

**Biotechnology, Chemical
and Materials Engineering III**

Edited by
Wen-Pei Sung and Ran Chen



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Biotechnology, Chemical and Materials Engineering III

Edited by
Wen-Pei Sung
Ran Chen

Biotechnology, Chemical and Materials Engineering III

Selected, peer reviewed papers from the
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December 12-13, 2013, Hong Kong, China

Edited by

Wen-Pei Sung and Ran Chen



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Preface

2013 International Conference on Biotechnology, Chemical and Materials Engineering (CBCME 2013) will be held in HongKong during December 12-13, 2013. CBCME 2013 is sponsored by Hong Kong Control Engineering and Information Science Research Association (CEIS), International Frontiers of Science and Technology Research Association (IFST) and Trans tech publications inc. The aim is to provide a platform for researchers, engineers, academicians as well as industrial professionals from all over the world to present their research results and development activities in Biotechnology, Chemical and Materials Engineering.

In this conference, we received more than 400 submissions from email and electronic submission system, which were reviewed by international experts, and about 159 papers have been selected for presentation, representing 9 national and international organizations. This high level of interest truly reflects the worldwide importance of Biotechnology, Chemical and Materials Engineering.

I think that CBCME 2013 will be the most comprehensive Conference focused on the Biotechnology, Chemical and Materials Engineering. The conference will promote the development of Biotechnology, Chemical and Materials Engineering, strengthening the international academic cooperation and communications, and exchanging research ideas.

We would like to thank the conference chairs, organization staff, the authors and the members of International Technological Committees for their hard work. Thanks are also given to Trans Tech Publications.

We hope that CBCME 2013 will be successful and enjoyable to all participants. We look forward to seeing all of you next year at the CBCME 2014.

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CHAPTER 1:

Chemical Materials and Technologies

A Green Method for Synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidine Derivatives Catalyzed by [Hnmp]HSO₄ Ionic Liquid

Si-jie Liu^{a*}, Ran Zhou^b, Hong-kun Yue^c, Lan-xiang Shi^d

College of Chemical Engineering, Shijiazhuang University, Shijiazhuang 050035, People's Republic of China

^aliusijie1982@163.com, ^bhelly30072004@163.com, ^cyuehongkuna@163.com, ^dkedashilanxiang@163.com

Keywords: 5*H*-thiazolo[3,2-*a*]pyrimidine, [Hnmp]HSO₄ ionic liquid, Multi-Component Reaction, Green chemistry, Cyclization

Abstract. An efficient and green approach to the synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidine derivatives using N-methyl pyrrolidone hydrosulfate ([Hnmp]HSO₄) ionic liquid as the catalyst is described. This green catalytic system can be recycled several times without any substantial decrease in the yields and reaction rates. The catalyst loading are high.

Introduction

In recent years, ionic liquids have become a powerful alternative to conventional molecular organic solvents due to their particular properties, such as undetectable vapor pressure and the ability to dissolve many organic and inorganic substances [1]. Environmental consciousness promotes significant efforts to find an alternative reaction medium in green chemistry. Ionic liquids have been extensively tested as environmentally friendly solvents for a large variety of reactions [2].

In our foregoing work, 5*H*-thiazolo[3,2-*a*]pyrimidine were designed and synthesized, which showed inhibitory activity against acetylcholinesterase [3-5]. In continuation of our studies on the development of new routes for the synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidine derivatives using ionic liquids, we developed the synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidines **5** via the four-component condensation of aryl aldehydes **1**, acetylacetone **2**, thiourea **3** and 2-bromoacetophenones **4** in [Hnmp]HSO₄ as the solvent and promotor (Fig. 1).

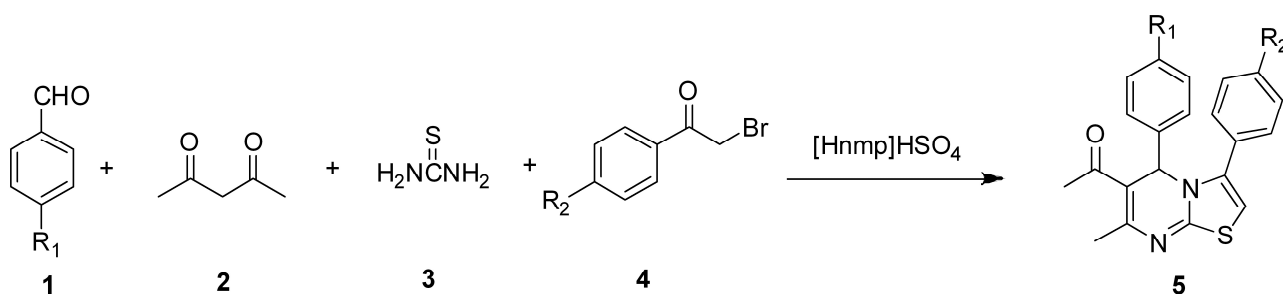


Fig.1. The synthetic route of 5*H*-thiazolo[3,2-*a*]pyrimidine derivatives

Results and Discussion

The reaction of 4-hydroxybenzaldehyde, acetylacetone, thiourea and 2-bromoacetophenone was selected as a model reaction to find an optimal loading amount of catalyst for the synthesis of **5b**, the amount of [Hnmp]HSO₄ was reduced from 0.8 to 0.1 equivalent. The results were collected in Table 1. Increasing the amount of [Hnmp]HSO₄ from 0.4 to 0.8 equiv., expected improvement in yield had not been observed. Thus, we chose 0.4 equiv. as an optimal amount of catalyst for further experiments.

Table 1. Results of varying the amount of [Hnmp]HSO₄ for the synthesis of **5b** in the solvent-free condensation at 80 °C

Entry	[Hnmp]HSO ₄ (mol%)	Time (h)	Yield (%)
1	10	2	58
2	20	2	78
3	40	2	90
4	60	2	90
5	80	2	91

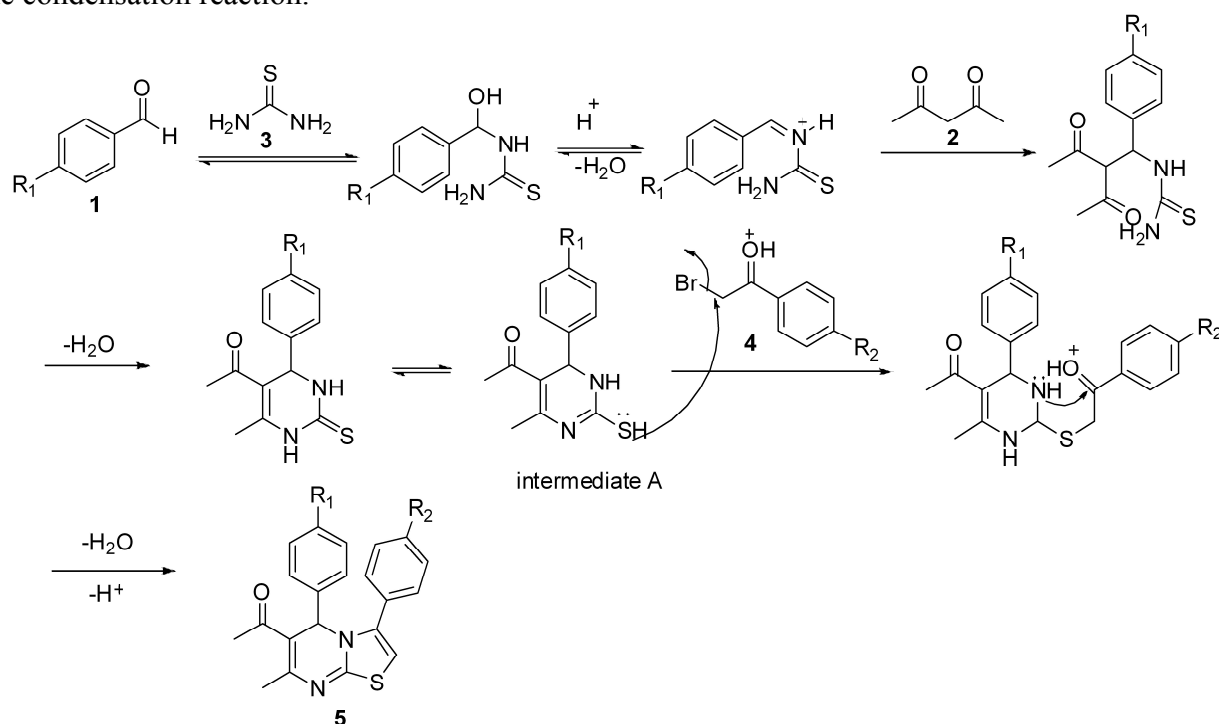
To explore the scope and limitations of this reaction, we extended it to various aryl aldehydes and 2-bromoacetophenones in the presence of [Hnmp]HSO₄. As indicated in Table 2, the reaction proceeds efficiently with all of them. One of the advantages of ionic liquids is their ability to function as a recyclable reaction medium. We were able to separate [Hnmp]HSO₄ from the reaction medium easily by washing with water, evaporating the solvent under vacuum, and reuse it for subsequent reactions (Table 2, **5e**).

Table 2. One-pot synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidines in 40 mol% [Hnmp]HSO₄ at 80 °C

Product	R ₁	R ₂	Time (h)	Yield (%)
5a	OCH ₃	OH	2	89
5b	OH	H	1.5	90
5c	OH	OCH ₃	2	85
5d	OH	CH ₃	2.5	88
5e	OH	Cl	2	93, 91, 87, 85 ^a

^a The same [Hnmp]HSO₄ was used for each of the four runs

The proposed mechanism for the synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidine is shown in Fig.2. The condensation of aryl aldehydes, acetylacetone and thiourea may occur by a mechanism of Biginelli reaction to produce intermediate A, which could not isolate. 5*H*-thiazolo[3,2-*a*]pyrimidine **5a-5e** are prepared by the Hantzsch-type condensation reaction between intermediate A and with 2-bromoacetophenones. It was suggested that [Hnmp]HSO₄ will act as an organic acid and promote the condensation reaction.

**Fig.2.** The proposed mechanism

Experimental

All reagents and solvents were purchased from common commercial suppliers and were used without further purification. All melting points were taken in open capillary tubes and the thermometer was uncorrected. The MS were obtained by electrospray (ESI) in a Waters spectrometer at 3.5kV spray voltage, acetonitrile was used for solvent. The IR spectra were determined using a Bruker AFS55 spectrometer. The NMR spectra were recorded in DMSO- d_6 solutions, using Bruker 400 MHz spectrometers.

General procedure for synthesis of 5*H*-thiazolo[3,2-*a*]pyrimidines. Aryl aldehydes **1** (1 mmol), acetylacetone **2** (1 mmol) and thiourea **3** (1 mmol) were mixed together in the presence of [Hnmp]HSO₄ (0.4 mmol), then stirred at 80 °C. An hour later, 2-bromoacetophenones **4** (1.1 mmol) was added. Upon the completion of the reaction, the reaction mixture was poured into water and the precipitate formed 5*H*-thiazolo[3,2-*a*]pyrimidines **5** was filtered, washed and crystallized from ethanol. The residue solution containing [Hnmp]HSO₄ was reused for subsequent reactions.

3-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-6-acetyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine (5a). Mp: 217-218 °C; ESI-MS (*m/z*): 394.1 (*M*+*H*)⁺; IR (KBr): 3441, 1629.06, 1383, 1252, 1176 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ: 7.28 (1H, s), 7.23 (2H, d, *J*=8.7), 7.07 (2H, d, *J*=8.7), 6.70 (2H, d, *J*=8.7), 6.57 (2H, d, *J*=8.7), 6.27 (1H, s), 4.02 (2H, m), 3.83 (3H, s), 3.65 (3H, s), 2.48 (3H, s), 1.09 (3H, t).

3-Phenyl-5-(4-hydroxyphenyl)-6-acetyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine (5b). Mp: 221-222 °C; ESI-MS (*m/z*): 363.5 (*M*+*H*)⁺, 747.3 (2*M*+Na)⁺; IR (KBr): 3430, 3200, 2927, 1610, 1512, 1383, 1279, 1239, 1168, 834, 755, 706 cm⁻¹; ¹H-NMR (400 MHz, DMSO-*d*₆) δ: 9.60 (1H, br, s), 7.62 (1H, m), 7.56 (2H, m), 7.46 (1H, s), 7.39 (2H, d, *J*=7.6 Hz), 6.50 (2H, d, *J*=8.4 Hz), 6.40 (2H, d, *J*=8.4 Hz), 6.37 (1H, s), 2.52 (3H, s), 2.27 (3H, s).

3-(4-Methoxyphenyl)-5-(4-hydroxyphenyl)-6-acetyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine (5c). Mp: 230-231 °C; ESI-MS (*m/z*): 393.9 (*M*+*H*)⁺; IR (KBr): 3412, 3107, 2732, 1636, 1611, 1516, 1384, 1252, 1182, 1028, 836 cm⁻¹; ¹H-NMR (400 MHz, DMSO-*d*₆) δ: 9.70 (1H, br, s), 7.33 (3H, m), 7.09 (1H, d, *J*=8.8 Hz), 6.53 (2H, d, *J*=8.4 Hz), 6.42 (2H, d, *J*=8.4 Hz), 6.35 (1H, s), 3.85 (3H, s), 2.54 (3H, s), 2.27 (3H, s).

3-(4-Methylphenyl)-5-(4-hydroxyphenyl)-6-acetyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine (5d). Mp: 230-231 °C; ESI-MS (*m/z*): 377.6 (*M*+*H*)⁺, 775.2 (2*M*+Na)⁺; IR (KBr): 3414, 1608, 1384, 1248, 1170, 830 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.70 (1H, br, s), 7.36 (3H, t), 7.28 (2H, d, *J*=8.0), 6.52 (2H, d, *J*=8.4), 6.42 (2H, d, *J*=8.4), 6.38 (1H, s), 2.54 (3H, s), 2.42 (3H, s), 2.27 (3H, s).

3-(4-Chlorophenyl)-5-(4-hydroxyphenyl)-6-acetyl-7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine (5e). Mp: 229-230 °C; ESI-MS (*m/z*): 397.3 (*M*+*H*)⁺; IR (KBr): 3433, 3089, 2668, 1635, 1515, 1384, 1290, 1250, 1093, 821 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.78 (1H, br, s), 7.62 (2H, d, *J*=8.4), 7.46 (1H, s), 7.43 (2H, d, *J*=8.4), 6.54 (2H, d, *J*=8.8), 6.45 (2H, d, *J*=8.8), 6.32 (1H, s), 2.54 (3H, s), 2.27 (3H, s).

Conclusion

In conclusion, we developed a novel, mild and effective one-pot method for the synthesis of substituted 5*H*-thiazolo[3,2-*a*]pyrimidines derivatives utilizing [Hnmp]HSO₄.

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A Kind of Novel Chemical Plugging Removal Technology Study for Polymer Flooding Wells

Yuan Jing-Shu^{1, a}, Cao Guang-Sheng^{1, b}, Chen Ping^{2, c}, Gao Yang^{3, d}

¹College of Petroleum Engineering, North East Petroleum University, Daqing, Heilongjiang, 163318,
P. R. of China

²North East Petroleum University, Daqing, Heilongjiang, 163318,
P. R. of China

³School of Computer and Information Technology, NorthEast Petroleum University, Daqing,
Heilongjiang, 163318 P.R. of China

^a337539754@qq.com

^bcaoguangsheng@nepu.edu.cn

^cchenping6806@126.com

^d1609995729@qq.com

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Abstract. Aiming at plugging removal issues of polymer flooding well, first of all, the mechanism of formation plugging is analyzed, and then, we discuss the reasons of bottom borehole block in polymer water flooding well and block laws. Finally, some typical indoor experiments are designed, during testing; some chemicals are tested, such as CJN-x, sodium nitrite, sodium sulfite etc. are tested. Through these experiments, these different effect of materials reducing viscosity is compared, among them, the CJN-1x and hydrogen peroxide possess better effect of plugging removal for polymer flooding wells.

1. Introduction

With the development of tertiary recovery, polymer flooding and ASP flooding technique [1][2] have obtained better achievement. The tertiary recovery scale of popularization is increasing, but the increasing injection rate of polymer makes stem long time assemble on the bottom hole, the issue of block in polymer water flooding well becomes extremely serious[3]. The polymer resort in rich hole medium through chemical adsorption and mechanical catching causing flowing section of hole decreased, the increasing of fluid resistance causes the stratum block in polymer water flooding well. Nowadays, there are many methods of plugging removal, but these methods have some disadvantages. In this paper, a kind of novel chemical plugging removal technology is proposed and studied. The content is organized as follows: section 2 introduces the mechanism of plugging of polymer flooding well; section 3 gives some typical plugging removal methods, some experiments are tested and discusses the experiments' results. Finally, section 5 gives the conclusion and next study work.

2. Mechanism of Plugging of Polymer Flooding Wells

Through research and theory analyzing on polymer flooding, some reasons resulting plugging of polymer flooding wells are summarized. Firstly, polymer has mechanical catching [4]: carboxylic acid groups of high polymer can act with electric charges, which can generate particle clusters and plugging at pore throat. Because the polymer itself has ability of high catching minute particles, in general, these colloidal particles should not have been precipitated also precipitated. Secondly, the polymer itself sorting and adsorption action, under the microscope, we can observe that the clay in formation primarily distributes on the surface of pore, particularly, on the pore throat. Because the

polymer has intensively surrounding ability to clay, thicker polymer adsorption layer will be formed on the surface of pore throat and wall. If the polymer still carries migrating flocculated particles, it should coil and form plugging particles group, and which will adsorb on formation pore, therefore, resulting in plugging formation. Even if the polymer does not catch minute particles, it will form plugging around the pore, which will make pore become narrow, resulting in reducing formation permeability. Thirdly, during water being injected, those water swellable minute particles and impurities will assemble together and form particle group structure, which will plug pore of oil formation, therefore, resulting in decreasing formation permeability. And finally, because of ferric iron existing in pipeline and container, which will be cross-linked with polymer and micro-organisms, form rigid cross-linking materials. These gels are important ingredient plugging formation. Therefore, only these different plugging principles are understood, good measures can be researched. In the next section, all kinds of plugging removal methods will be discussed.

3. Study on Plugging Removal Method for Polymer Flooding Formation

So far, in sum, there are two kinds of plugging removal method [5][6], the one is physical plugging removal, the other is chemical plugging removal method, during the application, we must choose appropriate method. Here, chemical plugging removal method will be discussed primarily, which mainly include three classes, firstly, thermo-chemistry plugging removal method[7] uses chemical reaction releasing heat to degrade some materials, such as wax, gum, pitch, etc., which can restore formation permeability. Because there are some disadvantage influence factors, the method of thermo-chemistry plugging removal is not a kind of ideal one. Secondly, hot gas acid plugging removal method [8] uses thermo-chemistry and oxidizing to remove the plugging removal, the application practice proves that this method has definite limitations, during the application, it will enhance cost, and this method is not fit for large scale extending. The finally, the chlorine dioxide plugging removal method: chlorine dioxide is an unstable oxidant, which can effectively remove bacteria, iron sulfide, polymer corrosion and plugging materials, on the one hand, its disadvantage is chlorine dioxide having instability, and on the other hand, chlorine dioxide must be used with hydrochloric acid, therefore, this kind of method has many aspects to be improved.

4. Indoor Experiment and Results Analyze

In this section, we try to find a new formulation of plugging removal, in order to reduce polymer viscosity, during the experiment, oxidant oxidized is employed, several type of oxidants are tested. Through these tests, wish to discovery a kind of effective formulation of plugging removal which possesses optimal performance-cost ratio.

4.1 The Chemicals and Instruments

During the experiment, many chemicals are used, such as CJN-1 (Analytical Reagent: AR), CJN-2 (AR), CJN-3 (AR), hydrogen peroxide(AR), sodium chlorate(AR), sodium sulfite(AR), sodium nitrite(AR), hydrochloric acid(AR), HPAM and hydrofluoric acid(AR). These instruments are used, such as DNJ-1 rotating viscometer, measuring cylinder, timer, photoelectric analytical balance, and fluid mixer, constant temperature heating box, test tube, jar, pipeline, volumetric flask and suction pipette.

4.2 Experiment for reducing viscosity effect of gel breaker

Below, as one of gel breakers, CJN-1 will be tested; we will observe how the reducing viscosity effect is. In this paper, without any special specification, the polymer molecular weight is 1.2millions; the polymer concentration is 5 g/L.

4.2.1 The test of CJN-1 optimal concentration

The five group testing jars are fetched, in every jars, 60mL polymer is added, respectively. Every group is numbered from one to five in turn. The 10ml, 1% to 5% CJN-1 is respectively added into no.1 to no. 5 jar. Next, firstly, the mother liquor and five group samples are heated to 40°C, the mother liquor and the five group sample viscosity is measured respectively. Then, After the five group sample

in water path is heated to 40°C, these five group samples are heated for 10min, 20min, 30min, 60min, 90min and 120min, respectively, every sample viscosity is measured respectively, these measured results are showed in Fig 1. From the Fig 1, we can observe that the group 4 sample and the group 5 sample viscosity reduce below 10 mPa · s about 20min, about 30min, the effect is similar, therefore, we select the fourth group, optimal concentration of CJN-1 is 4%.

4.2.2 The test of CJN-1 comparison of polymer

Like above, we fetch five jars, these jars are numbered from one to five, in turn. 12mL, 4% CJN-1 is added into the first jar, 6mL, 4% CJN-1 is added into second jar, 4mL, 4% CJN-1 is added into third jar, 3mL, 4% CJN-1 is added into fourth jar, and finally, 2.4mL 4% CJN-1 is added into fifth jar. Next firstly, the mother liquor and the five group samples are heated to 40°C, the mother liquor and the five group sample viscosity is measured respectively. Then, After the five group samples in water path are heated to 40°C, these five group samples are heated for 10min, 20min, 30min, 60min, 90min, 120min and 240min, every group sample viscosity is measured respectively, these measured results are showed in Fig 2. The Fig 2 shows that viscosity of the first group sample and the second group sample reduce to about 10 mPa·s after 30min, these two group samples can flow, therefore, optimal CJN-1 comparison of polymer is 10:1. From above testing, we can observe that reducing polymer viscosity effect of gel breaker is very obvious; furthermore, velocity of reducing polymer viscosity is faster. By means of the same testing way, we test the reducing viscosity effect of CJN-2 and CJN-3, like the CJN-1, the other two gel breaker, CJN-2 and CJN-3 have the same effect in reducing polymer viscosity aspect too.

4.3 Experiment for reducing viscosity effect of weak oxidant

Below, we will do a test to check reducing viscosity effect of weak oxidant, in the test; the sodium nitrite is used as weak oxidant.

4.3.1 Experiment for reducing viscosity effect of sodium nitrite

In this test, the polymer and sodium nitrite proportion is 6:1.

From the reference materials, we know that the sodium nitrite possesses higher solubility; therefore, the higher concentration solution of sodium nitrite is compounded. In order to check the reducing viscosity effect of the sodium nitrite, primarily, the lower concentration sodium nitrite solution makes chemical reaction.

(1) The test of sodium nitrite concentration

The five group jars are fetched, respectively, and every jars is added into 60mL polymer, every jar of the five jars is numbered from one to five, in turn. The NDJ-1 of rotating viscometer is used to measure the solution viscosity, the solution viscosity is 1460 mPa·s. Next, 10mL, from 1% to 5% sodium nitrite solution is added into the first to fifth jar, in turn. Then, the mother liquor and the five group samples are heated to 40°C, the mother liquor and the five group sample viscosity is measured respectively. Then, After the five group samples in water path are heated to 40°C, these five group samples are heated for 10min, 20min, 30min, 60min, 90min, 120min and 240min, every group sample

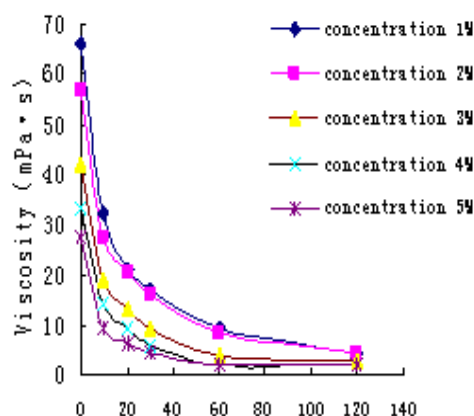


Figure 1. Optimal Concentration test curve of CJN-1

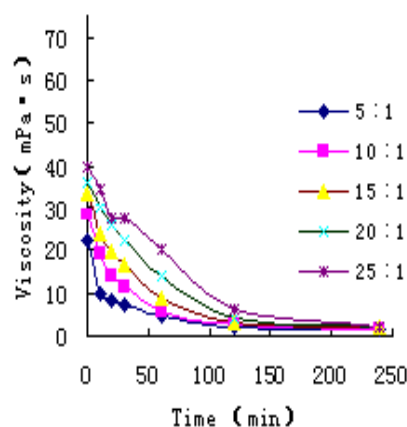


Figure 2. The curve of optimal CJN-1 comparison of polymer

viscosity is measured respectively, these measured results is showed in Fig 3. The Fig 3 shows that the solution viscosity is reduced after the sodium nitrite is added, but after while, every sample solution viscosity becomes balance tendency, namely, the solution viscosity does not reduce, no longer. Why this kind of result accurse, two reasons may exist, the one is that the sodium nitrite is a kind of weak oxidant, it does not completely oxidize polymer, the other is that the sodium nitrite concentration may be too low, it also does not completely oxidize polymer. Finally, test shows that it is not oxidant itself concentration, but oxidant itself oxidability is too weaker; therefore, it results in reducing viscosity inefficient effect.

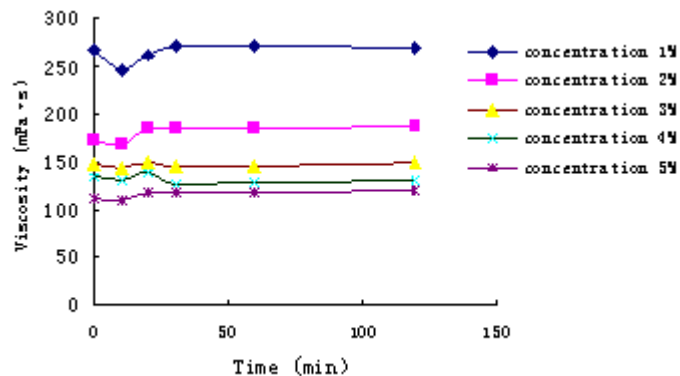


Figure 3. The Curve 1 of sodium nitrite concentration

(2) Comparison with reducing viscosity effect of all kinds of oxidants

Like above test, Firstly, The five group jars are fetched, respectively, and every jar is added into 60mL polymer, its viscosity is 1460 mPa · s. Next, 10mL, 5% sodium sulfite, 10mL, 5% sodium chlorate, 10mL, 5% CJN-3, 10mL, 5% hydrogen peroxide is added into jar form No.1 to No. 4, and finally, 10mL, 5% sodium nitrite and CJN-1 compounded solution is added into the fifth jar. Then, the mother liquor and the five group samples are heated to 40 °C, the mother liquor and every group sample viscosity is measured respectively. Then, After the five group samples in water path are heated to 40 °C, very group sample is heated for 10min, 20min, 30min, 60min, 120min and 240min, every group sample viscosity is measured respectively, these measured results are showed in Fig 4. The Fig 4 shows that reducing viscosity effect of the weak oxidants of sodium nitrite, the sodium chlorate and others are not obvious. Reducing viscosity effect of CJN-3 is very obvious, reducing viscosity effect of hydrogen peroxide is obvious, but it needs longer time. From Fig 4, the sodium sulfite and the sodium chlorate can reduce the polymer viscosity at shorter time. From above series of experiments, some oxidants and gel breaker are compared; it shows that some chemicals can be acted as plugging removals. Among them, the CJN-1, CJN-2, CJN-3 and hydrogen peroxide possess better effect of plugging removal.

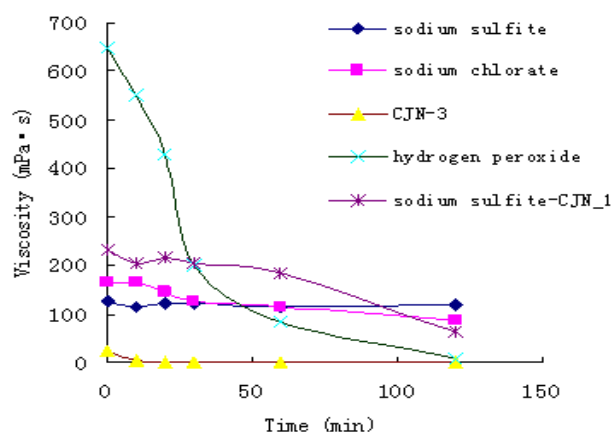


Figure 4. Reducing viscosity effect Comparison of drugs

5. Conclusions and Next Work

Through above experiments, CJN-x and hydrogen peroxide can be used as plugging removal. Considering that the CJN-3 will react with acid to generate chlorine and nitrogen when it meets acid gas in the formation of borehole. These gases will threaten security of worker and well, hence, the CJN-3 is not used as plugging removal. The CJN-2 not only possesses better plugging removal effect, but it has not any insecurity factors, however, if it is ionized, it will generate flu silicate which will result in plugging formation again, hence, the CJN-2 is not used as plugging removal either. As to the hydrogen peroxide, on the one hand, it needs to react for longer time, on the other hand, it will generate oxygen which will threaten oil well security, therefore, the hydrogen peroxide is not used as

plugging removal either. Among these chemicals, only the rest of CJN-1 is able to satisfy requirements, the CJN-1 not only possesses better plugging removal effect, but it has not any security hidden trouble, and meanwhile, it does not generate plugging to formation again, consequently, the CJN-1 is a kind of ideal plugging removal.

There are many factors which will influence effect of plugging removal, such as temperature, acid liquid, and molecular weight of polymer and so on; next, these issues will be further studied. Meanwhile, the plugging removal effect will be further studied under the formation conditions.

Acknowledgements

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A study of Oxalic acid adsorption on the surface of natural mica

Meizhen Ke^{1,a}, Qinghua Chen^{2,b}, Weiming Zhou^{1,c}, Nan Wu^{2,d},

Qingrong Qian^{2,e}, Zhanhui Yuan^{3,f}, Xiaomin Huang^{2,g}

¹ College of Materials Science and Engineering, Fujian Normal University, Fuzhou, China

² College of Environmental Science and Engineering, Fujian Normal University, Fuzhou, China

³ Fuzhou Kuncai Fine Chemicals Co., Ltd, Fuqing, China

^a 757412608@qq.com (M Ke), ^b cqhuar@126.com (Q. Chen),

^c zhouweiming721@126.com (W. Zhou), ^d 270732913@qq.com (N Wu),

^e qrqian@fjnu.edu.cn (Q. Qian), ^f zhanhui.yuan@fzkuncai.com (Z Yuan),

^g 864093945@qq.com (X Huang)

Keywords: Natural mica; Surface adsorption; Oxalic acid; Organic silicon coupling agent KH550; silane; Polyethylene glycol

Abstract: This paper reports an increment of conformal metal oxides or nonmetal oxides films with good crystallinity coating on natural mica synthesized by liquid phase deposition. PEG1000 and KH550 were used to increase the adsorption of oxalic acid on the mica surface. Hence, the metal ions can react with the oxalic acid, resulting in uniform and compact thick films. The potasrmanganate titration and infrared ssium pepectroscopy were adopted to obtain the optimum dosage of PEG1000 and KH550. It is shown that the condition with the usage of PEG1000 of 0.4 g/L, KH550 of 9.76 g/L, temperature of 30 °C and mixing of 4 hours is appropriate.

Introduction

Mica pearlescent pigment based on mica flakes covered with surface oxide layer of different metals or nonmetals, organic pigments, dyes, etc [1] is usually prepared by liquid phase deposition (LPD) [2]. The LPD has the advantage that itself can produce crystallized films owing to stepwise hydrolysis and slow rate of deposition[3]. However, it can't form uniform and dense membranes on the mica surface due to the weak surface adhesion between the mica and the metal oxides or nonmetal oxides because of the weak polarity of the metal oxides or nonmetal oxides.

Recently, the organic acid method was also used to make the mica pearl pigment[4-5], in which the coating is through the precipitation by organic acid. Oxalic acid, one kind of excellent precipitant, can combine metal ions to form membranes. However, the precipitates being free in solution can't form an uniform and compact layer with the use of oxalic acid. Because oxalic acid and metal ions form small particles in solution, and the force between deposited metal oxalate and mica is weak.

In our work, the natural mica soaks in the saturated oxalic acid, and then the coupling agent 3 - ammonia propyl triethoxy silane (KH550) and dispersant PEG1000 are added into the the solution. The work aims to study the adsorption capacity of oxalate in mica surface to screen the optimum condition with the best adsorption of oxalic acid.

Experimental

Raw materials and reagents. All materials used in the experiments were analytic reagents and without further purification. The oxalic acid was purchased from Tianjin Fuchen Chemical Reagents Factory; the polyethylene glycol (PEG) 1000 was obtained from Chengdu union chemical industry reagent research institute; the 3-ammonia propyl triethoxy silane was bought from Shanghai Zhongyi Plastic Product Factory; the potassium permanganate and sulfuric acid from Hengyang city kaixin chemical reagent co., LTD.

Preparation process. A certain amount of natural mica, KH550 and PEG1000 (see Table 1) were mixed together, then 50 ml of saturated oxalic acid was added into the above solution under stirring at a certain temperature. The obtained preliminary product was filtered and washed with 50 mL of warm water, and then transferred to the conical flask and washed it with 50mL of distilled water. Subsequently, 0.02 mL of concentrated sulfuric acid was added and mixed homogeneously. The following added 2.00 mL, 0.01 mol/L potassium permanganate into the preliminary product suspensions and heated it until boiling by the electric jacket. Then a 0.01 mol/L potassium permanganate was used to titrate and record the results.

Table. 1 The amount of KH550 and PEG1000

condition	1	2	3	4
PEG1000	0	optimum	0	optimum
KH550	0	0	optimum	optimum

Results and discussion

Influence of dispersant PEG1000. The effect of dispersant on the quantity of oxalic acid adsorption in natural mica is shown in Fig. 1. When the amount of PEG1000 is 0.02 g, the largest adsorption on the surface of the mica is achieved. PEG1000 is one kind of stabilizer to the space steric hindrance. Once added into the solution, the end of polymer chain closely adsorbs on the surface of particles while the other side of chain in PEG1000 tries to extend in the solution to reduce the attraction between particles [6-7]. So the increment of space and time of oxalic acid adsorption can be realized.

When the addition of PEG1000 is too much, it could make long polymer chains intertwine together, greatly restricting the movement of the particles, increasing the viscosity, forming aggregation and sedimentation, and thus reducing the surface adsorption of oxalic acid.

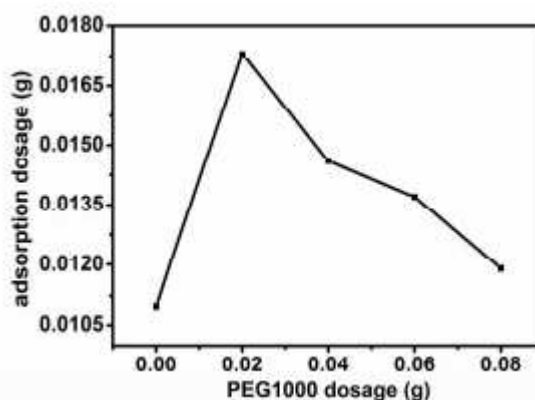


Figure. 1 The effect of dispersant on the quantity of oxalic acid adsorption in natural mica surface (Process conditions: 10.0 g natural mica (39% water), KH550 0.4880 g, 50 ml saturated oxalic acid, water bath temperature is 80 °C, stirring time 4 h.)

Influence of coupling agent KH550. The effect of coupling agent on the quantity of oxalic acid adsorption on natural mica is shown in Fig. 2. It is seen that the adsorption amount of oxalic acid increases with the increment of KH550 and reaches a maximum when the content of KH550 is 0.4880 g. The ethoxy groups of KH550 hydrolyze to produce silanol and then combine with inorganic substance to form a siloxane. The amino of the KH550, reactive group, can react with the organic, which builds a "bridge" between the interface of oxalic acid and natural mica, improving the properties of natural mica surface.

However, if the amount of KH550 is too much, crosslinking reaction occurs after hydrolysis. It reduces the useful effective ratio of the coupling agent in natural mica, leading to a decrease in the adsorption of oxalic acid on mica. When the amount of KH550 is too little, there is so little "molecular bridge" for oxalic acid adsorption on mica[8-9].

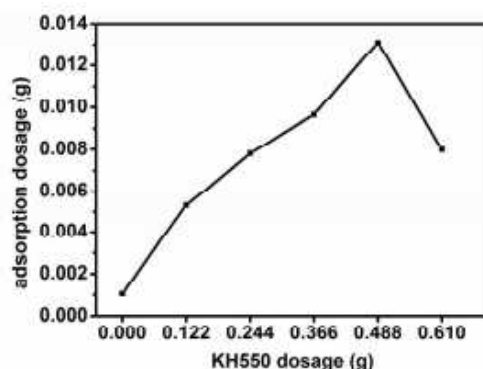


Figure. 2 The effect of coupling agent on the quantity of oxalic acid in natural mica surface adsorption (Process conditions: KH550 0.4880 g (9.76 g/L), PEG1000 0.02 g (0.4 g/L), 50 ml saturated oxalic acid, water bath temperature is 80 °C, stirring time 4 h.)

Decrement of Calcination weight. Fixed conditions: 10 g natural mica, 50 ml saturated oxalic acid. Other conditions are the same as in Table 1. The sample is treated by soaking for 4 h, washed with 50 mL of distilled water, and finally heated at 800 °C for 90 min.

Table. 2 Calcination weight's reduction

Condition	1	2	3	4
Not alcination quality	2.9647	2.5706	1.9228	2.0993
Weight loss	0.1329	0.1156	0.0937	0.1087
Percentage of weight loss %	4.48	4.50	4.87	5.18

The results of Table 2 illustrates that under optimum conditions, the surface of mica was adsorbed with silane coupling agent and oxalic acid, which goes well with the titration results.

Analysis of Infrared spectrum. Fig. 3 shows the IR spectra of saturated oxalic acid soaking natural mica at different conditions of processing. Strong absorption peak at 3400 cm^{-1} , 1600 cm^{-1} , 1000 cm^{-1} , 500 cm^{-1} and 470 cm^{-1} are observed. The band at 3400 cm^{-1} is due to stretching vibration of O-H bond and the one at 1600 cm^{-1} is due to bending vibration of O-H bond. It is known that natural mica have wool stoma or physical adsorption of water. The band at 1000 cm^{-1} and 470 cm^{-1} are caused by the stretching vibration and bending vibration of Si-O bond, respectively. In addition, obvious absorption peaks at 800 cm^{-1} and 690 cm^{-1} can be seen in the fingerprint area of 900~500 cm^{-1} , which are ascribed to the vibration of the Si-O-Al bond. In Fig.3 b and c, the peaks at 400 cm^{-1} and 1600 cm^{-1} are contributed to the scaling and bending vibration of O-H of PEG adsorbing on the natural mica, respectively. And the peak near 3600 cm^{-1} is due to the hydroxyl absorption.

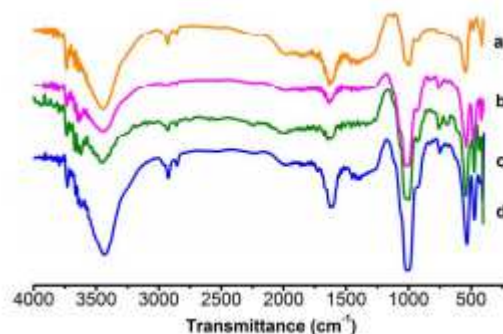


Figure. 3 The IR spectra of saturated oxalic acid soaking natural mica at different conditions of processing (a: KH550 processing; b: PEG processing; c: KH550 and PEG processing; d: No processing)

Conclusions

1) Appropriate amounts of KH550 and PEG1000 can effectively increase the adsorption quantity of oxalic acid on the mica surface. The optimum reaction condition is using 0.02 g 0.4 g/L of PEG1000, 0.4880 g 9.76 g/L of KH550 at 30 °C with 4 hours of mixing when the mica is 10 g.

2) The addition of dispersant leads to a good dispersion performance of the natural mica, promoting the adsorption capacity of oxalic acid. On the other hand, the addition of silane coupling agent favors forming an organic layer on the natural mica surface, which increases interface adsorption capacity.

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Adsorption Breakthrough Curves for Alkaline-earth Metal Ions on the Resins in a Fixed-bed Column

LIU Haining^{1,2}, ZHANG Huifang², GAO Can^{2,3}, YE Xiushen^{2,a}
and WU Zhijian^{2,b}

¹State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

²Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

³Graduate University of Chinese Academy of Sciences, Beijing 100049, China

^aE-mail: yexs@isl.ac.cn, ^bE-mail: zjw6512@hotmail.com

Keywords: Alkaline earth metal ion. Resin. Breakthrough curve. Adsorption.

Abstract. A column sorption study was carried out by using four resins (D113, D001, LS-1000, LS-5000) for the adsorption of alkaline-earth metal ions from aqueous solutions. The breakthrough curve was obtained as a function of feed flow rate, and the total and breakthrough capacity values of the resins were calculated. Four kinetic models: Adams-Bohart, Wolborska and Thomas models were applied to experimental data to predict the breakthrough curves of Na-form resins and to determine the characteristic parameters of the column useful for process design. All models were found suitable for describing the whole or a definite part of the dynamic behavior of the column with respect to flow rate and inlet ion concentration. The results obtained would be helpful for the understanding of the competitive adsorption processes and the recovery or removal of one or more alkaline-earth metal ions from aqueous solutions.

Introduction

Many compounds of alkali-earth metals, such as magnesium, calcium and strontium are important inorganic chemicals, And these elements are of great importance for both material and environmental sciences, especially Sr. Due to special physical and chemical properties, Sr and its compounds have been widely applied in the field of electronic engineering, chemical industry, metallurgical engineering, military industry and light industry etc. [1-3].

Several techniques have been proposed to remove strontium ions from aqueous solutions, such as solvent extraction [4], membrane [5], ion exchange [6] and electrocoagulation [7]. However, all these methods cannot obtain ideal effect, when large amounts of other elements such as magnesium, calcium coexist with strontium. According to reported, adsorption method has been proved to be an attractive way to remove calcium, magnesium or strontium offering significant advantages like the cheapest, easy availability and easy operation, especially from an environmental view [6-8]. So far, lots of works have been focused on the adsorption of metal ions from aqueous media and most of studies are static adsorption experiment. However, adsorption capacities from batch studies, although useful, may not provide accurate scale-up information for column systems due to a number of factors [9].

The aim of the present work was to study and model the extract of alkali-earth metal from aqueous solutions by resins in fixed-bed columns. In order to better understand the adsorption behaviour of alkali-earth metal ions from aqueous systems onto resins, a series of column studies have been undertaken. And four resins (D113, D001, LS-1000, LS-5000) were used to adsorb alkaline-earth metals elements Mg^{2+} , Ca^{2+} , Sr^{2+} from aqueous solutions. Breakthrough curves were generated and the Adams-Bohart, Wolborska and Thomas models are employed to analyze the breakthrough curve for the adsorption of single metal ion.

Experimental Details

Materials.

Four resins (D113, D001, LS-1000, LS-5000) used in this study were bought from Xi'an LanShen Special Resin Ltd., and their primary character were described in Table 1. The Mg^{2+} , Ca^{2+} ,

Sr^{2+} solutions were prepared using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd.) with the concentration of 0.01 mol L^{-1} , respectively. The ion concentrations were measured using an ISC-1100 Ion Chromatography (Thermo Fisher Scientific Inc.)

Table 1 Resins and their properties

Resins	Functional groups	Exchanged ions	Water content [%]	pH range
D113	$-\text{COO}^-$	Na	61.95	0-14
D001	$-\text{SO}_3^-$	Na	51.77	0-14
LS-1000	$-\text{N}(\text{CH}_2\text{COO}^-)_2$	Na	62.38	0-14
LS-5000	$-\text{NHCH}_2\text{PO}_3^{2-}$	Na	58.99	0-14

Experiments.

The column tests were carried out on a glass column with a 1.0 cm diameter and 20 cm height. And it was filled with resins up to a height of 15 cm. The solutions of Mg^{2+} , Ca^{2+} , Sr^{2+} at a known concentration (0.01 mol L^{-1}) and flow rate ($4.625 \text{ mL min}^{-1}$) was passed continuously through the stationary bed of resins. The flow rate was regulated with a peristaltic pump. Samples were taken from the effluent at time intervals and analyzed as described below. The experiment was continued until a constant concentration of alkaline-earth metal ions was obtained.

Results and discussion

The area under the breakthrough curve obtained by integrating the adsorbed concentration versus the throughput volume plot can be used to find the total adsorbed alkaline earth metal ions quantity (maximum column capacity). Sorption capacity of the bed (q , mmol g^{-1}) is calculated from Eq.1 [9,10]:

$$q = \int_0^{V_r} \frac{(C_0 - C)dV}{m} \quad (1)$$

where m is the mass of the ion-exchange resin (g).

Breakthrough curves of the alkaline earth metal ions on the resins in single solutions.

The experimental breakthrough curves of the three ions on Na-form resins are presented in Fig. 1. The adsorption amounts of the ions on the Na-form resins are listed in Table 2.

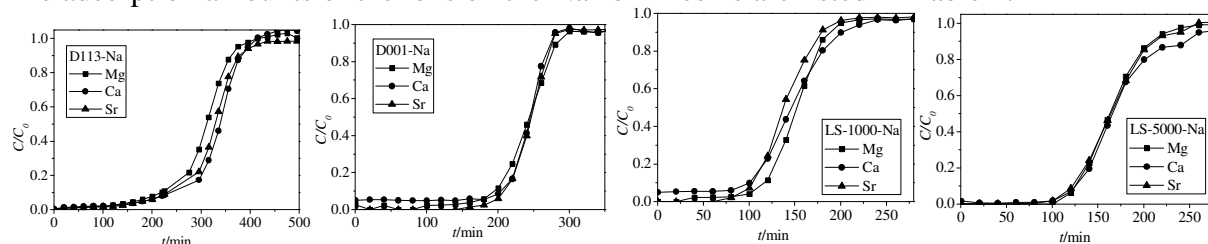


Fig. 1 Breakthrough curves of the Na-form resins

Table 2 The adsorption amounts of the ions on the Na-form resins.

Ions	Adsorption amounts [mmol g^{-1}]			
	D113-Na	D001-Na	LS-1000-Na	LS-5000-Na
Mg	3.889	2.268	2.350	2.051
Ca	3.702	2.217	1.955	2.124
Sr	3.885	2.402	1.948	1.961

Mathematical description of comparative adsorption.

(1) Application of the Adams-Bohart and the Wolborska models

The Adams-Bohart model [11-13] is used for the description of the initial part of the breakthrough curve, expressed as:

$$\ln \frac{C}{C_0} = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \quad (2)$$

where C_0 and C are the inlet and effluent concentrations (mol L^{-1}), respectively. k_{AB} is the kinetic constant ($\text{L mmol}^{-1} \text{min}^{-1}$). N_0 is the saturation concentration (mg L^{-1}). t is the flow time (min), Z is the height of the column (cm) and U_0 is superficial velocity (cm min^{-1}).

The Wolborska model [14-16] has the following form:

$$\ln \frac{C}{C_0} = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a Z}{U_0} \quad (3)$$

The expression of the Wolborska solution is equivalent to the Adams-Bohart relation if the coefficient k_{AB} is equal to β_a/N_0 . So the drawing of $\ln C/C_0$ versus t would also give information on this model [17,18].

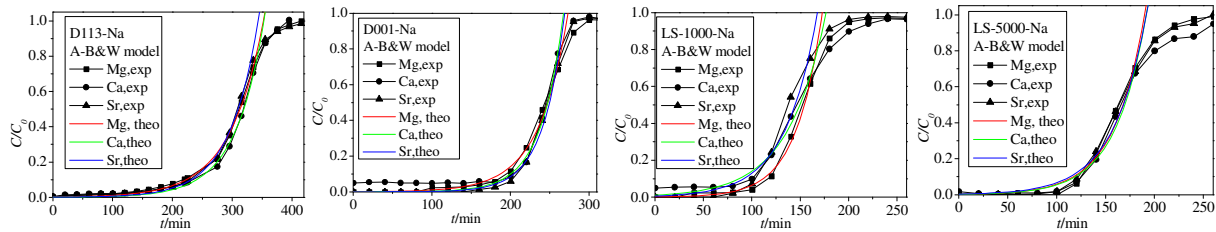


Fig. 5 Comparison of the experimental and predicted breakthrough curves to the Adams-Bohart (or Wolborska) model (temperature, 25°C; initial pH, 6.0; $C_0 = 0.01 \text{ mol L}^{-1}$).

Table 3 Parameters predicted from the Adams-Bohart and Wolborska models for alkaline-earth metal ions adsorption to the resins

		Adams-Bohart model			Wolborska model		
		$k_{AB} [\text{L mmol}^{-1} \text{min}^{-1}]$	$N_0 [\text{mmol L}^{-1}]$	$q_{0,cal} [\text{mmol g}^{-1}]$	$\beta_a [\text{min}^{-1}]$	R	$q_{0,exp} [\text{mmol g}^{-1}]$
D113	Mg	1.225	398.9	5.107	488.6	0.985	3.889
	Ca	1.040	448.4	5.552	466.3	0.968	3.702
	Sr	1.203	424.7	5.322	510.9	0.989	3.885
D001	Mg	1.983	305.5	2.903	605.8	0.949	2.268
	Ca	2.054	299.2	2.793	614.6	0.916	2.217
	Sr	4.323	259.1	2.498	1120	0.996	2.402
LS-1000	Mg	3.580	175.1	2.420	626.8	0.975	2.350
	Ca	3.116	168.3	2.226	524.4	0.993	1.955
	Sr	5.478	146.9	1.984	804.7	0.996	1.948
LS-5000	Mg	4.009	181.1	2.175	726.0	0.970	2.051
	Ca	3.850	186.3	2.200	717.2	0.983	2.124
	Sr	5.564	167.8	2.037	933.6	0.992	1.961

After applying Eq. 2 (or Eq. 3) to the experimental data for all the ions and resins, a linear relationship between $\ln C/C_0$ and t was obtained for the relative concentration region up to 0.5, i.e. up to 50% breakthrough. Respective values of N_0 , k_{AB} and β_a were calculated from the $\ln C/C_0$ versus t plots are presented in Table 3 together with the correlation coefficients. Predicted and experimental breakthrough curves are shown in Fig. 2. It is clear that there is a good agreement between the experimental and predicted values, suggesting that the Adams-Bohart (or Wolborska) model is valid for the relative concentration region up to 0.5 where large discrepancies were found between the experimental and predicted curves above this level for the ions adsorption in immobilized cell column.

(2) Application of the Thomas model

The expression by Thomas for an adsorption column is given below [19-21]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{Th} q_0 m}{\theta} - k_{Th} C_0 t\right)} \quad (4)$$

Where k_{Th} is the Thomas rate constant ($\text{mL mmol}^{-1} \text{min}^{-1}$), and θ is the volumetric flow rate (mL min^{-1}). The kinetic coefficient k_{Th} and the sorption capacity of the bed q_0 can be determined from a plot of $\ln[(C_0/C)-1]$ against t for the given resin.

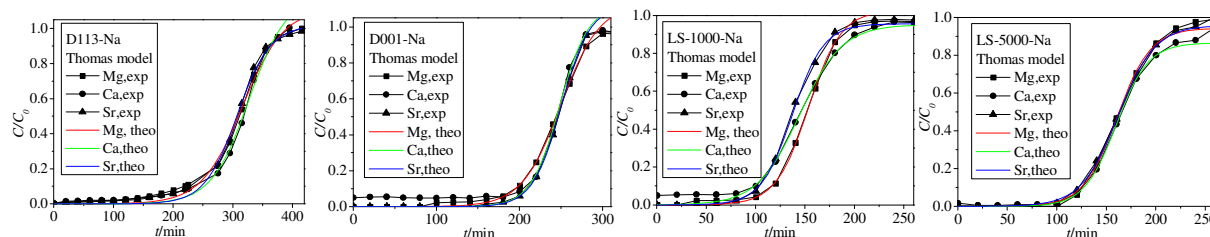


Fig. 3 Comparison of the experimental and predicted breakthrough curves to the Thomas model (temperature, 25°C; initial pH, 6.0; $C_0 = 0.01 \text{ mol L}^{-1}$).

Table 4 Parameters predicted from the Thomas models for alkaline-earth metal ions adsorption to the resins

		Thomas model			
		$k_T [\text{mL mmol}^{-1} \text{min}^{-1}]$	$q_{0,cal} [\text{mmol g}^{-1}]$	R	$q_{0,exp} [\text{mmol g}^{-1}]$
D113	Mg	2.882	3.675	0.971	3.889
	Ca	2.470	3.907	0.949	3.702
	Sr	2.655	3.819	0.983	3.885
D001	Mg	3.602	2.201	0.963	2.268
	Ca	6.102	2.178	0.985	2.217
	Sr	5.998	2.281	0.991	2.402
LS-1000	Mg	5.121	2.101	0.982	2.350
	Ca	3.971	1.941	0.997	1.955
	Sr	5.545	1.900	0.993	1.948
LS-5000	Mg	5.127	1.959	0.997	2.051
	Ca	3.581	2.171	0.980	2.124
	Sr	5.378	2.035	0.993	1.961

Application of Thomas model to the data at C/C_0 ratios higher than 0.05 and lower than 0.97 enabled the determination of the kinetic coefficients in this system [22]. The values of k_{Th} and q_0 are presented in Table 4. A comparison of values of q_0 obtained from calculation and experiment showed that they were close for given experimental conditions. The predicted curves at various experimental conditions according to the Thomas model are shown in Fig. 3. It is clear that there is a good agreement between the experimental and predicted normalized concentration values. The Thomas model is suitable for adsorption processes where the external and internal diffusions will not be the limiting step.

Conclusions

- (1) The adsorption of alkaline-earth metal ions (Mg^{2+} , Ca^{2+} , Sr^{2+}) from aqueous solution on four Na-form resins (D113, D001, LS-1000, LS-5000) was investigated in a continuous packed bed column. The breakthrough curves for column sorption of ions from dilute solutions to resins have been measured at a known concentration and flow rate at 25°C.
- (2) The Adams-Bohart (or Wolborska) and the Thomas models were applied to experimental data obtained from dynamic studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The initial region of breakthrough curve was defined by the Adams-Bohart (or Wolborska) model studied while the full description of breakthrough could be accomplished by the Thomas model. The model constants belonging to each model were determined by linear and non-linear regression techniques and were proposed for the use in column design.

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Analysis of Certain Phenomena in Tussah Silk

Dye-free Coloration

SHI Huibei^a, CUI Yongzhu^b, YE Fang^c, WANG Xiao^d, LV Lihua^e

School of Textile and Material Engineering, Dalian Polytechnic University,

Dalian 116034, China

^ashihuibei.no.1@163.com, ^byjcui1108@aliyun.com, ^cyidi999@163.com,

^dwangxiao@dlpu.edu.cn, ^eLvLh@dlpu.edu.cn

Key words: Dye-free; Tussah silk; Phenomenon; Analysis; Benzaldehyde

Abstract. Different color tussah fabric was got applied by dye-free coloration technology. When tussah fabric was treated with *p*-hydroxybenzaldehyde, red tussah fabric was obtained by coloration directly and two-step for deeper color, and brown color fabric was shown in one-bath coloration. In this paper, some phenomena showing in different processes of dye-free colorations was analyzed.

Introduction

The tussah fabrics in markets are mostly primary or colored by acidic dyes, which has bright color, and lack of tussah connate softness. The products of tussah fabrics dyed by chromogenic technology without dye has showed soft colors, good wear ability and soft in feel^[1]. In recent years, scholars had some research on the dye free technique^[2]. They experimented with different derivatives of benzaldehyde to achieve a series of chromogenic protein fibers^[3,4]. In order to their contributions, the process of *p*-hydroxybenzaldehyde to dye silk has been relatively mature^[5,6]. Tussah silk showed different phenomena during the different process, such as the order of color, the depth of color yield, and so on. In this paper, we will focus on three different color process and study and analyze certain phenomena in those color process.

Experiment

Materials and Instruments. Commercially available Tussah fabric (120g/m²), Hydrochloric acid, Tryptophan, Hydrogen peroxide, Hydroxybenzaldehyde, which are all in grade analytically pure. Instrument: X • rite SpectroEye colorimeter (kaicong Color Management Ltd.), JEOL JSM-6460LV scanning electron microscope (JEOL Ltd.).

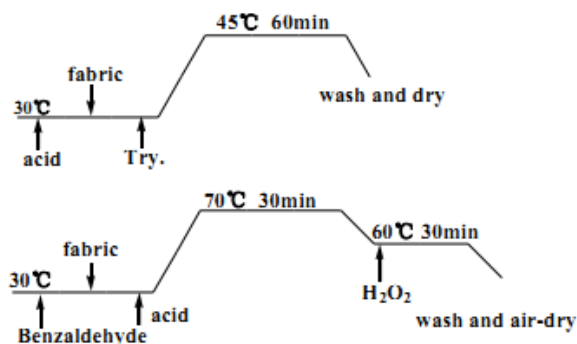


Fig. 1 Curve of two-step- process

Experiment method. Three groups of tussah fabric were colored using different color process. The first group were colored by direct chromogenic method, the second group were treated with tryptophan pretreatment and then color-step approach, and the third group used the one-bath tryptophan color chromogenic method. Specific process curves were shown in Fig. 1 and Fig. 2. Direct chromogenic process was the same as the second part of two-step process.

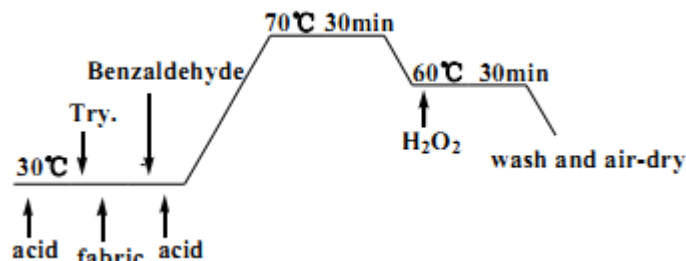


Fig. 2 Curve of one-bath process

Acid added to the system created the acidic environment for this reaction. H^+ of ionization promoted the reaction between benzaldehyde and tryptophan to a colorless substance. Under the oxidizing action of hydrogen peroxide, the reactive group such as hydroxyl of the product further oxidized and intramolecular rearrangement occurred. So that the length of the conjugated double bonds in products greatly increased, and the fabric put color on. The tryptophan applied promoted such reactions in greater extent by increasing the tryptophan content of the fabric, which made the chromogenic fabric deeper and more saturated.

Testing. In the conditions of GB/T7921-2008, ΔE values of dyed and undyed samples were measured through automatic color measurement (X • rite SpectroEye colorimeter). The surface characterization was analyzed by scanning electron microscopy (JEOL JSM-6460LV). The treated samples were tested for fastness to washing and rubbing. The progress were executed under GB/T 3921-2008 Color fastness to washing testing methods and GB/T 3920-2008 Color fastness to rubbing fastness standard.

Phenomenon and Discussion

Phenomenon 1. The fabric pretreated by tryptophan showed a pale yellow color with increased a^* , b^* and reduced L^* value (showed in Tab.1).

Tab. 1 The color change of tussah pretreated by tryptophan

No.	ΔL^*	Δa^*	Δb^*	ΔE
1	-6.97	1.09	11.50	13.49
	-6.35	0.96	11.06	12.78
	-7.09	0.89	11.13	13.22
2	-6.65	1.23	12.01	13.78
	-6.00	0.99	11.04	12.61
	-7.10	1.22	11.55	13.61
3	-7.27	1.07	11.61	13.74
	-7.12	1.35	12.28	14.21
	-7.52	1.05	11.48	13.76
Mean	-6.90	1.09	11.52	13.47

The yellow color may be caused of the residual acid within fabric, which causes some reaction at high temperature. Another, the reaction between tryptophan added and phenolic hydroxyl residues of tyrosine in amorphous region is possible to make the fibers to show a certain color. Author

prefers the latter. This reaction between tryptophan added and fabric itself makes a covalent bond through chemical action, which gives a hand to keep the added tryptophan staying inside. This theory can be verified from the fastness to washing of chromogenic fabric (showed in Tab. 2).

Tab. 2 Results of fabric color fastness test

	Color fastness to washing	Color fastness to crocking	
		dry	wet
chromogenic fabric of direct	4-5	5	4-5
chromogenic fabric of two-step	4	4-5	4-5

Phenomenon 2. The tussah silk pretreatment with tryptophan was first colored when being treated in the same conditions. Then the color gradually deepened with time. The content of tryptophan in it is higher than the other groups, having more substrates for this reaction, so the initial rate is higher. The samples dye-free directly has no color change basically before adding H_2O_2 , which illustrated that acid provided acidic environment just for the reaction, having no contributions to the oxidation.

Phenomenon 3. The color of tussah in one-bath deepened rapidly after adding hydrogen peroxide, meanwhile the reddish brown of dye gradually faded to clear. The oxidized reaction product, being more stable with larger and more complex structure, was gradually gathered in the fabric surface in the shape of flocculent precipitate (showed in Fig.3). Thus, fabric color deepened and dye liquor color fade.

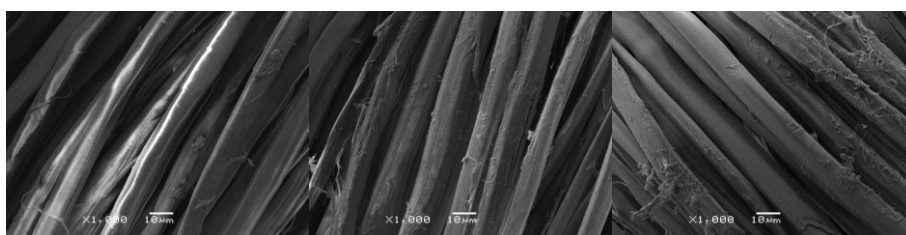


Fig. 3 SEM of colored tussah fabric

Left: directly; Middle: two-step; Right: one-bath

Phenomenon 4. All of samples had small bubbles coming out from the bottom of beakers with some irritating odor. This may be the product of hydrogen peroxide and hydrochloric acid in dye, chlorine or hypochlorite. With the oxidation of both, the specimen color continued deepen. This reaction can be verified from the yellow-green solution. The reaction can be represented by the following formula:



Phenomenon 5. Three samples have different degrees of shrinkage, two-step the largest, while one-bath almost no shrinkage (showed in Tab. 3).

Tab. 3 Shrinkage variation of fabric treated by Tryptophan

No.	shrinkage/ %	No.	shrinkage /%	No.	shrinkage /%	No.	shrinkage /%
1	15.4	6	15.40	11	7.88	16	13.52
2	7.88	7	24.40	12	17.20	17	6.00
3	21.04	8	11.68	13	13.70	18	15.36
4	13.52	9	19.16	14	8.00	19	15.40
5	17.28	10	17.20	15	8.00	mean	14.11

Tussah fabric showed shrinkage obviously in two-step color process. Tryptophan entered the interior of the fiber under the action of ions and fine water, and made a partial binding with the

amino acid residues in the amorphous region. The entering of tryptophan disrupted the original combination such as hydrogen bonds between macromolecules internal fiber. Then new hydrogen bonds formed in new location under wet and heat condition. Thus the appearance characteristics of the original fabric was changed.

Conclusion

The silk has different color reaction with benzaldehyde under different color process; tussah fabric performance differences and has not the same shades of color after different treatments. In future studies, different fabric color and performance can be obtained by controlling conditions in different processes.

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Application of Molecular Simulation on Wettability and Its Alteration

Minghui Zhou^{1, 2, 3, a}, Wenjie Sun^{1, 3, b}

¹School of Earth and Space Sciences, Peking U., Beijing, China

²State Key Laboratory of EOR, RIPED, PetroChina, Beijing, China

³Research Institute of Petroleum Exploration and Development, Beijing, China

^aahuiiam@pku.edu.cn, ^bspot1@126.com

Keywords: Molecular Simulation, Wettability, Surface Tension

Abstract. As the mechanical mechanism in interfacial phenomenon, interfacial forces are known as important but difficult to measure experimentally. In recent years, molecular simulation has been rapidly developed to give novel way in inter-molecular forces. In this study, molecular simulation is introduced into wettability and several formulas are presented to model forces and their microscopic effect among water, vapor and quartz phases. A novel dynamic method is proposed to determine the reasonable value of the cutoff distance to calculate the contact angles in vapor-water-quartz systems with and without fluorocarbon surfactants treated using molecular simulation. With other improvement in molecular simulation, the results of the contact angles are closely consistent with the measured data.

Introduction

Much attention has been paid to wettability alteration to preferential gas-wetness in porous media since researchers [1-3] reported the possibility to do so experimentally. Wettability alteration to preferential gas-wetness has many applications in petroleum industry such as enhancing gas production, water shut off, and reducing formation damage by drilling or stimulation measures. However, the effects of the concentration and novel chemicals available for wettability alteration on recovery in reservoir cores have not been investigated. It is not clear how the fluids distribute in porous media and what the difference in distribution of liquid saturation by different chemicals after the wettability is altered to preferential gas-wetness in gas-liquid (oil or water)-rock systems. It is not clear either how the chemical is bonded on the surface of rock to change the wettability of gas-liquid-rock systems. On the other hand, the chemicals used to change the wettability are still expensive. Understanding the mechanism of wettability alteration to preferential gas-wetness will be helpful to developing cheaper chemicals and improving the industrial applications.

In this study we introduce molecular simulation into wettability and several formulas are presented to model forces and their microscopic effect among water, vapor and quartz phases. A novel method is also proposed to determine the suitable value of the cutoff distance to calculate the contact angles in gas-water-quartz systems with and without fluorocarbon surfactants treated using molecular modeling. With other improvements in molecular modeling, the new model results of the contact angles are closely consistent with the measured data.

Molecular Simulation Improvements

Dynamic Modeling of Water

Because of the complex hydrogen bond, it is still a big challenge in molecular simulation to characterize inter-molecule forces and model its phase characters. In many cases, the modeling surface tension of water is much higher than experimental data. We considered it might be caused by the approach in modeling water. In ideal model, water molecules were put together as a matrix, which is not the most stable state.