Comments and Suggestions for Authors

This article reports a study to investigate the performance of a material on cadmium adsorption associated with system optimization. Concrete results were shown from carefully performed experiments and analyses. However, very obvious and important problems are found. Please see the comments shown below. In addition, line numbers should be placed throughout the article.

General comments:

The authors described the results, but did not make adequate discussion. In-depth discussion related to mechanisms is definitely necessary.

Ans: Many thanks for your time and valuable input. Line numbers are added in the revised manuscript. A new section "Section 4.8" is added, and the adsorption mechanism is discussed elaborately with a schematic diagram in Figure 11a. Moreover, a graphical plot Figure 11b showing the comparison of percentage removal of Cd using (KAC and CS-KAC-Ag) is also added. There were various other changes made across the manuscript, using red fonts, and engineering mechanisms that support the statistical findings have been added and described in the text.

When making discussion, please try to compare the results to previous studies and please show references.

Ans: Thank you for your input. New references are added and cited in the text (old manuscript: 35 references – revised manuscript: 43 references). Table 7 and the associated discussion reflects such a comparison. Moreover, a detailed discussion under Results & discussion section is added. Other changes were made across the revised manuscript to reflect such comparison, with a focus on indicating how our manuscript differentiates itself from prior studies.

Specific comments:

Page 1, Abstract, "The lab data were also corroborated from tests conducted using the actual water samples collected from mining sites in Mexico": Do you mean that the results shown previously were from artificial water? Please indicate this clearly.

Ans: Thank you for your input. Cadmium stock solution was prepared in the lab. We have made revisions and it is highlighted in red.

Page 1, the last line, “Several studies suggested that adsorption was one of the most effective…”: You could start a new paragraph from here.

Ans : A new paragraph was inserted per the reviewer’s suggestion.

Page 2, “Recently, silver nanoparticle (AgNPs) loaded commercial AC matrix … and mixed metals from industrial wastewater [18, 19]”: The logic and coherence of this part should be improved. It reads like you just placed some discrete sentences there.

Ans: The paragraph has been rewritten, and all the added or changed lines are highlighted in red.

Page 4, “The wastewater sample was first filtered using a Whatman 44 filter paper to remove suspended particulate matter”: Indicate the pore size of the filter.

Ans: Many thanks for your input. The pore size of the filter is now indicated Section 3.4

Page 4, “…for a contact time of 120 minutes at room temperature”: Why did you use 120 min? Did the adsorption reach equilibrium?

Ans: Many thanks for your valuable input. At 120 minutes the absorption reached the equilibrium, and it is added to our revised manuscript. 3.1 Adsorption Section.

Page 4, “… because of its operational factor optimization capacity”: Show more information of the merit of this method.

Ans: Many thanks for your valuable input. New information regarding the merit of this method is added and highlighted in red Section -3.5 Design of Experiments.

Page 5, Table 1: The contents in the same row should be at the same level.

Ans: Thank you, it was changed accordingly in the revised manuscript.

Page 5, Table 2: Table 2 contains results. It may not be good to show results in this section. It would be better to divide the table into two.

Ans: Thank you for your valuable insight. We have moved Table 2 into the Results section (Section 4.3) and we have split Table 2 into two separate tables, Table 4 (Predicted Design Results) and Table 5 (Experimental results).

Page 5, "The UV–vis spectra of CS-KAC-Ag are shown in Figure 1, the changes in color of the CS-KAC-Ag sample after 15 minutes (Inset Figure 1a) and 40 minutes…": Why did you show the pictures at 15 and 40 min? Do you show them as examples? Or is there any special reason? Please indicate this. At what time point of the adsorption corresponds to the spectra in Figure 1? Can the colour shown in the insets be analyzed using professional instruments, rather than naked eyes? After showing the results, please make necessary discussion.

Ans: Many thanks for your input. Following lines are added 'The bio reduction of the Ag^{+} ions was monitored by periodic sampling of 1mL of the aliquots using a UV-Vis spectrophotometer (Model No: Perkin-Elmer Lambda-900) at 15, 30 minutes, and 40 minutes. A detailed description is added in the revised manuscript -Section 4.1.1. The procedure for getting the plasmon resonance at 424 nm is added and highlighted in red (~Lines 216-219).

Page 6, Table 3: Please show standard deviations of the results.

Ans: Thank you for your input. We wanted to study the physical/chemical characteristics such as the pore size/pore volume of raw kenaf-activated carbon prepared from the raw biomass kenaf and nanobiocomposite. As these are physical quantities, we did not take repeat measurements or any other statistical measurements that would allow us to compute standard deviations. However, we would keep this suggestion in mind for future studies.

Page 6, "This suggested that the surface pores were blocked by AgNPs or silver ions during the growth of AgNPs within the KAC matrix": Is this blockage good or not for adsorption capacity?

Ans: Thank you for your input. We have added a detailed explanation in the new Section 4.8. to explain the presence of different functional groups in fabricated bionanocomposites facilitated the adsorption mechanism. Additional discussion is also added in section 4.1.4

Page 7, "The functional group of KAC and CS-KAC-Ag nanobiocomposite can be better understood from the FT-IR study": Please improve the writing of this paragraph. It is wordy and boring. A table or figure could be good to represent what is discussed here clearly. When discussing the observation, you need to show references.

Ans: Thank you for your time and valuable input. Table 2 was split now into Table 4 (Predicted Design Results) and Table 5 (Experimental results), and moved into a different section, which triggered a re-numbering of all tables in the revised manuscript. New tables have been added as well. As a result, there are 7 tables now in the revised manuscript and we added all the FTIR

discussions under section 4 (Results and Discussion). The references have been added and the section was edited, with the revised lines in red fonts.

Page 7, "…would be ascribed to the presence of cellulose and hemicellulose": Discussion like this, not limited to this discussion, should be expanded. Please explain why and how you drew this conclusion from the observation. Please indicate the references. Please check the whole article according to this comment to make improvements.

Ans: Thank you for your time and valuable input. Expanded explanations are added. New references are added, and the FTIR spectrum is discussed giving detailed explanation of various absorption peaks in Section 4 (Results and Discussion), with the lines changed in red fonts.

Page 7, "…which were attributed to the chemical interaction between the functional groups of AC, chitosan molecules, and silver ions": Again, discussion like this should be expanded. Indicate how you got this conclusion, any mechanisms, and the references. Please check the whole article for this comment.

Ans: Thank you for your time and valuable input. FTIR spectrum mechanism and conclusion are added in detail and new references are also added and highlighted in red. .For example Reference-26, 27,29,30 31.

Page 8, "The resulting regression expression is provided in Eq. (8) used to predict the response variable Ypred in Table 2 considering the coded variables to preserve the orthogonality of the design": The model like this is very site-specific. It cannot be used in other situations. Please make discussion on what the model would be like in general.

Ans : The orthogonal experimental design is a widely accepted statistical modeling method with excellent and widely accepted external validity since 1935 (Fisher, 1935). The main advantage of the orthogonal design is that it allows testing the effectiveness of many treatments (interventions) simultaneously in a single experiment (and possibly identifying some of their interactions) with far fewer experimental units than it would take to exhaust all possible treatment combinations. The Box-Behnken design (BBD) adopted in this research study is an orthogonal design by its nature (the way it is structured). It is a widely used method by researchers in various fields e.g., chemical, pharmaceuticals, bioprocessing, engineering, etc. (Ahmad et al., 2015; Maran et al., 2013; Yetilmezsoy et al., 2009; Ferreira et al., 2007; Aslan et al., 2007). Therefore, the internal validity and external validity of the BBD method are ensured inherently by the experimental design structure (which we adopted in this study), and we believe that the model (regression equation Eq. 8 in the manuscript) can be used in other situations with similar and generally accepted results. We hope that this answer satisfactorily addresses the reviewer's concern.

References:

Fisher, R. A. (1935). The design of experiments. Oliver and Boyd. Edinburgh, London, UK

Yetilmezsoy, K., Demirel, S., & Vanderbei, R. J. (2009). Response surface modeling of Pb (II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design. Journal of hazardous materials, 171(1-3), 551-562.

Ahmad, A., Alkharfy, K. M., Wani, T. A., & Raish, M. (2015). Application of Box–Behnken design for ultrasonic-assisted extraction of polysaccharides from Paeonia emodi. International journal of biological macromolecules, 72, 990-997.

Maran, J. P., Manikandan, S., Thirugnanasambandham, K., Nivetha, C. V., & Dinesh, R. (2013). Box–Behnken design based statistical modeling for ultrasound-assisted extraction of corn silk polysaccharide. Carbohydrate polymers, 92(1), 604-611.

Ferreira, S. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandão, G. C., ... & Dos Santos, W. N. L. (2007). Box-Behnken design: an alternative for the optimization of analytical methods. Analytica chimica acta, 597(2), 179-186.

Aslan, N. E. V. Z. A. T., & Cebeci, Y. A. K. U. P. (2007). Application of Box–Behnken design and response surface methodology for modeling of some Turkish coals. Fuel, 86(1-2), 90-97.

Page 9, Table 4: It would be better to indicate what X1, X2, and X3 mean in the table to facilitate understanding.

Ans : Thank you for your feedback. Table 4 in the original manuscript is now Table 3, and it was updated to include these indicators, as suggested by the reviewer.

Page 9, “The plot showed that the X1*X1 and X1* X2 effects were not significant…were consistent with the ANOVA results in Table 4”: What mechanisms lead to such results? Please make discussion. You primarily described the results but did not make in-depth discussion, especially that related to mechanisms. In addition, when possible, please make a comparison to other relevant studies.

Ans: Table 4 is now Table 3 in the revised manuscript, and we have added and expanded on the statistical and mechanisms discussions, with the changes in red fonts. For example, the statistical discussion was expanded with additions in page numbers around 320 -340. And we have added and expanded the discussion of the mechanisms confirming our statistical results, for example under the Adsorption kinetics section (Lines 411-413)

Page 10, Figure 4: Figure 4 needs a title. When possible, please show statistical analysis results, such as confidence intervals.

Ans : Figure 4 in the original manuscript now corresponds to Figures 5a, 5b, and 5c in the revised manuscript and titles have been added where missing.

Page 10, Figure 4c: Do you really need A, B, and C? X1 to X3 are already quite simple. You need to indicate what X1 to X3 stand for.

Ans: It is indicated now in the Figure 5c plot. The Pareto chart was generated in Minitab, and it uses the A, B, and C notations. This is a Minitab tool artifact that we have no control over. However, we have indicated the A/B/C to $X_1/X_2/X_3$ mapping in the legend that was added to the Pareto chart plot.

Page 11, "The surface and contour plots shown in Figure 5a and Figure 5b demonstrate the impact of two factors while keeping the third factor constant at the center point": Again, you described the results in this paragraph, but did not make adequate discussion. Please discuss the reasons/mechanisms that could lead to such results.

Ans: We have greatly expanded the discussion of the statistical results (including the interactions) and the supporting mechanisms are discussed now in the Adsorption kinetics section). All changes are highlighted in red fonts.

Page 11, "It was observed that the Cd2+ removal rate increased with the increase in pH of the solution and decreased with the increase in metal ion concentration": Is this consistent with other studies? Please discuss this.

Ans: Many thanks for your valuable input. In this piece of research work, we have used kenaf-based activated carbon with chitosan and silver nanoparticles. We do not have enough research work on kenaf based nanobiocomposites but we found a similar work done and we have added a reference to support our results.

Page 11, "… which led to a repulsion between Cd2+ and active sites on the surface of the nanocomposite": For this kind of discussion, you used mechanisms developed in other studies. Please show references.

Ans: Thank you. A new reference is added [35] to support our results.

Page 12, “The optimum coded values for the initial metal concentration…which delivered a removal rate of 97.9 %”: X1 was -1, which means the optimal conditions could be out of the range tested. Please discuss how you respond to this issue.

Ans: X_1 is -1, but that is a coded value. The corresponding actual value for -1 is 10 mg/L, and we tested some of these values according to the BBD experimental design requirements. However, not all the values were tested as BBD does not require one to test them all. This is the main advantage of an orthogonal design such as BBD, see my explanation above on orthogonal designs (“The main advantage of the orthogonal design is that it allows testing the effectiveness of many treatments (interventions) simultaneously in a single experiment (and possibly identify some of their interactions) with far fewer experimental units than it would take to exhaust all possible treatment combinations”). Even if we did not test the actual optimal combination, we feel confident about the validity and generalizability of our results because we have used a scientifically sound, widely accepted, and widely used method to analyze and interpret the results.

Also, we have tested in this study the 10/6/120 and 10/9/70 combinations and obtained an experimental result of 89.89% and 87.49% removal, respectively (a 90% range). If we use these two values as proxies for the optimal combination of 10/6.9393/83.635, it is not unreasonable to believe that a 98% range (relatively close to the 90% range of the proxies) can be achieved when the parameters X1, X2, and X3 are tuned to these optimal values.

Page 13, “It was observed from Figure 7 that the adsorption rate increased rapidly with the time”: It seems not right. Please double check this statement.

Ans: It is observed from Figure 8 (new numbering) in the revised manuscript that the removal (~ 70 %) increased rapidly from 0 within the first 40 minutes. We double checked our experimental data, and the trend is confirmed

Page 14, Figure 8: Why did you not show the first-order model in the figure? The figure seems very simple. It can be removed.

Ans: Thank you for your valuable input. The figure is removed in the revised manuscript.

Page 14, “Table 5 showed that the R2 values of pseudo-first-order and pseudo-second-order models…”: Please review other studies to discuss whether second-order model is appropriate or not, as indicated by other studies.

Ans: An explanation for the selection of the pseudo-second-order model is added and highlighted in red.Table 5 is now 6 and additional lines are added to establish the accord with pseudo-second-order models

Page 14, “Figure 9 shows the removal percentage of the three metals using KAC, CAC, and nano-biocomposites CS-KAC-Ag”: Based on Figure 9, the three absorbents have similar efficiency. So why did you propose this new material?

Ans: Thank you for your input. The main objective of the research was to find an adsorbent that can act as a superior adsorbent to remove cadmium from water. A comparative study with KAC revealed that nanobiocomposite was effective in removing cadmium. To check its multifunctional efficacy mining water was collected and treated with KAC, CAC, and nano-biocomposites CS-KAC-Ag. And in all these cases, CS-KAC-Ag exhibited better results.

Page 14, “The removal efficiency of Cr (VI) 91.7 % >Ni (II) 84.4 % > Co(II) 80.5 % was observed with the nano-biocomposites”: Is the results consistent with other studies? Why is the efficiency for Cr higher than Ni and Co? Please discuss the mechanism.

Ans: The results are consistent with other studies. A new reference [37] is added to affirm our results and we explained our observation.

Page 15, Figure 9: Please show error bars to represent standard deviations.

Ans: Error bars are shown

Page 16, Figure 10: Improve this figure. The blue bars are not necessary. A curve is better than the histogram.

Ans: In Figure 10 Blue bars are removed, and the figure is improved.

Page 16, “It was observed that the adsorption efficiency of our synthesized material was high…”: Please discuss the mechanism why your method is better.

Ans: To highlight the superior property in terms of adsorption of our synthesized material we added a new section 4.8 to explain the mechanism. A schematic diagram is also added. We have added a graphical plot to show a comparative study of the effectiveness of our fabricated sustainable nanosadsorbent. Moreover, a detailed explanation is also added under the FTIR Section 4.1.4.