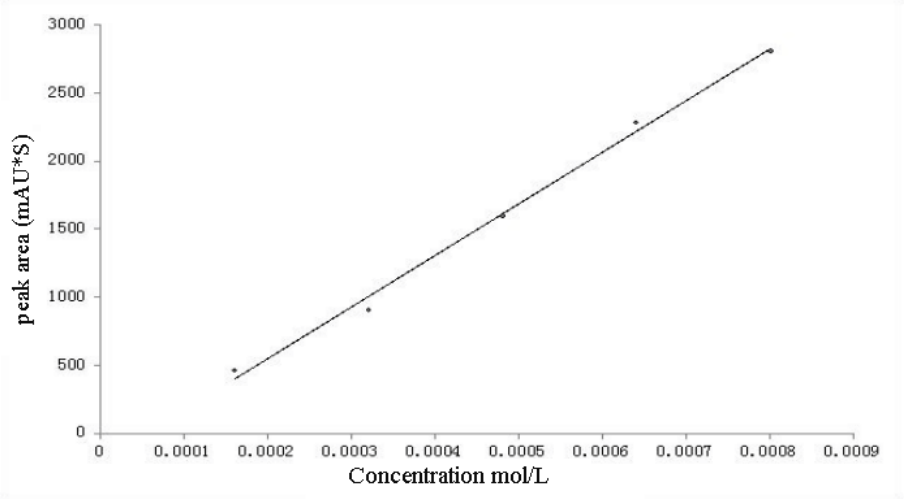

Figure 1 The standard curve of m-Aminobenzenesulfonic acid

The metanilic acid standard curve equation was: A=3.796×10^{6}C-207.78, correlation coefficient r = 0.9975. From the data analysis in Table 2, the optimum conditions of the reaction temperature is 60^{o}C, pH 8.0, the mass ratio of ferrous sulfate/m-nitrobenzene sulfonic acid 1:1, the amount of iron mud is 0.3g. Under these conditions, the average of yield of metanilic acid was maximized. Five parallel experiments were then carried out under such optimal conditions to obtain the yield of metanilic acid. Since yield under optimal conditions was generated on the basis of the results in the yield table, so when measure peak area of metanilic acid by HPLC, need to draw standard curve for twice. Respectively dilute 0.80mL, 1.20mL, 1.60mL, 2.00mL and 2.50mL of 0.01mol/L of metanilic acid to corresponding concentration of 0.00032mol/L, 0.00048mol/L, 0.00064mol/L, 0.0008mol/L, and 0.001mol/L, The standard curve of metanilic acid made from the above data was shown in Figure 2, standard curve equation: A = 4.744×10^6 C-839.41, the correlation coefficient r = 0.9993, which showed a good linear relationship.

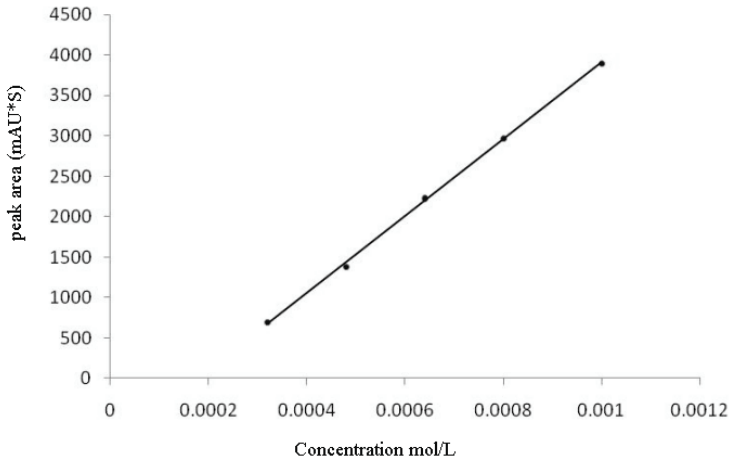

Figure 2 The standard curve of m-Aminobenzenesulfonic acid

Table 3 showed parallel experiment results for yield of metanilic acid under optimum conditions, it can be seen from Table 3, all yields of metanilic acid reached more than 92% and with good reproducibility.

Table 3 Parallel experiment results for yield of metanilic acid under optimum conditions

Experiment	1	2	3	4	5	average
Yield of metanilic acid	93.65	92.79	93.71	92.69	93.73	93.31

CONCLUSION

Based on studies on the optimum reaction conditions for iron mud reducing 3-Nitrobenzene Sulfonic Acid with orthogonal method, it was concluded that, in the reaction reducing 3-Nitrobenzene Sulfonic Acid by iron mud, when pH at 8.0, temperature at 60^{o}C, mass ratio of ferrous sulfate/3-nitrobenzene sulfonic acid as 1:1, amount of iron mud as 0.3g, the yield of metanilic acid can reach more than 92%, and with good reproducibility.

Acknowledgement
The project was financially supported by the science and technology project of Hebei Province，15213815

REFERENCES

[1] K Y Peng, *Xiangtan Chemical* .**1991**, 20 (1): 23-24.
[2] B H Jeon; B A Dempsey; W D Burgos, *Environmental Science technology*, **2003**, 37(15): 3309-3315
[3] J Klausen; S P Trober; S B Haderlein; et al, *Environmental Science Technology*, **1995**, 29(9):2396-2404.
[4] J Li; L Xie; J Sheng; etc, *Research Progress in Earth Science* .**2009**, 24, (1): 25- 32.
[5] L Tong; X J Bi; G B Tang, *Renewable Resources Research*, **2005**, 1: 28.
[6] S T Zhang; Y S Sun; X Chen; etc, *Environmental Protection*, **1997**, 8: 17.
[7] Y D Wang, *China Ocean University Journal*. **2006**, 5: 131.
[8] J H Fan; W Y Xu; T Y Gao; etc, *Environmental Pollution and Control*, **2005**, 27.
[9] J F Wei; D Q Wu, *Research Progress in Earth Science*, **2000**, (1): 90-96.
[10] X X Feng; S Wu; X K Wu, *Shanghai Environment Section Science*, **2003**, 22 (02): 109-111.
[11] State Environmental Protection Administration. Monitoring analysis methods for water and wastewater, 4th edition, China Environmental Science Press, Beijing, **2002**.