Preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater

Jian Meng, Jianlan Cui, Siyuan Yu, Hui Jiang, Congshan Zhong and Ji Hongshun

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Review timeline
Original submission: 14 November 2018
1st revised submission: 10 January 2019
2nd revised submission: 23 January 2019
Final acceptance: 25 January 2019

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History
RSOS-181923.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
No

Are the interpretations and conclusions justified by the results?
No

Is the language acceptable?
No

Is it clear how to access all supporting data?
Yes

Do you have any ethical concerns with this paper?
No
Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Reject

Comments to the Author(s)
1. There are several, but very important issues, have not been present in the manuscript. Like "the disperse property of the MSs", "the surface area (BET) information", "the recycle properties of the dye adsorbent"...
2. SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory.
3. Abstract, should contain some important quantitative findings

Introduction, first paragraph, need to put these references:
Carbohydrate polymers 113, 115-130 (2014).
Journal of hazardous materials 177 (1), 70-80 (2010).
Royal Society open science, 4(9), 170697 (2017)

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
No

Is the language acceptable?
Yes

Is it clear how to access all supporting data?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Major revision is needed (please make suggestions in comments)

Comments to the Author(s)
In the research the authors were studied the preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater. They investigated Characterization of chitosan microspheres with the analysis such as FT-IR, XRD, SEM, TG and EDS, and they also investigated adsorption kinetic constants for chitosan microspheres, thermodynamics parameters and the effects of parameters such as pH on the adsorption process.
1. More quantitative measurements be mentioned in the abstract
2. Summary of the section on the conclusion is also presented in the abstract
3. In the introduction section used more literature. The following references should be cited in this section for upgrading the quality of the manuscript:

3.1. Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide, Environment Protection Engineering, 42(1), pp. 149-168.
3.2. Synthesis of nanochitosan for the removal of fluoride from aqueous solutions: A study of isotherms, kinetics, and thermodynamics, Fluoride, 50(2), pp. 256-268.
3.3. Synthesis and performance evaluation of chitosan prepared from Persian gulf shrimp shell in removal of reactive blue 29 dye from aqueous solution (Isotherm, thermodynamic and kinetic study), Iranian Journal of Chemistry and Chemical Engineering, 36(3), pp. 25-36.
3.4. Optimization of humic acid removal by adsorption onto bentonite and montmorillonite nanoparticles. Journal of Molecular Liquids, 259, pp. 76-81
3.5. Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions. Desalination and Water Treatment, 70, pp. 355-363.
3.6. Equilibrium and kinetics study of reactive dyes removal from aqueous solutions by bentonite nanoparticles. Desalination and Water Treatment, 97, pp. 329-377

4. For characterization of adsorbents, because the process was adsorption, so the analysis BET must be made to determine the surface area of the particles.
5. Formulas related to calculation of kinetics and thermodynamics in the section of experimental expressed not in the results section.
6. The conclusion is poorly written and must be rewritten.

Decision letter (RSOS-181923.R0)

11-Dec-2018

Dear Mr Yu:

Manuscript ID: RSOS-181923
Title: "Preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater"

Thank you for submitting the above manuscript to Royal Society Open Science. Your paper was sent to reviewers and their comments are included at the bottom of this letter.

In view of the concerns raised by the reviewers, the manuscript has been rejected in its current form. However, a new manuscript may be submitted which takes into consideration these comments.

Please note that resubmitting your manuscript does not guarantee eventual acceptance, and that your resubmission will be subject to peer review before a decision is made.

You will be unable to make your revisions on the originally submitted version of your manuscript. Instead, revise your manuscript and upload the files via your author centre.

Once you have revised your manuscript, go to https://mc.manuscriptcentral.com/rsos and login to your Author Center. Click on "Manuscripts with Decisions," and then click on "Create a
Resubmission” located next to the manuscript number. Then, follow the steps for resubmitting your manuscript.

Your resubmitted manuscript should be submitted by 10-Jun-2019. If you are unable to submit by this date please contact the Editorial Office.

We look forward to receiving your resubmission.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Ya-Wen Wang

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REVIEWER(S) REPORTS:
Associate Editor Comments to Author ():
RSC Associate Editor:
Comments to the Author:
(There are no comments.)

RSC Subject Editor:
Comments to the Author:
(There are no comments.)

Reviewers’ Comments to Author:
Reviewer: 1

Comments to the Author(s)
1. There are several, but very important issues, have not been present in the manuscript. Like "the disperse property of the MSs", "the surface area (BET) information", "the recycle properties of the dye adsorbent"...
2. SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory.
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In the research the authors were studied the preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater. They investigated Characterization of chitosan microspheres with the analysis such as FT-IR, XRD, SEM, TG and EDS, and they also investigated adsorption kinetic constants for chitosan microspheres, thermodynamics parameters and the effects of parameters such as pH on the adsorption process.

1. More quantitative measurements be mentioned in the abstract
2. Summary of the section on the conclusion is also presented in the abstract
3. In the introduction section used more literature. The following references should be cited in this section for upgrading the quality of the manuscript:
   3.1. Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide, Environment Protection Engineering, 42(1), pp. 149-168.
   3.2. Synthesis of nanochitosan for the removal of fluoride from aqueous solutions: A study of isotherms, kinetics, and thermodynamics, Fluoride, 50(2), pp. 256-268.
   3.3. Synthesis and performance evaluation of chitosan prepared from Persian gulf shrimp shell in removal of reactive blue 29 dye from aqueous solution (Isotherm, thermodynamic and kinetic study), Iranian Journal of Chemistry and Chemical Engineering, 36(3), pp. 25-36.
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   3.5. Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions. Desalination and Water Treatment, 70, pp. 355-363.
   3.6. Equilibrium and kinetics study of reactive dyes removal from aqueous solutions by bentonite nanoparticles. Desalination and Water Treatment, 97, pp. 329-377

4. For characterization of adsorbents, because the process was adsorption, so the analysis BET must be made to determine the surface area of the particles.
5. Formulas related to calculation of kinetics and thermodynamics in the section of experimental expressed not in the results section.
6. The conclusion is poorly written and must be rewritten.

Author’s Response to Decision Letter for (RSOS-181923.R0)

See Appendix A.
Are the interpretations and conclusions justified by the results?  
No

Is the language acceptable?  
Yes

Is it clear how to access all supporting data?  
Not Applicable

Do you have any ethical concerns with this paper?  
No

Have you any concerns about statistical analyses in this paper?  
No

Recommendation?  
Major revision is needed (please make suggestions in comments)

Comments to the Author(s)
1. BET should give data and graphs according to the style in the literature, not screen shots. Ref (1) Chem. Mater. 2001, 13, 3169-3183; (2) Journal of Industrial and Engineering Chemistry, Volume 21, 25 January 2015, Pages 369-377; (3) Colloid Polym Sci (2018) 296:59-70
2. My foregoing question of "SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory."

Author’s reply: During the preparation of the aminated microspheres, due to the addition of the polyamine-based substances TETA and PEI, the degree of cross-linking between the molecular chains was increased, causing aggregation. But the amino group content on the same surface area was significantly increased, which in turn leaded to a higher adsorption amount.

Thus, please provide evidence data about "the amino group content on the same surface area was significantly increased". This claimed conclusion should be proved by Solid data, not description.

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?  
Yes

Are the interpretations and conclusions justified by the results?  
Yes

Is the language acceptable?  
Yes

Is it clear how to access all supporting data?  
Yes

Do you have any ethical concerns with this paper?  
No
Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
Now the manuscript can be accepted for publication.

Decision letter (RSOS-182226.R0)

21-Jan-2019

Dear Mr Yu:

Title: Preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater
Manuscript ID: RSOS-182226

Thank you for your submission to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The editor assigned to your paper has now received comments from reviewers. We would like you to revise your paper in accordance with the referee and Subject Editor suggestions which can be found below (not including confidential reports to the Editor). Please note this decision does not guarantee eventual acceptance.

Please submit a copy of your revised paper before 13-Feb-2019. Please note that the revision deadline will expire at 00.00am on this date. If we do not hear from you within this time then it will be assumed that the paper has been withdrawn. In exceptional circumstances, extensions may be possible if agreed with the Editorial Office in advance. We do not allow multiple rounds of revision so we urge you to make every effort to fully address all of the comments at this stage. If deemed necessary by the Editors, your manuscript will be sent back to one or more of the original reviewers for assessment. If the original reviewers are not available we may invite new reviewers.

To revise your manuscript, log into http://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under "Manuscripts with Decisions." Under "Actions," click on "Create a Revision." Your manuscript number has been appended to denote a revision. Revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you must respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". Please use this to document how you have responded to the comments, and the adjustments you have made. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response.

Please also include the following statements alongside the other end statements. As we cannot
publish your manuscript without these end statements included, if you feel that a given heading is not relevant to your paper, please nevertheless include the heading and explicitly state that it is not relevant to your work.

• Ethics statement
Please clarify whether you received ethical approval from a local ethics committee to carry out your study. If so please include details of this, including the name of the committee that gave consent in a Research Ethics section after your main text. Please also clarify whether you received informed consent for the participants to participate in the study and state this in your Research Ethics section.
*OR*
Please clarify whether you obtained the necessary licences and approvals from your institutional animal ethics committee before conducting your research. Please provide details of these licences and approvals in an Animal Ethics section after your main text.
*OR*
Please clarify whether you obtained the appropriate permissions and licences to conduct the fieldwork detailed in your study. Please provide details of these in your methods section.

Once again, thank you for submitting your manuscript to Royal Society Open Science and I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Ya-Wen Wang.

*******************************************************************************

RSC Associate Editor
Comments to the Author:
(There are no comments.)

*******************************************************************************

Reviewers' Comments to Author:
Reviewer: 2

Comments to the Author(s)
Now the manuscript can be accepted for publication.
Reviewer: 1

Comments to the Author(s)
1. BET should give data and graphs according to the style in the literature, not screen shots. Ref (1) Chem. Mater. 2001, 13, 3169-3183; (2) Journal of Industrial and Engineering Chemistry, Volume 21, 25 January 2015, Pages 369-377; (3) Colloid Polym Sci (2018) 296:59–70
2. My foregoing question of "SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory."

Author’s reply: During the preparation of the aminated microspheres, due to the addition of the polyamine-based substances TETA and PEI, the degree of cross-linking between the molecular chains was increased, causing aggregation. But the amino group content on the same surface area was significantly increased, which in turn leaded to a higher adsorption amount.

Thus, please provide evidence data about "the amino group content on the same surface area was significantly increased". This claimed conclusion should be proved by Solid data, not description.

Author's Response to Decision Letter for (RSOS-182226.R0)
See Appendix B.

Decision letter (RSOS-182226.R1)

25-Jan-2019

Dear Mr Yu:

Title: Preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater
Manuscript ID: RSOS-182226.R1

It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals
On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Ya-Wen Wang.

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Review(s)' Comments to Author:
Appendix A

Dear Editor,

Thank you so much for your time and suggestion on our manuscript (RSOS-181923). We have revised the manuscript thoroughly as you and the reviewers suggested. Each concern raised by the reviewers has been seriously considered and addressed in our response as below. All the significant changes have been highlighted in colors in the revised manuscript. We would greatly appreciate it if you could approve the publication of the revised manuscript. If you have any more questions or advice, please let us know.

We clarify that the screen shoots of Excel spreadsheets are not previously reported. Per the instructions for authors, the data supporting the conclusions drawn in our manuscript has been provided via electronic supplementary materials according to your requirement.

Yours sincerely,

Prof. Jianlan Cui
**Reviewer #1: Comments to the Author(s)**

**Author’s reply:** We highly appreciate the reviewer’s time and constructive suggestions on our manuscript. All the corrections have been made following the reviewer’s suggestions and highlighted in RED in the revised manuscript.

1. There are several, but very important issues, have not been present in the manuscript. Like "the disperse property of the MSs", "the surface area (BET) information", "the recycle properties of the dye adsorbent".

**Author’s reply:** The SEM images (Fig. 4) showed that the dispersion of the microspheres TETA-CTSms and PEI-CTSms was worse than that of the microspheres CTSms. Meanwhile, the particle size distribution curve of aminated microspheres was presented in Fig. 6. This may be because during the crosslinking of the polyamine substance, the degree of crosslinking increased due to a large amount of amino groups, and the dispersibility of the microspheres deteriorated.

The surface area of the MSs was characterized by N$_2$ adsorption/desorption isotherms at 77 K on Accelerated Surface Area and Porosimetry System (ASAP 2020M, Micromeritics Company), and the surface area obtained by the test was almost absent. This may be due to the tight entanglement between the molecular chains of chitosan during the process of crosslinking and precipitation when adding NaOH solution. The BET test data of CTSms, TETA-CTSms and PEI-CTSms microspheres were given.
A laser particle size distribution analyzer (BT-2002, Dandong Bettersize Co., Ltd. China) is used to measure the particle size distribution of the microspheres according to the diffraction and scattering phenomenon of the laser, while obtaining the surface
area of the MSs by particle size fitting.

In this work, we mainly prepare polyamine-based microspheres by one-pot method. Next, we prepare to further optimize the preparation process of the aminated microspheres, including reactant feed ratio, reaction temperature, reaction time and the additive amount of glutaraldehyde. In the next adsorption experiment, we will further study the binary and ternary adsorption processes, and the recycling performance of the materials will be studied in detail in the next work.

2. SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory.

Author’s reply: During the preparation of the aminated microspheres, due to the addition of the polyamine-based substances TETA and PEI, the degree of cross-linking between the molecular chains was increased, causing aggregation. But the amino group content on the same surface area was significantly increased, which in turn leaded to a higher adsorption amount.

3. Abstract, should contain some important quantitative findings

Author’s reply: The comments pointed out above have been revised.

4. Introduction, first paragraph, need to put these references:

Carbohydrate polymers 113, 115-130 (2014).

Journal of hazardous materials 177 (1), 70-80 (2010).

Royal Society Open Science, 4(9), 170697 (2017)

Author’s reply: The comments pointed out above have been revised. We have cited these references in the Introduction and first paragraph.
Reviewer #2: Comments to the Author(s)

In the research the authors were studied the preparation of aminated chitosan microspheres by one-pot method and their adsorption properties for dye wastewater. They investigated Characterization of chitosan microspheres with the analysis such as FT-IR, XRD, SEM, TG and EDS, and they also investigated adsorption kinetic constants for chitosan microspheres, thermodynamics parameters and the effects of parameters such as pH on the adsorption process.

Author’s reply: We highly appreciate the reviewer’s time and constructive suggestions on our manuscript. All the corrections have been made following the reviewer’s suggestions and highlighted in BLUE in the revised manuscript.

1. More quantitative measurements be mentioned in the abstract.
Author’s reply: The comments pointed out above have been revised.

2. Summary of the section on the conclusion is also presented in the abstract.
Author’s reply: The comments pointed out above have been revised. Summary of the section on the conclusion has been presented in the abstract.

3. In the introduction section used more literature. The following references should be cited in this section for upgrading the quality of the manuscript:

   3.1 Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide, Environment Protection Engineering, 42(1), pp. 149-168.

   3.2 Synthesis of nanochitosan for the removal of fluoride from aqueous solutions: A study of isotherms, kinetics, and thermodynamics, Fluoride, 50(2), pp. 256-268.

   3.3 Synthesis and performance evaluation of chitosan prepared from Persian gulf shrimp shell in removal of reactive blue 29 dye from aqueous solution (Isotherm, thermodynamic and kinetic study). Iranian Journal of Chemistry and Chemical Engineering, 36(3), pp. 25-36.

   3.4 Optimization of humic acid removal by adsorption onto bentonite and montmorillonite nanoparticles. Journal of Molecular Liquids, 259, pp. 76-81.
3.5 Investigation of equilibrium, kinetics and thermodynamics of extracted chitin from shrimp shell in reactive blue 29 (RB-29) removal from aqueous solutions. Desalination and Water Treatment, 70, pp. 355-363.

3.6 Equilibrium and kinetics study of reactive dyes removal from aqueous solutions by bentonite nanoparticles. Desalination and Water Treatment, 97, pp. 329-377.

**Author’s reply:** The comments pointed out above have been revised. We have cited these references in the Introduction and first paragraph.

4. For characterization of adsorbents, because the process was adsorption, so the analysis BET must be made to determine the surface area of the particles.

**Author’s reply:** The surface area of the MSs was characterized by N₂ adsorption/desorption isotherms at 77 K on Accelerated Surface Area and Porosimetry System (ASAP 2020M, Micromeritics Company), and the surface area obtained by the test was almost absent. This may be due to the tight entanglement between the molecular chains of chitosan during the process of crosslinking and precipitation when adding NaOH solution. The BET test data of CTSms, TETA-CTSms and PEI-CTSms microspheres were given.
5. Formulas related to calculation of kinetics and thermodynamics in the section of experimental expressed not in the results section.

Author’s reply: The comments pointed out above have been revised.

6. The conclusion is poorly written and must be rewritten.

Author’s reply: The comments pointed out above have been revised. The conclusion has been rewritten.
Appendix B

Dear Editor,

We deeply appreciate the time and effort you have spent in reviewing our manuscript (RSOS-182226). Per your instruction, we have included Ethics statement alongside the other end statements.

The manuscript has been revised after reading the comments provided by the two reviewers. All the changes have been highlighted in RED in the revised manuscript. We would greatly appreciate it if you could approve the publication of the revised manuscript.

Should you have any more questions or advice, please let us know.

Yours sincerely,

Prof. Dr. Jianlan Cui
Reviewer #1: Comments to the Author(s)

Author’s reply: We highly appreciate the reviewer’s time and constructive suggestions on our manuscript.

1. BET should give data and graphs according to the style in the literature, not screen shots. Ref (1) Chem. Mater. 2001, 13, 3169-3183; (2) Journal of Industrial and Engineering Chemistry, Volume 21, 25 January 2015, Pages 369-377; (3) Colloid Polym Sci (2018) 296:59–70

Author’s reply: The surface area obtained by the BET test was almost absent. The BET test data of the microspheres CTSms, TETA-CTSms and PEI-CTSms are given in attached Excel files (supplementary materials).

2. My foregoing question of "SEM in Fig 4 show those MSs were seriously agglomerated as they been produced. The agglomerated adsorbents present perfect dye remove performance. The conclusion is seemed contradictory."

Author’s reply: During the preparation of the aminated microspheres, due to the addition of the polyamine-based substances TETA and PEI, the degree of cross-linking between the molecular chains was increased, causing aggregation. But the amino group content on the same surface area was significantly increased, which in turn leaded to a higher adsorption amount.

Thus, please provide evidence data about "the amino group content on the same surface area was significantly increased". This claimed conclusion should be proved by Solid data, not description.

Author’s reply: The comments pointed out above have been revised. As shown in Fig. 5 in the revised manuscript, the N content of the microspheres PEI-CTSms and TETA-CTSms increased significantly after the crosslinking reaction.

![Fig. 5 EDS for CTSms, PEI-CTSms and TETA-CTSms](image-url)
Reviewer #2: Comments to the Author(s)

Now the manuscript can be accepted for publication.

Author’s reply: We highly appreciate the reviewer’s time and constructive suggestions on our manuscript.