**Manuscript Title:** “Synthesis, characterization and adsorption studies of nanocomposite hydrogels and SiO2 effect on removal capacity of methylene blue dye'" (JSCS-PM-8227)

Dear Editor:

We wish to express our appreciation to the Referees for their comments. We are pleased to respond point-by-point to the reviewers’ comments in this first evaluation. The detailed responses to the specific comments/suggestions/queries are presented below.

***Referee 1.***

The Manuscript covers the original work dealing with preparation and
application of acrylic acid-co-vinyl pyrrolidone hydrogel loaded with SiO2
nanoparticles. The hydrogel was then used for removal of dye methylene blue.
The research shows potential; however, presented results and discussion on
characterization and removal of dye is sloppy. The references should be
updated and the majority of references date from some years ago. English in
the Manuscript is not at the satisfactory level and is should be thoroughly
checked and corrected. Overall, the Manuscript needs to be significantly
improved before I could recommend it to be published in Journal of the
Serbian Chemical Society.

The list the essential specific points:

**1.** In Abstract, Authors claim that “Nanocomposite hydrogels were used for
the adsorption and desorption of methylene blue dye from waste water”, but
they actually prepared dye solution in distilled water. Wastewater has much
more complex composition and those components affect the removal process.

**Response:** Used water sample were described as: “Nanocomposite hydrogels were used for the adsorption and desorption of methylene blue dye from wastewater. Wastewater was refered as a distilled water which contained methylene blue dye at laboratory conditions.” in Abstract section.

**2.** In Abstract and in Conclusion, Authors are mentioning BET and Langmuir
isotherms that are not actually presented in the manuscript. This should be
corrected.

**Response:** Abstract and Conclusion sections have been reviewed and corrected.

**3.** Line 69, experimental part, names of the used chemicals should be
corrected; this should also be corrected through whole text.

**Response:** Used chemicals have been corrected as:For this purpose, hydrogel samples were synthesized by crosslinking copolymerization of N-vinylpyrrolidone with N, N-methylene bis-acrylamide (MBA) in aqueous solution and using ammonium persulfate (APS) as a radical initiator.” in Experimental section.

**4.** Section “Preparation of hydrogels and SiO2 doped nanocomposite
hydrogels”, hydrogel synthesis should be explained in much more details
and list or table of all prepared samples should be included in the
Manuscript.

**Response:** Preparation of hydrogels and SiO2 doped nanocomposite
hydrogels section have been reviewed and List 1. Have been added to the manuscript as:

List 1.

Formulations for hydrogel synthesis

|  |  |  |  |
| --- | --- | --- | --- |
| Hydrogel ID | AA (M) | VP (M) | Nanoparticle (SiO2)(wt%) |
| AA | 5.5 | - | - |
| AA-SiO2(0.05) | 5.5 | - | 0.05 |
| AA-SiO2(0.5) | 5.5 | - | 0.5 |
| AA-SiO2(1) | 5.5 | - | 1 |
| AA-VP(3:1) | 4.125 | 1.375 | - |
| AA-VP(2:2) | 2.75 | 2.75 | - |
| AA-VP(1:3) | 1.375 | 4.125 | - |
| AA-VP-SiO2(0.05) | 4.125 | 1.375 | 0.05 |
| AA-VP-SiO2(0.5) | 4.125 | 1.375 | 0.5 |
| AA-VP-SiO2(1) | 4.125 | 1.375 | 1 |
| 0.05M MBA (cross-linking agent) |
| 0.01M APS (initiator) |

**5.** Section “Swelling behavior”, first two lines should be deleted or
moved in Results and Discussion.

**Response:** In swelling behavior section, first two lines have been deleted.

**6.** Section “Methylene blue (MB) adsorption”: equations and explanation
how was MB concentration calculated should be added.

**Response:** Because of the page number restriction, MB concentration calculation have not been added. This calculation can be found in analytical chemistry books, easily.

**7.** In Section “Desorption and reusability”, experimental procedure
should be better explained. It is not clear which solution was used for
desorption and which concentration is measured by UV-VIS. Authors should
rewrite this part.

**Response:** “Desorption studies of SiO2 doped and undoped AA homopolymeric nanocomposite hydrogels containing 2, 4, 6, 8 and 10 mg L-1 dye concentration were performed. The effect of SiO2 addition on desorption was investigated.” have been added to Desorption and reusability part to provide additional information about experimental procedure.

**8.** Regarding result of swelling of hydrogels, Authors state that they
prepared samples with different AA:VP ratio. In this part, only one ratio is
evaluated. How do you explain this? Also, swelling curve of this AA-co-VP
(3:1) sample is missing on the graph. How do the Authors explain
significant increase in swelling degree for the copolymer sample with 1% of
SiO2? This is the only sample that shows similar behavior as the monopolymer
hydrogels do.

 **Response:** The additional comments have been added to swelling behavior part as: “According to Fig.1, as expected, hydrogel (AA hydrogel) and co-polymeric hydrogel (AA-*co*-VP (3: 1) hydrogel) had the highest swelling value. Unexpected results for AA-*co*-VP-1%SiO2 showed that 1% nanoparticles were agglomerated non-homogenously in hydrogel pores. SiO2 nanoparticles that dispersed in the pores of hydrogels, increased the surface area and reduced pore diameter. In that case, doped hydrogels exhibited lower swelling behavior than undoped hydrogels.”

**9.** Authors state that they performed FTIR measurements of the samples, but
only IR spectra presented in the paper was of hydrogel AA-co-VP (no ratio
specified). FTIR analysis should be much better analyzed and discussed.
Also, additional IR spectra should be presented.

 **Response:**

Additional comments have been added to manuscript as: “In Fig. 2, the FT-IR spectrum of the methylene blue dye (black line) and the FT-IR spectrum of the non-adsorbed AA-co-VP (3: 1) hydrogel (red line) are shown in the same graphic. The single-spectrum graphic in Fig.2 belongs to the structure of methylene blue dye once adsorption onto AA*-co*-VP (3: 1) hydrogel. FT-IR spectra of other hydrogel and nanocomposite hydrogels which were synthesized in the study is given in S1.” And the FTIR results for other produced hydrogels have been given in Supplementary data as:



**S1.** FT-IR spectrum of not-adsorbed MB dye on hydrogels and nanocomposite hydrogels

**10.** Like in the case of FTIR, SEM analysis should be better described.

 **Response:** The additional SEM images have been added to Supplementary data file.

**11.** Fig. 4. SEM images of (a) before MB adsorption, (b) after MB adsorption
on hydrogels. Which hydrogel? Monopolymer or copolymer hydrogel? Again, more
micrographs of both hydrogels and nanocomposites should be inserted.

**Response:** The additional comments and details have been added as: “The morphological structure of the MB dye not-adsorbed / adsorbed on AA mono polymeric hydrogels was seen in Fig 4(a), (b). AA mono polymeric hydrogel was chosen for SEM analysis, because of the absence N% in their chemical structure. Therefore, differences between doped/undoped hydrogels were determined by EDX analysis.”

**12.** The whole characterization part of the Manuscript needs to be checked.
For each method of characterization different sample was used which leads to
the inability to make one clear conclusion of the properties of prepared
sample.

**Response:** The characterization part of the manuscript has been reviewed andcharacterization result belongs to which sample is clearly indicated in the relevant section.

**13.** Again, which hydrogel was used for this test of element content? In the
case of copolymer hydrogel, content of N cannot be 0 as it is given in Table
1?

**Response:** The caption of Table 1. have been rewritten as: “TABLE 1. Elemental contents of before and after MB adsorption on AA mono polymeric hydrogels”.

**14.** Line 231, “The adsorption efficiency of the co-polymeric and
homo-polymeric hydrogels decreased in the high concentration dye
contents.” This statement is not in good correlation with results showed
in the table 2. In case of copolymer hydrogels, the highest removal was
achieved in highest MB concentration. Also, Removal values oscillate in
small %, so it is not recommended to make such strong statement.

**Response:** The comments have been added to this part as: “The SiO2 addition (wt%; 1; 0.5 and 0.05%) in the hydrogels was kept in low amounts due to agglomeration. Therefore, the adsorption amount of hydrogels did not change much at varying MB dye concentrations (2, 4, 6, 8 and 10 mg L-1).”

**15.** Section “Adsorption isotherms”. Authors claim that 70 mg of
adsorbent is optimized. How can you confirm this? What other weights of
adsorbent were tested or this is the result presented in previous paper. If
so, it is necessary to insert reference.  Also, the whole paragraph need to
be rewritten.

**Response:** The writers have misrepresented the explanation. The sentence has been rewritten as: “Adsorption isotherm studies were carried out by without shaking a series of vials by adding the chosen quantity of adsorbent (~70 mg) and 10 mL of MB solution of different concentrations (2-4-6-8-10 mg L-1) at 25 ºC until they reached to equilibrium.”

**16.** Section “Reusability of hydrogels”. If desorption of dye is such an
easy process in distilled water, how can Authors claim that they removed
between 80% and 98% of dye in Section Adsorption studies?  In that case,
parallel process of adsorption and desorption is occurring.

**Response:** The statement has been added to the Reusability of hydrogels section as: “Although there was MB dye adhesion on the hydrogel obtained in the range of 80-98% in adsorption studies (pH 8.4), they achieved a maximum release of 40% in pH 6.8. It is envisaged that the release efficiency will be increased for the dyed hydrogels in different pH environments.”

**17.** Section “Elemental Analysis (C, H, N)”. This results presented are
not in the good correlation with the results given in Tab.2. How do the
Authors explain this?

**Response:** In Table 1, AA mono polymeric hydrogel was chosen for EDX analysis because of the absence N% in their chemical structure. Therefore, differences between doped/undoped hydrogels have been determined. The statement has been added to FTIR and FESEM Analyses part as: “AA mono polymeric hydrogel was chosen for SEM analysis, because of the absence N% in their chemical structure. Therefore, differences between doped/undoped hydrogels were determined by EDX analysis.” In Figure 7, there is a comparing study about nitrogen amounts of the hydrogel samples to determine nitrogen (% N) distribution of non-adsorbed hydrogel and MB adsorbed hydrogel.

**18.** Section “Conclusion”. The whole section needs to be rewritten. More
discussion is given here than in the “Results and discussion” part.
Also, it is clear that Lines 292-299 are not supposed to be inserted in the
Manuscript and that they should be removed.

**Response:** Conclusion section has been rewritten and the new comments have been written in red color.

**19.** Reference list should be up-to-dated. Majority of the references are
dating until 2013.

**Response:** New studies have been added to manuscript and reference section.

**20.** English in the Manuscript should be thoroughly checked and corrected.
For the most part Manuscript should be rewritten. There is a large number of
typos and grammatical errors.

**Response:** Language of the manuscript have been checked and corrected.Typos and grammatical errors have also been corrected and written in red color.

***Referee 2.***

The authors present an interesting work concerned with the synthesis and
characterization of acrylic/vinylpyrrolidone-based hydrogels with silica
nanofiller, which were successfully tested as absorbers of methylene blue.
The studied materials hence possess an promising application potential in
the field of wastewater treatment. The work is dedicated to an attractive
topic, is clearly written and its conclusions are logical and well-supported
by experiments.

The reviewer hence suggests the publication of this manuscript, after adding
some experimental information, and after addressing some other (rather
minor) questions and issues listed below.

1) Experimental Part:

-the type of SiO2 nanoparticles obtained from Sigma-Aldrich should be
specified more precisely (also size and shape could be mentioned).

**Response:** The size of SiO2 nanoparticles have been given as: “20-30 nm” in Materials section.
-the synthesis description should contain mg amounts (ev. also mmol) of
reactants and other components for a typical synthesis batch.

**Response:** The synthesis description has been revised as:“The ratio of AA-*co*-VP was optimized in 3 mL:1 mL, 2 mL:2 mL and 1 mL:3 mL values.” and “0.002 g, 0.021 g and 0.041 g SiO2 nanoparticles was added to achieve 0.05%, 0.5% and 1% (w:w) nano SiO2 doping on AA and AA-*co*-VP (3:1) hydrogels.”

-the description of SiO2 dispersion is missing (simple stirring for x min?
or more sophisticated?).

**Response:** The description of SiO2 dispersion has been added as: “The dispersion of SiO2 in the solution was carried out at the same time as the polymerization process.” In Preparation of hydrogels and SiO2 doped nanocomposite hydrogels part.

-freeze-drying as (probable) sample preparation for SEM imaging should be
mentioned.

**Response:** Freeze drying as sample preparation have been mentioned as: “For better examination of the pore structures of the nanocomposite hydrogels, the water adsorbed hydrogels were put in a freezer (kept at -18 °C) for 12 h, then placed in a vacuum device with frozen states (instrument: Labconco, Freezone 2.5 (Canada) lyophilizer). Hydrogels that have been pressurized in the apparatus for 16 h were examined in FESEM without deformation by the water separation inside.”

2) Results and discussion – Synthesis:

-it would increase the attractivity of the paper, if the structure of the
(co-) polymer would be depicted, eventually the whole synthesis scheme.

**Response:** The authors have cited to previous study.

-generally:  What was the reason for introducing the vinylpyrrolidone
co-monomer (VP) in some gels?  A brief introducing comment would be useful.

**Response:** The reason for introducing the vinylpyrrolidone
co-monomer (VP) in some gels has been added to manuscript as: “Copolymers (AA-*co*-VP (3:1)) have the same behavior as the homo polymer with some new characteristics, which are based on interaction between the monomers. In addition to this, they can be reacted with Si-O groups in SiO2 nanoparticles which dilute in aqueous solution” in Conclusion part.

3) Fig.1 (swelling behavior):

-lines of some samples are poorly visible, an improved legend, which would
note overlapping curves would be useful.

**Response:** Fig. 1 has been revised, the exact swelling values have been added to the Figure.

-a comment concerning the small swelling step near 25–32h of swelling is
missing – is this a gel property or an artifact caused by equipment (after
what is presumably a night pause)?

**Response:** The swelling of the gels has been completed at 25th hours. So, the statement “The equilibrium of the swollen was achieved 25 hours later.” Have been added to swelling behavior part.

4) FT-IR:

-a Table with peak assignment + a shorter text discussing only the most
important trends would be more reader-friendly.

**Response:** Because of the page restriction, unfortunately, a Table have not been added.

5) Porosity discussion (line 205–208):

-It seems from the preparation description, that the studied gels were
originally obtained as homogeneous ones; also their drying prior to swelling
(absorption) with methylene blue solution occurred under very mild
conditions; hence the porosity is likely the result of freeze-drying which
is usually carried out prior to SEM of hydrogels; different final porosities
likely are related to different properties of the samples ‘original’ and
‘after absorption’.

**Response:** The additional SEM images have been given in Supplementary data.

-Involved samples (names) should be mentioned.

**Response:** All the samples have been listed as:

List 1.

Formulations for hydrogel synthesis

|  |  |  |  |
| --- | --- | --- | --- |
| Hydrogel ID | AA (M) | VP (M) | Nanoparticle (SiO2)(wt%) |
| AA | 5.5 | - | - |
| AA-SiO2(0.05) | 5.5 | - | 0.05 |
| AA-SiO2(0.5) | 5.5 | - | 0.5 |
| AA-SiO2(1) | 5.5 | - | 1 |
| AA-VP(3:1) | 4.125 | 1.375 | - |
| AA-VP(2:2) | 2.75 | 2.75 | - |
| AA-VP(1:3) | 1.375 | 4.125 | - |
| AA-VP-SiO2(0.05) | 4.125 | 1.375 | 0.05 |
| AA-VP-SiO2(0.5) | 4.125 | 1.375 | 0.5 |
| AA-VP-SiO2(1) | 4.125 | 1.375 | 1 |
| 0.05M MBA (cross-linking agent) |
| 0.01M APS (initiator) |

6) Nitrogen content (lines 212-214):

The name of the gel in Table 1 should be specified (in case of gels
containing vinylpyrrolidone co-monomer (VP) an initial N-content would be
namely expected).

**Response:** The title of the Table 1. Has been revised as: “TABLE 1. Elemental contents of before and after MB adsorption on AA mono polymeric hydrogels”.

7) Reusability of hydrogels:

It should be mentioned also in the Discussion, that 8 extraction cycles for
removing methylene blue were applied. What was the correct pH value during the dye extraction? 6.4 (as reported in Experimental Part) or 6.8 (reported in Discussion)?

**Response:** pH value has been corrected as: “The desorption studies of the hydrogels were carried out with equilibrated hydrogel in 2-4-6-8 and 10 mg L-1 dye concentration at 25 hours in distilled water (pH 6.4).” in Reusability of hydrogel part.

***Referee 3.***

In the submitted manuscript “Synthesis, characterization and adsorption studies of nanocomposite hydrogels and SiO2 effect on removal capacity of methylene blue dye”, prepared by S. TEMEL et all, the authors synthesized nanocomposite hydrogels by free radical polymerization of acrylic acid and vinyl pyrrolidone in the presence of SiO2 nanoparticles, with aim to be used for adsorption and desorption of methylene blue dye from waste waters. Although there are a lot of measurement performed and presented in the work, based on the presented results and explanation, with regret, by my opinion the submitted manuscript in the presented form is not acceptable to be published in the appreciated Journal, JSCS. The main reasons for such decision are given in the comments.

**Response:** Dear Referee 3, thank you for your valuable comments. The manuscript has been improved according to your advices.

Sincerely