**Manuscript Title:** “Synthesis, characterization and adsorption studies of nanocomposite hydrogels and SiO2 effect on removal capacity of methylene blue dye'" (JSCS-PM-8227R1)

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 second evaluation. The detailed responses to the specific comments/suggestions/queries are presented below.

**Referee 1.**

With responses to the reviewers’ comments given upon revision, and after
the revision performed regarding typos and grammar corrections, the authors
significantly improved the manuscript. Experiments and results are better
discussed. Some crucial figures are added to the manuscript. Nevertheless,
some corrections still need to be performed. Although, Conclusion was
corrected it is still not at the satisfactory level. It is far too long; it
contains unnecessary data and even one reference. In the Conclusion only
substantial results and findings have to be presented. It should be clearly
and concisely written. Again, there is a small number of typos throughout
the text that needs to be corrected. To my opinion and based on results
showed, I can recommend this paper for publication after minor revision in
Journal of Serbian Chemical Society.

**Response:** Dear Referee 1, thank you for your valuable advice. Conclusion part has been revised. Unnecessary data and the reference have been removed. It has been rewritten more clearly.

**Referee 2.**

The Authors considerably improved the Manuscript and partly addressed the
reviewers’ previous suggestions. However, the reviewer still has some
strong reservations concerning the text of the Revised Manuscript, which
should be addressed prior to publication and which are listed below. To save
time, nearly all corrections are suggested in full-text-form, which could be
used directly (and which do not contradict the suggestions of the other
reviewers). In one case, the drawing of a scheme symbolically depicting the
starting compounds and the final structure of a representative gel is
strongly suggested, in order to increase the appeal of this special
Manuscript to the readers of the appreciated JSCS Journal. Some of the
suggested text corrections address the important issue of the gels’
porosity.

Remark:
In future work, it might be interesting to test the rate of swelling, as
well as the MB adsorption capacity of freeze dried gels, especially of the
ones which showed large pores after freeze drying.

List of strongly suggested changes:

1) Introduction, concerning aim of work and co-monomers choice:
Last paragraph of the Introduction should be modified to:
“In this work, nano SiO2 doped AA and AA-co-VP nanocomposite hydrogels
have been synthesized with the purpose of the adsorption of MB dye from
wastewater. AA was chosen as a highly hydrophilic co-monomer which supports
high swelling, VP as a polar hydrophilic co-monomer which could provide
polar interaction with dyes, while the SiO2 nanofiller should enhance the
adsorption of dyes and other polar compounds. The effect of copolymerization
and doping ratio of nano SiO2 in hydrogels were optimized to get the highest
adsorption capacity of nanocomposite hydrogels.”

**Response:** Last paragraph of the Introduction has been rewritten.

2) Experimental Part, synthesis description should be modified to (for
achieving standard reader-friendliness):

“Preparation of hydrogels and SiO2 doped nanocomposite hydrogels The AA
and AA-co-VP hydrogels were synthesized by free radical polymerization in
the presence of an initiator and crosslinking agent in aqueous solution. All
chemicals according to List 1 were mixed at the same time by brief stirring
and filled in PVC straws. PVC straws were placed in a water bath which was
set at 80 oC. The ratio of AA-co-VP was optimized to values of  3:1,  2:2
and 1:3. The concentration of polymerizable double bonds (including the
crosslinker) was always kept constant at 5.6M. The initiator concentration
was allways 0.01M. The reaction mixtures were held at 80 oC for 4h. After
the reaction is completed, the PVC straws were cooled down to room
temperature and hydrogels were released from the straws. The obtained
hydrogels were cut in the same diameter (3-4 mm) and dried in a room
condition for 24 h.

The SiO2 doped nanocomposite hydrogels were synthesized the same way like
the SiO2 – free ones. The only synthesis difference was the addition of
nano- SiO2 (see amounts in List 1). The dispersion of SiO2 in the solution
was achieved during the initial brief stirring of the components of the
reaction mixture. Experimental details were given in previous study25.

List 1.

Formulations for hydrogel synthesis
Hydrogel ID    AA  (g)    AA (mmol)    VP  (g)    VP  (mmol)    SiO2 nanoparticles  (g)
AA        1.59    22        -    -        -
AA-SiO2(0.05)    1.59    22        -    -        0.002
AA-SiO2(0.5)    1.59    22        -    -        0.021
AA-SiO2(1)    1.59    22        -    -        0.041
AA-VP(3:1)    1.19    16.5        0.61    5.5        -
AA-VP(2:2)    0.79    11        1.22    11        -
AA-VP(1:3)    0.40    5.5        1.83    16.5        -
AA-VP-SiO2(0.05) 1.19    16.5        0.61    5.5        0.002
AA-VP-SiO2(0.5)    1.19    16.5        0.61    5.5        0.021
AA-VP-SiO2(1)    1.19    16.5        0.61    5.5        0.041
Additionally:
0.0308 g MBA (cross-linking agent)

0.0091 g APS (initiator) and water filled-up to 4 mL of total volume of the reaction mixture

**Response:** Synthesis description in experimental part has been modified. List 1 has also been revised by using the units: AA(g), AA (mmol), VP (g), VP (mmol) and Nanoparticle (SiO2)(g).

3) Page 4, text concerning electron microscopy should be modified to:
“The morphology of hydrogel surface and elemental analysis were
investigated using a Field Emission Scanning Electron Microscopy (Zeiss,
Supra 40VP) under a 15-kV electron acceleration voltage after Au/Pd (80/20)
coating of the sample. Prior to observation, the swollen hydrogels were put
in a freezer (kept at -18 °C) for 12 h, then placed in a vacuum device in
the frozen state (instrument: Labconco, Freezone 2.5 (Canada) lyophilizer).
After 16 h of freeze-drying, the hydrogels were examined by ESEM.”

**Response:** The text about FESEM has been rewritten.

4) Results and discussion – first paragraph about synthesis:

Original reviewers’ note:

-it would increase the attractivity of the paper, if the structure of the
(co-) polymer would be depicted, eventually the whole synthesis scheme.
Authors‘ response to first review:

The authors have cited to previous study.

Rewiewer’s present reply:

The reviewer still insists, that such a scheme should be included in the
present full paper (the present Manuscript is not just an appendix to the
previous publication but a new interesting work).

**Response:** Schematic representation of the polymerization reactions have been added as Sheme 1 on Experimental part. As: schematic representation of possible structure of homo- and co-polymeric hydrogels is given in Scheme 1.



**Scheme 1.** Schematic illustration of the preparation of crosslinked homo/co-polymeric hydrogels

5) Discussion of nitrogen content on Page 8:

Line 3 below Fig. 3 should be modified to:

“analysis, because of the absence nitrogen in their chemical structure.
…” (“nitrogen” in place of N%)

**Response:** The sentence has been changed to: “AA mono polymeric hydrogel was chosen for SEM analysis, because of the absence nitrogen in their chemical structure.”

6) Discussion of nitrogen content, TABLE 1 on Page 9:

Please specify in the caption whether atom % or wt% are meant; mention that
Hydrogen is not evaluated; suggested Caption texts:
“TABLE 1. Elemental contents except hydrogen (atom %) of before and”
or “TABLE 1. Elemental contents except hydrogen (wt%) of before and”
**Response:** The caption of Table 1 has been changed to: “TABLE 1. Elemental contents except hydrogen (wt%) of before and after MB adsorption on AA mono polymeric hydrogels”.

7) The revised text discussing morphology and porosity on page 8:
“Despite, the surface of MB unattached hydrogel was homogenous,
dye-attached hydrogels have lost their both elasticity and pore homogeneity
(Fig 4(b)). The loss of elasticity was due to dye-monomer interactions. 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.” should be replaced by: “The hydrogels which absorbed MB have lost their elasticity. Also the porous structure generated by freeze-drying of the gels loaded with MB was a different and less homogeneous one, than the porous structure generated by
freeze-drying of MB-free gels (compare Fig. 4(a) and 4(b)). The different
porosity of the MB-loaded dried gels well correlates with their observed
stiffness in the swollen state.”

**Response:** The paragraph has been rewritten.

Remarks:
(The description of the freeze-drying process and equipment was suggested to
be moved to the Experimental Part). Presence of porosity prior to freeze drying is not possible due to the homogeneous reaction mixture and the high hydrophilicity of both the
involved monomers and polymers (copolymers).

**Response:** The descriptions of the freeze-drying process and equipment have been moved to the Experimental Part.

8) Re-usability of hydrogels top paragraph on Page 11: The paragraph should
be corrected to following corrected text:

“The MB desorption studies were carried out with hydrogels previously
equilibrated in 2, 4, 6, 8 and 10 mg L-1  MB dye solutions at pH = 8.4. The
desorption was carried out in distilled water (pH 6.4) in eight cycles of 24
hours per each cycle. The amount of desorbed MB dye was determined by UV/Vis
spectrometry. The recovery range was between 25-40% for various dye loadings
(Fig.6). At lower concentrations, the dye recovery in the range of 35-40%
(Fig.6). The maximum recovery values were obtained from undoped (SiO2-free)
hydrogels. As the amount of SiO2 increased, the recovery was reduced by
about 5% (Fig. 6). The SiO2 nanoparticles obviously bonded methylene more
strongly than the (AA, AA-co-VP) polymer chains. While at pH = 8.4 the
adsorption was highly efficient (80-98% observed), in case of the distilled
water at pH = 6.8 the reverse process (desorption) is moderately favored:
maximum released MB amounts of 40% are achieved. This demonstrates the
pH-sensitivity of the adsorption process.”

**Response:** The paragraph has been rewritten.

9) Elemental analysis on Page 11 and in Caption of Fig. 7 on Page 12:
it should be again specified if wt% or atom % are meant and that Hydrogen
content was excluded from the % values.

**Response:** Elemental analysis on Page 11 has been rewritten as: **“**C, H and N weight content of dye adsorbed hydrogels were characterized by Elemental Analysis. The nitrogen value of MB was determined in both homo and co-polymeric doped and undoped SiO2 hydrogels. C, H and N (wt%) elemental distribution of dye adsorbed hydrogels was given in Fig.7. In that case, the most dye attached to AA-*co*-VP / %1-SiO2 co-polymeric hydrogel. The amount of nitrogen showed the presence of the dye on all hydrogels with different amounts.” and the caption of Fig.7 has been rewritten as: “Fig 7. Nitrogen (wt%) distribution of non-adsorbed hydrogel and MB adsorbed hydrogel”.

10) CONCLUSION section:

10a)
“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 solution9.” change to
“Copolymers (AA-co-VP (3:1)) show a similar behavior like the homopolymer
but they possess some new characteristics, which are based on interaction
between the co-monomers and the dyes which are adsorbed. In addition to
this, the interactions between polymer chains and SiO2 nanoparticles are
also modified by the presence of the VP co-monomer9.”

**Response:** The paragraph has been rewritten.

10b)
“Both homo-polymeric and co-polymeric hydrogels showed more swelling
behavior than SiO2 doped nanocomposite hydrogels, due to SiO2 nanoparticles
located in the pore structures. On the other hand, the homopolymeric
hydrogels had higher swelling behavior than nanocomposite hydrogels because
of the interaction between nanoparticles and cross-linked polymer chains.”
change to “The SiO2-free (both homo-polymeric and co-polymeric) hydrogels showed a
higher swelling than SiO2-doped nanocomposite hydrogels, due to some
physical crosslinking by SiO2 nanoparticles in the nanocomposite
hydrogels.”

**Response:** The paragraph has been rewritten.

10c)
“SEM images were consistent with the swelling behavior of hydrogels.”
change to “SEM images of gel samples with porosity generated by freeze drying were
consistent with the swelling behavior of hydrogels (with higher swelling
gels being softer).”

**Response:** The paragraph has been rewritten.

10d)
“Adsorption of methylene blue on other hydrogels and nanocomposite
hydrogels …” change to  “Adsorption of methylene blue on SiO2-free and on nanocomposite hydrogels…”
**Response:** The sentence has been rewritten.

10e)
“All nanocomposite hydrogels showed adsorption affinity to MB dye in the
aqueous solution.” this sentence should be deleted (it was already said in different words in
the Conclusion text above).

**Response:** The sentence has been deleted.

Referee 3.

In the submitted revised form of the 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 made revisions covering the comments of Reviewer 1 and
Reviewer 2. On the other side, from the point of view of my side, designed
as a Reviewer 3, the Authors completely neglected all the comments and
suggestion, without providing any response.

Therefore, unfortunately, my decision, as a Reviewer 3, is that the
submitted manuscript in the presented form is not acceptable to be published
in Your appreciated Journal, JSCS.

**Response:** In first reviewer report, the third referee has rejected the manuscript by commenting as: “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.” Although there were only the reasons why sir/madam has rejected the manuscript, there was no any advice/request to the authors. In this second reviewer report, the third referee didn’t request any correction. He/she again rejected the manuscript without giving a chance to the authors.

Sincerely,

Dr. Fatma Özge GÖKMEN