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Original citation & hyperlink:

Rashid, T, Iqbal, D, Hazafa, A, Hussain, S, Sher, F & Sher, F 2020, 'Formulation of zeolite supported nano-metallic catalyst and applications in textile effluent treatment', Journal of Environmental Chemical Engineering, vol. 8, no. 4, 104023.

<https://dx.doi.org/10.1016/j.jece.2020.104023>

DOI 10.1016/j.jece.2020.104023

ISSN 2213-3437

Publisher: Elsevier

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DOI: 10.1016/j.jece.2020.104023

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Formulation of zeolite supported nano-metallic catalyst and applications in textile effluent treatment

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Highlights

- The borohydride method was used to synthesize a novel natural zeolite-supported nano-zerovalent iron (NZ-nZVI) catalyst.
- The unprocessed naturally mined zeolite was used as support for nZVI to decrease the aggregation and cost.
- The synthetic acid orange 52 dye was removed over 94.86% after 180 min treatment with novel natural zeolite modified nZVI.
- More than 60% of dye removal was observed within the first 10 min of treatment with NZ-nZVI at 15 mg/L concentration.
- NZ-nZVI/SPC Fenton system also effectively removed the green, magenta, and blended colour from the actual textile effluents.

31 **Abstract**

32 Textile industry is one of the major industries worldwide and produces a huge amount of coloured
33 effluents. The presence of coloured compounds (dyes) in water change its aesthetic value and cause
34 serious health and environmental consequences. However, the present investigation was carried
35 out to minimize and reduce the colour compounds discharged by the textile industries through a
36 nano-scaled catalyst. This study is mainly focused on the explanation of nanoparticles aggregation
37 by deposition on natural zeolite, and utilization of this natural zeolite as supported material to nano
38 zerovalent iron (NZ-nZVI) in the form of liquid slurry with sodium percarbonate acting as an
39 oxidant in a Fenton like system for the removal of synthetic CI acid orange 52 (AO52) azo dye, in
40 textile effluent. The nano-scaled zerovalent irons were synthesized by borohydride method in
41 ethanolic medium. UV-vis spectrophotometry, FTIR, EDX, SEM, and XRD (powdered) analysis
42 were used for the investigations of surface morphology, composition, and properties of natural
43 zeolite supported nZVI and study the dye removal mechanism. The XRD spectrum revealed that
44 clinoptilolite is the major component of natural zeolite used, while EDX found that the iron content
45 of NZ-nZVI was about 9.5%. The introduction of natural zeolite as supporting material in the
46 formation of iron nanoparticle resulted in the partial reduction of aggregation of zerovalent iron
47 nanoparticles. The findings revealed that the 94.86% removal of CI acid orange 52 dye was
48 obtained after 180 min treatment at 15 mg/L initial dye concentration. The highest rapid dye
49 removal of about 60% was achieved within the first 10 min of treatment at the same dye
50 concentration. Furthermore, the actual dyeing effluent including green, magenta, and the blended
51 colour was successfully decolourized by natural zeolite-supported nZVI/SPC Fenton process. It is
52 concluded that the acceleration of corrosion of NZ-nZVI, breaking of azo bond, and consumption
53 of Fe^{2+} were the possible mechanisms behind the removal of AO52 dye. It is also recommended

54 that NZ-nZVI/SPC Fenton process could be a viable option for effluent and groundwater
55 remediation.

56

57 **Keywords:** Fenton process; Natural zeolite; nano zerovalent iron; CI acid orange 52 dye; dye
58 removal; and Textile dyeing wastewater.

59 **1 Introduction**

60 The textile industry is one of the major industries worldwide and the highest consumer of raw
61 water. This sector is growing proportionally with an increasing demand for textile products
62 worldwide. This increase is also causing an increase in water demand and consequently increased
63 effluent discharge [1, 2]. The major operations involved in the textile industry are spinning
64 (twisting of fibres to form thread), weaving (arranging two different sets of threads perpendicular
65 to each other to form fabric), and finishing. Finishing steps might contain several elements,
66 including washing, bleaching, stabilizing and dyeing operations [3]. The inappropriate discarding
67 of industrial wastes including dyes causes serious health and environmental problems [4].
68 According to accumulated data, worldwide there is 7–10 million ton annual dye production and
69 commercially more than one million types of dyes exist [1]. In this total dye production >2.8
70 million tons of textile dyes are discharged as industrial wastes [5]. Dyes are usually classified
71 according to their usage and application method. Among all dyes including reactive, direct, vat,
72 disperse, azo, acid and anthraquinone dyes, the azo dye holds up to 70% market share of all organic
73 dyes [6-8].

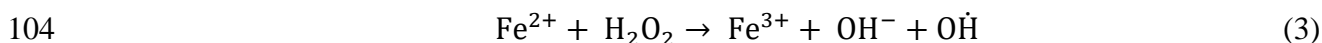
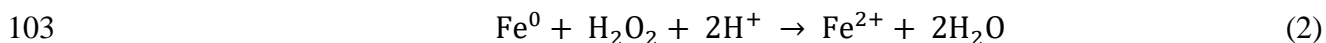
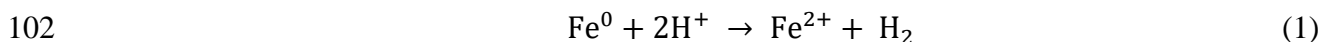
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75 Major constituents of textile effluent are colour, total dissolved solids (TDS), chemical oxygen
76 demand (COD), turbidity, and pH. The presence of dyes in the effluent affects the aesthetic value

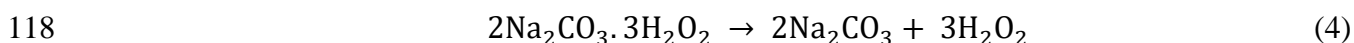
77 of the water and possesses severe environmental and health threats. They tend to adversely affect
78 aquatic life and are carcinogenic for human beings [9]. Several prominent azo dyes are degradable
79 into amines in an intestinal environment, which are proven carcinogens [10]. Carcinogenic threats
80 are not only limited to azo family dyes. The anthraquinone dyes, such as Disperse Blue 3 is also
81 found to have severe toxic effects [11, 12]. The removal of colouring ingredients from the
82 wastewater poses a major challenge. According to current industrial practices, different methods
83 are being applied for the removal of dyes from wastewater, including physical
84 (powdered/granulated activated carbon and adsorption), chemical (coagulation), and biological
85 (fungal decolourization or microbial degradation). However, due to low biodegradability, high
86 cost, low efficiency and toxic byproducts (DBPs), these methods attain less attention [9, 13, 14].
87 The advanced oxidation process (AOP) is an alternative method for the removal of dyes from
88 industrial effluent [15].

89
90 The advanced oxidation process (AOP) relies on the oxidation of organic contaminants by
91 involving highly reactive species such as hydroxyl radical (OH), hydrogen peroxide (H₂O₂), ozone
92 (O₃) and sulfate radical (SO₄^{·-}), for the removal of dyes. Furthermore, AOP has the potential to
93 offer complete or satisfactory degradation of textile dyes and other contaminants, unlike other
94 conventional methods [9, 16]. AOP includes Fenton process, per-ozonation, H₂O₂/UV, photo-
95 Fenton, O₃/UV, and Sono-AOP. Due to high reactivity and efficient remediation of contaminants,
96 the Fenton process is being focused upon as AOP of choice among all processes. Fenton process
97 includes disintegration of hydrogen peroxide (H₂O₂) by ferrous ion (Fe²⁺) to generate hydroxyl
98 radical which further binds with organic impurities to remove dyes/colour from water according
99 to following Eqs. (1–3) [17, 18]. In the last few decades, many heterogeneous catalysts including

100 Fe₂O₃, Ag₂O, ZnO, and TiO₂ have been used to depollute water from toxic metal ions (Cr^{VI}) and
101 other pollutants like dyes [19, 20].



105
106 The nanotechnology for dye removal has achieved special attention in the scientific community
107 since the last decade. Nano-zerovalent iron (nZVI) got more focus due to superior dye removal
108 efficiency, less toxicity, and cost-effective characteristics. nZVI particles have less than 100 nm
109 size, due to their smaller particle size; they possess higher surface area (29 m²/g) and display higher
110 reactivity than mZVI (micro nano-zerovalent iron). Due to its high surface area, it can be
111 effectively used as an adsorbent for textile dye removal [21]. According to previously published
112 literature, more than 90% of decolourization of methyl orange dye was observed with nZVI in 24
113 min treatment while only 25% of decolourization was achieved by mZVI with the same treatment
114 time [22]. Use of hydrogen peroxide can be difficult due to transportation, storage and usage
115 challenges. Recently, sodium percarbonate has been suggested as a novel source of H₂O₂. It
116 contains hydrogen peroxide within its matrix, which it releases on dissolution in water by the
117 following Eq. (4) [17, 18].



119
120 nZVI particles tend to aggregate due to their magnetic properties and Van der Waals attraction.
121 This is one of the two major inhibitors of nZVI's performance, the other being their rapid corrosion
122 on exposure to air. Aggregation of nZVI depends upon particle concentration, size of particles,
123 magnetic properties, surface area to volume ratio and pH [23]. Recently several support materials

124 have been used as good carriers to decrease the aggregation of nZVI including alumina, chitosan,
125 bentonite, graphene oxide, biochar, coral, kaolin, clinoptilolite, and activated carbon [24, 25].

126

127 In the previously published literature less reactive, high price and toxic by-products of these
128 supporting materials have been observed. Therefore, for the first time, the natural zeolite (due to
129 its high cation exchange capacity) as support material with nZVI to decrease its aggregation,
130 enhance biodegradability and efficiency to remove synthetic and textile dyes is used in the present
131 study. Shi and co-workers [26] reported the 86.4% removal of Rhodamine B dye within 20 min
132 by using nZVI particles with reduced graphene oxide (r-GO) as a supported carrier. They also
133 observed nanoparticles dispersion on the graphene oxide sheet with decreased aggregation.
134 However, some aggregation persisted even after the deposition of nZVI upon the r-GO sheet. Han
135 and his research group [27] used biochar as support material for nZVI in the removal process of
136 methyl orange dye. They observed an improved dispersion and reactivity of nanoparticles, as well
137 as enhanced adsorption capacity resulting in 98.5% dye removal at a composite dose of as low as
138 600 mg/L, at an optimum pH of 4 within 10 min. Jin and co-workers [28] suggested the use of
139 nZVI and kaolin in equal mass ratios, in a removal study of Direct Fast Black G dye and reported
140 99.8% removal of dye in 1 h even in the alkaline range of 9.4.

141

142 Another study found bentonite as a better option (92.7% dye removal) than native clay (92.1%)
143 and kaoline (91.6%) for remediation of an industrial azo dye [29]. Malik and co-workers reported
144 that nZVI, Fe and ozone pre-treatment on actual filtrated textile effluent showed significant results
145 of about 0.61 for biochemical and chemical oxygen demands (BOD/COD) with 87% of colour
146 removal, as compared to untreated effluent [30]. Similarly, ultrasonication supported the removal

147 of toxic Remazol black 133 dye up to 80% within 15 min treatment at an optimum pH range of 4–
148 10. They also noticed that one gram of nZVI removed approximately 749 mg of dye, by breaking
149 the azo group into an amino group. They also suggested that dye removal efficiency was increased
150 via increasing nanoparticles dosage [31]. Luo and coworkers demonstrated a complete removal of
151 orange II dye using rectorite (a natural clay), as support for nZVI in 10 min treatment, while only
152 35% dye removal was observed by using unsupported nZVI [32].

153
154 However, many supporting materials (kaolin, bentonite, biochar, alumina, and chitosan) have been
155 applied in combination with nZVI to decrease its aggregation and increase reactivity, but the
156 above-mentioned supported materials are expensive and produce toxic by-products like DBPs. To
157 overcome this problem, for the first time, this study investigates the synthesis of natural zeolite as
158 supported material of nano-zerovalent iron (NZ-nZVI) by using borohydride method to remove
159 the synthetic dye (CI Acid Orange 52) from textile waste. SEM, EDX, FTIR and UV/VIS analyses
160 were performed to evaluate the structure and performance of natural zeolite and synthesized NZ-
161 nZVI. Furthermore, present study also assessed the mutagenic dye remediation potential of NZ-
162 nZVI in a Fenton like process by using sodium percarbonate (SPC) as a source of reactive advance
163 oxidative species for both synthetic dye solution and actual textile effluents. To deal with the
164 corrosion of nZVI on exposure to ambient air, nZVI was synthesized and introduced to target
165 solution in the form of a liquid slurry.

166 **2 Materials and methods**

167 **2.1 Chemicals**

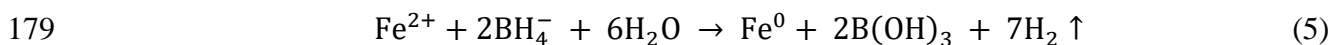
168 Sodium Borohydride (NaBH_4 : 97%) was procured from Deajung, Korea. Iron (II) Sulphate
169 Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and Ethanol (Absolute) were purchased from BDH. Natural Zeolite

170 was procured from Meiqi Trade Co. China. Sulfuric Acid (H₂SO₄), Sodium Percarbonate
171 (Na₂CO₃.1.5H₂O₂) and Sodium Hydroxide (NaOH) were purchased from Sigma Aldrich (USA).
172 CI Acid Orange 52 (methyl orange) dye was purchased from Sinochem, China. Actual dyeing
173 effluent was obtained from Multan Yarn Dyeing, located at home-tex export zone, Multan,
174 Pakistan.

175 **2.2 Preparation of NZ-nZVI catalyst**

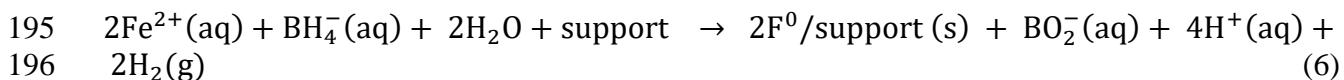
176 NZ-nZVI was synthesized by borohydride method, also known as reduction method, or liquid
177 phase reduction method according to the following Eq. (5) [33, 34]:

178



180 The preparation of NZ-nZVI was achieved by adding a 250 mL solution of ethanol in deionized
181 water (40%) made in a Pyrex beaker. The solution of FeSO₄.7H₂O was added into the ethanol-
182 water mixture, it is readily soluble in water and dissolved immediately with mild stirring. Then the
183 natural zeolite which is composed of clinoptilolite (85.7%), SiO₂ (65.5%), Al₂O₃ (12.3), Fe₂O₃
184 (1.49), CaO (3.97), MgO (0.92), and K₂O (1.54) [35] (pulverized and sieved < 63 μm) was added
185 with the ratio of 1:2 of FeSO₄.7H₂O and Zeolite. The pH was maintained at 4 and ultrasonicated
186 for 15 min; the pH of FeSO₄.7H₂O solution increased to around 5–5.5. To maintain the pH a few
187 drops of H₂SO₄ solution (approx. 0.4 M) were added to decrease the pH to 4. The ultrasonication
188 was used to breakdown iron sulfate agglomerates and effectively disperse the zeolite and iron
189 sulfate in an aqueous matrix to improve the iron sulfate adsorption on the zeolite surface.
190 The pH is a critical factor in the preparation of NZ-nZVI because as near neutral pH, the nZVI
191 starts to precipitate in the aqueous solution in the form of iron oxides and hydroxides. After the
192 homogenization of reaction mixture, 1 M NaBH₄ was added at a rate of 1.6–2 mL/min with

193 moderate stirring. The synthesis of nZVI on the support of natural zeolite (NZ) was achieved
194 according to the following Eq. (6) [36].



197
198 NZ-nZVI particles are formed almost immediately, indicating an initiation of the reduction
199 process. NaBH₄ gives off hydrogen gas in water, and hence its solution cannot be stocked. It must
200 be prepared 10 min before use. If NZ-nZVI made immediately prior to use, the emitting hydrogen
201 gas can cause heavy froth in the reaction mixture. The emitted hydrogen froth prevents the further
202 addition of NaBH₄ and reduces the zeolite supported iron in the aqueous solution and form nZVI
203 instead of NZ-nZVI. When the reduction of iron has completed, it was remained to settle down for
204 1 h and finally stored in the same reaction media. The nanoparticles must not be exposed to the
205 ambient air in order to prevent the corrosion of iron. Literature also recommends the storage of
206 nanoparticles in nitrogen environment to prevent rusting [36, 37].

207 **2.3 Preparation of synthetic methyl orange dye and actual dying effluents**

208 Dye removal studies were performed for both synthetic and actual textile effluent. Concentrated
209 dye stock solution of CI Acid Orange 52 (methyl orange) was prepared with a concentration of 35
210 ppm and various solutions for removal studies were prepared by serial dilutions. The dye stock
211 solution was prepared at least 24 h prior to use because some undissolved dye fragments remain
212 in the solution even after 2–3 h of mixing and may need a longer time to completely dissolve. The
213 preparation of dye was achieved by adding 250 mL of dye solution diluted up to the required
214 concentration in a Pyrex beaker, which served as the reaction vessel [38]. 40 mL of NZ-nZVI
215 slurry and sodium percarbonate was added into the reaction vessel and continuously stirred at 450

216 rpm. The synthetic dye solution was prepared by mixing Acid Orange 52 (AO52) dye, a bright
217 orange powder, with distilled water. Initially, a 35 pm stock solution was prepared, which was then
218 serially diluted to the required concentrations. The actual dyeing effluent was prepared by adding
219 250 mL of textile effluent sample in a Pyrex Erlenmeyer flask with deionized water. Erlenmeyer
220 flask is recommended, as high froth generation could be observed in the treatment of low pH dye
221 effluents. The NZ-nZVI slurry and sodium percarbonate (SPC) solution was added into the
222 Erlenmeyer flask and stirred at 450 rpm.

223 **2.4 Characterization of NZ-nZVI catalyst**

224 The nano zerovalent iron particles supported on natural zeolite were analyzed by using FEI Quanta
225 250 scanning electron microscopy (SEM) for studying the surface morphology along with energy-
226 dispersive X-ray spectroscopy, while the mineralogical content was studied using Malvern
227 Panalytical X-pert Pro XRD. Elemental composition was detected to confirm the iron loading on
228 natural zeolite by INCA X-Act Electron Back Scattered Diffraction System (Oxford Instruments,
229 U.K). Removal of dye from target dye solutions was recorded by UV-vis Spectrophotometry
230 (model V1100), while the functional groups found on the raw natural zeolite and NZ-nZVI were
231 studied using Fourier transform infrared spectroscopy (Perken Elmers Spectrum: FTIR).

232 **2.5 The percentage removal efficiency of CI Acid Orange 52 dye and actual dyeing** 233 **effluent**

234 Five different concentrations of synthetic dye solution (AO52) were synthesized as follows 5, 10,
235 15, 20, and 25 mg/L. UV-vis spectrophotometer was used to investigate the change in dye
236 concentration concerning time and its work according to the Beer-Lambert law. Deviation from
237 this law is observed on too high concentrations of analyte, possibly due to electrostatic interactions
238 of molecules. Hence, to ensure the accuracy of absorbance measurement, dye concentration was

239 limited to 25 mg/L. AO52 solutions (250 mL) were stored in dark, to avoid any UV oxidation.
240 Stirrer rpm, pH and temperature were kept constant during all runs. The dye (AO52) removal
241 efficiency was reported over the course of 180 min. multiple absorbance of each sample were
242 recorded at 465 nm, and the average value was reported.

243
244 In actual dyeing effluent, the dye removal study was performed on three samples as actual effluent
245 green (AEG), actual effluent magenta (AEM), and actual effluent blended (50% AEG + 50% AEM
246 = AEB). Samples were treated with NZ-nZVI/SPC system without any filtration or dilution. To
247 the best of our knowledge, this is unprecedented in scientific literature, as actual samples are often
248 diluted up to several times or passed through some polishing step prior to treatment. The dye
249 removal efficiency was reported over the course of 180 min at natural pH of effluent [39]. IR and
250 UV-vis absorbance spectra were used to understand the dye removal process. Periodically,
251 approximately a 4 mL sample was taken, filtered to remove NZ-nZVI particles and then filled into
252 the glass cuvette for absorption determination by UV-vis spectrophotometer. Absorption was
253 measured against distilled water (in case of actual effluents) and 9 mM sodium percarbonate (SPC)
254 solution (in case of AO52) as blanks. The removal efficiency was calculated by the following Eq.
255 (7).

$$256 \quad \quad \quad \% \text{ removal} = (A_0 - A_t) / A_0 \times 100 \quad (7)$$

257
258 where A_0 represents the initial values of synthetic dye (AO52) and actual effluent (green, magenta,
259 and blended) in mg/L, and A_t represents the values of synthetic dye and actual effluent at time t .
260

261 The heavy froth was observed by the addition of NZ-nZVI/SPC into the reaction vessel of actual
262 dye. Which might be due to the maximum reactivity of Fenton system that occurs at acidic pH.
263 Therefore, the Erlenmeyer flask is recommended to avoid any reagent loss by dropping froth out
264 of the reaction vessel.

265 **3 Results and discussion**

266 **3.1 Characterization study of NZ-nZVI**

267 The characterization studies were performed by scanning electron microscope (SEM), X-ray
268 diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-Ray
269 (EDX) Detector. SEM was used to study the surface morphology of zeolite particles and NZ-nZVI.
270 SEM analysis of samples was conducted at accelerating voltage within the 15–20 kV range, and a
271 dwell time of 30 micro-seconds (μs) as reported in **Fig. 1**. The surface area is a critical factor in
272 proper functioning of n-ZVI because the surface area is typically corresponding to the reactivity
273 of n-ZVI particle, and the measured surface area of n-ZVI is between 8.4–46.27 m^2/g by NaBH_4
274 method [40]. Zeolite particles were quasi-spherical in shape with 2–30 μm particle size. The
275 natural zeolite surface was comparatively smooth. The smaller particles were distributed all over
276 the larger ones. Chain-Like structures were present in NZ-nZVI, which covered the zeolite grains
277 [41]. After the utilization of NZ-nZVI particles in dye removal, they were filtered out and dried in
278 the form of fragile chunks of iron. These NZ-nZVI chunk were found to be highly porous.
279 Although impregnation of natural zeolite surface with nZVI significantly decreased the
280 aggregation, some nanoparticles attraction persisted, as the presence of individual particle entities
281 were slightly diminished. This existence in the form of an individual particle was seen again in the
282 case of used NZ-nZVI particles. However, the surface of used NZ-nZVI was rougher as compared

283 to unloaded natural zeolite, due to buildup of iron oxides on the surface during the removal process
284 [42].

285
286 The EDX detector results showed that the natural zeolite did not contain iron content, and it
287 appeared after the loading of nZVI onto the natural zeolite surface as presented in **Fig. 2**. Iron was
288 loaded in its nano zerovalent scale during the synthesis procedure. The loaded iron content was
289 9.5%, which is low as compared to most of the previously cited quantities in the literature [32, 43].
290 According to Luo et al. [32], the loaded iron content was 9.94% (w/w) in nZVI. The oxygen
291 content increased only after use, which indicates the corrosion of NZ-nZVI particles. Synthesized
292 NZ-nZVI contained sodium, which is expected to appear due to the use of NaBH₄ for reduction.
293 The negligible sulfur contents were also detected, due to the use of sulfuric acid for pH control.
294 Natural zeolite was free from sulfur as per EDX detection. No obvious peak of crystalline iron was
295 noticed in the sample, which indicates the dispersion of iron species. These iron species formed
296 very small-sized crystallites which were not detectable [32]. EDX detector was also used for the
297 elemental composition of samples that are illustrated in Error! Reference source not found..

298
299 XRD Spectrum of natural zeolite is shown in **Fig. 3**. The XRD was used to investigate the
300 mineralogical nature of the natural zeolite used as nZVI support. The characteristic strong peaks
301 appeared at 13, 22.37, 26.6, 28.15, and 32 intensity in the spectrum indicate that the natural zeolite
302 consists mostly of clinoptilolite [44]. It was observed that most of the peaks were fall in these three
303 spectra, which indicate the presence of clinoptilolite, and model structural formula could be
304 suggested as (Na, K, Ca)₆(Si, Al)₃₆O₇₂·20H₂O [45]. The natural zeolite also contained heulandite
305 confirmed by peaks appeared at 2theta values of 17.2, 26.6, and 35.86 in the spectra. The peak at

306 26.6 also shows the presence of quartz in the zeolite sample. A sufficient quantity of calcite was
307 also observed at 3θ that is in agreement with the recently stated study [46]. In addition, the small
308 quantity of phillipsite zeolite was also detected through its peaks appeared at 21.51 and 45.82
309 intensities [44]. Clinoptilolite is high silica-containing and one of the most common types of
310 natural zeolite. It has a negatively charged surface, which tends to attract cations, such as Na^+ .

311
312 FTIR spectra of natural zeolite and NZ-nZVI is represented in **Fig. 4**. The symmetric and
313 asymmetric stretching of the hydroxyl group is shown by the peak at 3366.69 cm^{-1} . This is expected
314 due to absorbed water present in the natural zeolite framework. The band at 1633 cm^{-1} represents
315 the water molecularly bound within the zeolite structure, as well as the metal-O bonding. The
316 aluminosilicate status of zeolite is evident from the peak at 1034 cm^{-1} , which is due to Al and/or
317 Si bonding with oxygen. This is once again shown in the fingerprint region, where the peaks at
318 799.3 cm^{-1} and 780.59 cm^{-1} represent the Si-Al-O bonding. The results of natural zeolite spectrum
319 are in good agreement with the previously reported IR studies [47, 48]. Ruiz-Baltazar and co-
320 workers [47] stated that zeolite has a large surface area due to allotropic phase of SiO_2 that is
321 recognized by the peak appeared at 797 cm^{-1} and is associated with O-Al and Si-O bonds, which
322 are characteristically tectosilicates.

323
324 The FTIR spectrum of used NZ-nZVI was also recorded and is presented in **Fig. 4**. Some
325 characteristic features of this spectrum are the significant increase in the depth of OH stretch band
326 at 1330 cm^{-1} and the C-O stretch band at 1030 cm^{-1} that might be due to the ethanol used in the
327 synthesis and storage process [49]. There is another shift in the spectrum, however, the direction
328 of this shift is opposite in the fingerprint region at left half. Furthermore, the shift in OH stretch is

329 due to the loading of nZVI on the natural zeolite, which causes the IR to be absorbed at
330 comparatively lower frequencies. The stretching and bending vibrotational band of OH in water
331 molecule adsorbed over the n-ZVI surface was observed as 3422 and 1600 cm^{-1} , respectively [50].
332 Moreover, two new peaks appeared at 2884.6 cm^{-1} and 2823.37 cm^{-1} represent the OH bonding in
333 the iron oxide shell, most likely due to FeOOH.

334 **3.2 Aggregation reduction study of NZ-nZVI**

335 Few batches of nZVI were also prepared to visually compare the aggregation behaviour of
336 supported and unsupported nZVI. The use of natural zeolite as support material for nZVI greatly
337 reduced nanoparticle aggregation. Some magnetic attraction existed between NZ-nZVI particles
338 which was trying to join with each other but were again separated by even very slight shear, while
339 the aggregated nZVI particles were able to resist even very vigorous mixing and therefore, had to
340 be ultrasonicated to separate [34]. Furthermore, the aggregation persisted even on vigorous manual
341 stirring. Aggregation dissipated when the liquid was subjected to ultrasonication for 20 min but
342 returned within 100 s when the ultrasonication was stopped. Therefore, once particles separated,
343 they aggregated immediately together. Natural zeolite supported nZVI demonstrated superior
344 dispersion in the aqueous media than their unsupported counterparts. The reduction in the
345 aggregation of nZVI by using support material is in agreement with several previously reported
346 studies [24, 51, 52]. Shahwan et al. [51] observed a partial reduction in the aggregation of iron
347 nanoparticles by intruding K10 as supporting material during the synthesis of nZVI particles.

348 3.3 Dye removal study

349 3.3.1 Removal of synthetic CI acid Orange 52 dye

350 Five different initial dye concentrations (5, 10, 15, 20, 25 mg/L) were used to check the synthetic
351 Acid Orange 52 (AO52) dye removal over 180 min treatment. The results of different initial dye
352 concentrations on synthetic AO52 dye removal are depicted in **Fig. 5**. Dye concentration drop over
353 time, as well as an increase in percentage removal, was observed as illustrated in **Fig. 6**. The
354 decrease in dye concentration over the treatment of 180 min was studied as a result of Fenton
355 system comprising of NZ-nZVI/SPC. Furthermore, to remove dye from the aqueous solution the
356 SPC and NZ-nZVI slurry were conveniently suspended in an aqueous matrix on slightest agitation
357 that stayed in suspension for a considerable period due to negligible gravitational pull and small
358 size of NZ-nZVI particles.

359

360 Moreover, visible decolourization of samples started after 10 min in all five concentrations (5, 10,
361 15, 20, 25 mg/L). Colour of the reaction mixture first turned from black to dark green tint and then
362 to dark red/ brown after 29 min. The reaction mixture completely changed its colour after 70 min.
363 The maximum rapid dye removal was observed within the first 10 min about 60% removal.
364 Further, decolourization rate drops considerably after 20 min and maximum dye removal (>90%)
365 was achieved after 180 min treatment at 15 mg/L concentration. More than 80% of dye removal
366 was noted within 30 min of operation at 15 mg/L initial dye concentration. These findings correlate
367 with the recently published research, which states 73.5% removal of atrazine by GO/nZVI within
368 the first 30 of min treatment and the removal efficiency increased up to 81.6% with total
369 elimination of atrazine after 240 min [53].

370

371 Dutta et al. [54] reported that more than 80% reduction of Remazol Brilliant Orange 3RID dye
372 was achieved within the first 15 min treatment with nZVI catalyst. They also stated that one gram
373 of nZVI significantly removed about 2207 mg of anthraquinone dye (RBMR) and 2757 mg of
374 Remazol Brilliant Orange 3RID dye. With 5 mg/L concentration, 89.3% removal was recorded in
375 the first 60 min. However, the following two hours resulted in only approximately 2.5% dye
376 removal. The maximum dye removal was 93.5% in the case of 10 mg/L initial concentration and
377 94.8% in the case of 15 mg/L concentration after 180 min treatment as represented in **Fig. 7**.
378 Comparable findings of a previous study stated that 96% decolourization of methyl orange dye
379 was achieved while using CFA (coal fly ash) as supporting material for nanoscale ZVI through
380 Fenton reaction at pH 3 [49].

381
382 A recent study reported about 80% removal of acid orange 7 (AO7) dye by using PMS/WMF as a
383 supported carrier with Z-nZVI. But surprisingly after three-times regeneration of zeolite, the
384 decolourization percentage of AO7 dye was improved and detected as 90% removal [34].
385 Similarly, a surprising rise in removal efficiency was observed at an initial dye concentration of
386 25 mg/L. Furthermore, 79.68 and 83.73% dye removal was recorded after 20 and 30 min of
387 operation respectively at 25 mg/L concentration, as compared to 68.5 and 74.28% in the case of
388 20 mg/L concentration. Most probably the reason for this behaviour is the negative surface of
389 clinoptilolite type natural zeolite used as NZ-nZVI support. Therefore, a 20 mg/L, the negative
390 ions of dissociated AO52 are repelled due to similar charge of zeolite. However, when the initial
391 concentration increases up to 25 mg/L the momentum of ions in motion overcomes the repelling
392 effect of zeolite and adsorption of dye on NZ-nZVI and consequent removal performance

393 improves. These results are in agreement with the findings of several other researches, which
394 reported remediation application of nZVI along with the advanced oxidation process [29, 55].

395
396 The overall dye removal percentage was decreased by increasing the an initial dye concentration
397 above 15 mg/L such as the removal percentage decreased from 94.8 to 85.9% in the case of 25
398 mg/L concentration after 180 min treatment. This drop in the dye removal performance with
399 respect to 15 mg/L concentration could be due to the high amount of dye molecules that are
400 remediated by the same amount of NZ-nZVI and SPC dosage. These findings are also in agreement
401 with those of Yang et al. [56], who stated a maximum 76.09% and minimum 41.74% removal of
402 methyl orange dye (MO) by using S-nZVI/BC system at an initial dye concentration of 0.05 and 1
403 mM after 240 min treatment. Although this removal rate can be deemed satisfactory to current
404 industrial practices when it comes to textile effluent decolourization, with the determination of
405 optimum concentration of SPC. However, performance can be improved by using a smaller
406 concentration amount and lesser treatment time [57].

407 ***3.3.2 Removal of actual dyeing effluents by NZ-nZVI/SPC Fenton system***

408 Three different actual textile effluent samples including AEG, AEM and AEB (green, magenta
409 and blended) were remediated by using NZ-nZVI/SPC Fenton system. Significant dye removal
410 was achieved within 10 min of treatment. The dye removal efficiency was calculated from
411 absorbances measured from the UV-vis spectrophotometer. Furthermore, the decrease in dye
412 concentration was confirmed from UV-vis spectra. In the absorption spectra for AEG, the UV-vis
413 spectras have been recorded from a wavelength range of 325–1000 nm using MAPADA V1100
414 Spectrophotometer. The highest peak in the pre-treatment spectra appears at 372 nm, which lies in
415 the UV range. The bleaching, scouring, de-sizing, and mercerizing are the most significant pre-

416 treatments which are directly used before dyeing (after yarn) [57]. The significant peak in the visible
417 range at 625 nm confirms the green colour of effluent as shown in **Fig. 8**. The unusual high peak
418 in UV range is due to the presence of several compounds in effluent, especially glacial acetic acid.
419 The post-treatment spectra showed a decrease in absorption across the spectral range. The peak
420 representing the green colour (pre-treatment) is completely flattened, indicating significant green
421 chromophore removal. Mao and his research group suggested that 98.5% reduction of malachite
422 green (MG) effluent was achieved from the textile dyeing solution by using microwave/nZVI with
423 16 mL/min influent flow rate [58].

424
425 Fenton system can mineralize the acetic acid, which is also evident from a decrease in UV region
426 peak height after treatment with NZ-nZVI/SPC system. Similar dye removal behaviour is also
427 observed in the case of AEM as presented in **Fig. 9**. The peak at 540 nm represents the
428 characteristic for a violet/magenta coloured liquid in the pretreatment spectra, while a similar
429 decrease in UV range peak was observed in post-treatment spectra. These results are correlated
430 with the findings of Kecic et al. [37] who reported that 84.06% reduction of Magenta colour from
431 aqueous solution after 60 min treatment with oak leaf nano-zerovalent iron (OAK-nZVI). They
432 also stated that the destruction of azo bond in chromophore is responsible for the decolourization
433 of dye solution. Therefore, to eliminate the effect of dilution the spectra was reproduced after
434 removal of 50% solvent.

435
436 The dye removal in blended effluent (AEB) was also studied by utilizing UV-vis spectra, due to
437 its comparatively simpler composition. In those cases where effluent is complex containing a large
438 number of different chromophores or other additives, then spectrophotometric determination

439 becomes unreliable and therefore techniques are recommended. In the pretreatment spectra, visible
440 peak appeared at 625 nm, while the UV range peak appeared at 358 nm. These results are
441 represented in **Fig. 10**. The NZ-nZVI system was also able to successfully remove dye from AEB
442 sample because of the flattening of visible spectrum peak. Similar findings that are reported in the
443 literature in agreement with the obtained results [59, 60]. Nidhi et al. [59] observed that 72.7%
444 decolourization of the actual untreated filtered wastewater by using resin-supported nZVI.

445
446 Surprisingly, the colour removal percentage decreased (72.7–67.3%) by increasing the solution
447 volume from 100 to 2600 mL. This could be because of unknown chemicals and auxiliaries in the
448 actual effluent. Similarly, another study reported that nZVI effectively removed the colour of azo
449 dye by breaking the azo linkage and generated free Fe^{2+} ions. This Fe^{2+} reacts with H_2O_2 through
450 Fenton oxidation and subsequently removed up to 67% of colour from azo dye with 125 mg/L
451 dose of nZVI [60]. Moreover, Fenton reactions provided dual function at a time including
452 coagulation and oxidation that significantly helped out in the decolorization of textile wastewater
453 [61].

454 **4 Conclusions**

455 The present study aimed to analyze textile dye removal potential of nZVI supported on natural
456 zeolite in a Fenton like system for the activation of sodium percarbonate (SPC), which served as a
457 source of hydroxyl radical generation. There was a significant reduction in the characteristic
458 aggregation behaviour, with the particles being efficiently distributed in aqueous media. Whereas
459 in previous literature, NZ-nZVI was filtered and dried in vacuum/nitrogen environment due to its
460 rapidly corroding tendency. NZ-nZVI was used as a slurry with dilute 70% ethanol solution that
461 served as an aqueous media of storage and transportation. The same method was utilized for the

462 removal of dye from undiluted and unfiltered actual effluent, which showed effective
463 decolorization within 30 min treatment. Both actual effluent and synthetic textile effluent were
464 decolorized by using NZ-nZVI/SPC catalyst. A maximum 94.86% decolorization of Acid Orange
465 52 (an azo dye) dye was achieved at 15 mg/L concentration after 180 min treatment. Moreover,
466 NZ-nZVI nanoparticles were also significantly removed from the actual textile effluent (AEG,
467 AEM, and AEB), as quantified by UV-vis absorption spectra. Owing to cheap, safer reagent, high
468 biodegradability, and significant decolorization potential within a short time the NZ-nZVI/SPC
469 system is recommended to be practically feasible for industrial effluent, ground and surface water
470 treatment. The output of nZVI/Fenton/SBH system can be fed into the conventional biological
471 treatment process to further polish the effluent being treated. Furthermore, borohydride synthesis
472 method results in the evolution of hydrogen gas, there are lack of studies to determine the potential
473 of this hydrogen gas as a possible energy source. Therefore, more studies are recommended to be
474 conducted to use this hydrogen gas for possible positive purposes. Moreover, nZVI in combination
475 with other processes such as photolysis, ozonation or ultrasonication could be an innovative option
476 to treat wastewater.

477 **Acknowledgement**

478 The authors are grateful for the financial support from Higher Education Commission of Pakistan,
479 under startup research grant programme (SRGP) project # 1530.

480

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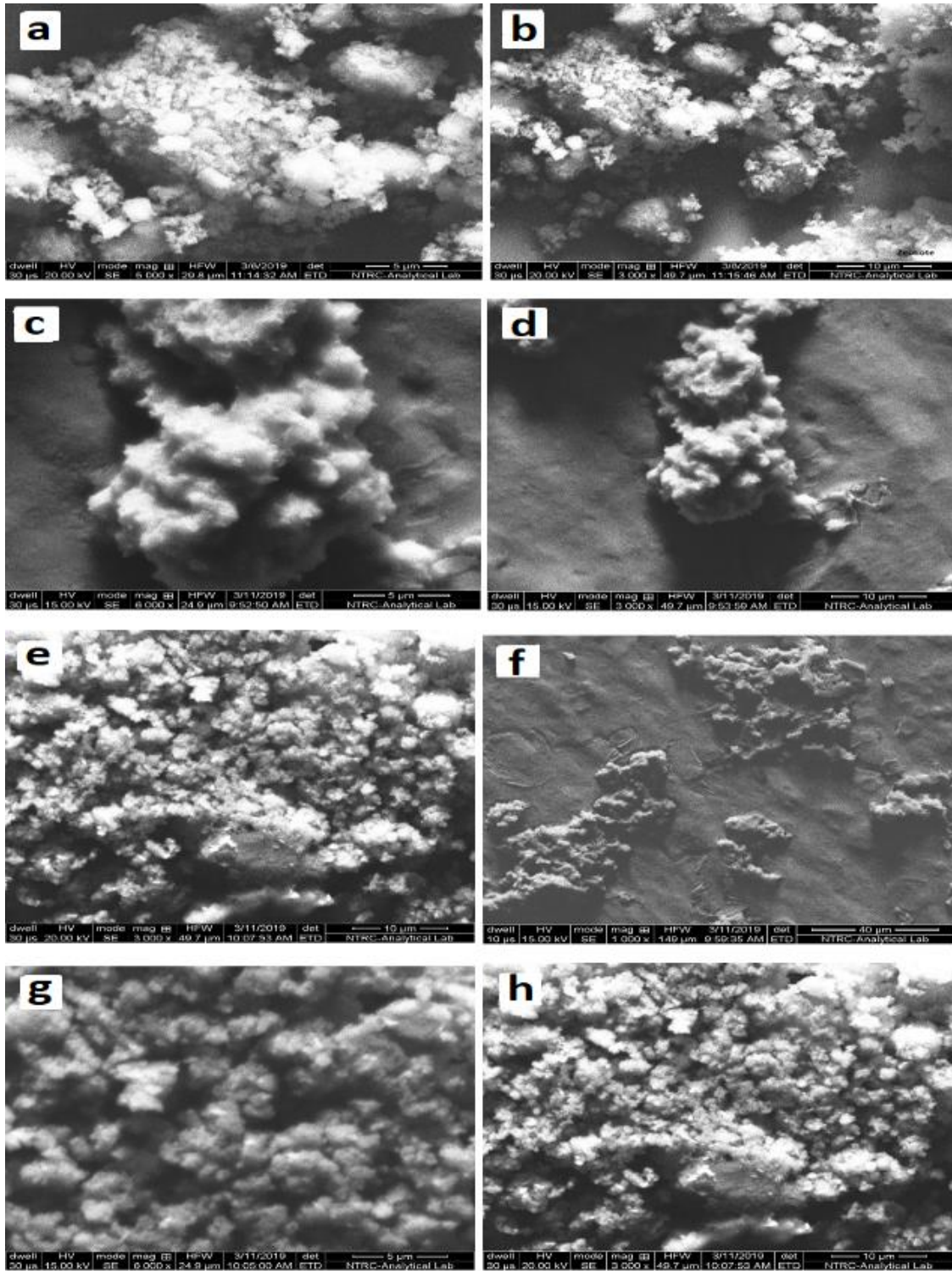
646 **Table 1.** The elemental compositions of natural zeolite, NZ-nZVI, and spent NZ-nZVI for
647 synthetic CI acid orange 52 dye removal by EDX.

Element	Natural Zeolite (%)	NZ-nZVI (%)	Spent NZ-nZVI (%)
Si	24.34	1.11	13.48
Al	5.23	23.98	3.12
O	67.64	59.40	68.45
Mg	1.10	0.00	0.55
K	0.64	-	-
Ca	1.05	-	0.95
Fe	0.00	1.38	9.50
Na	0.00	11.96	2.72
S	0.00	0.86	-

648

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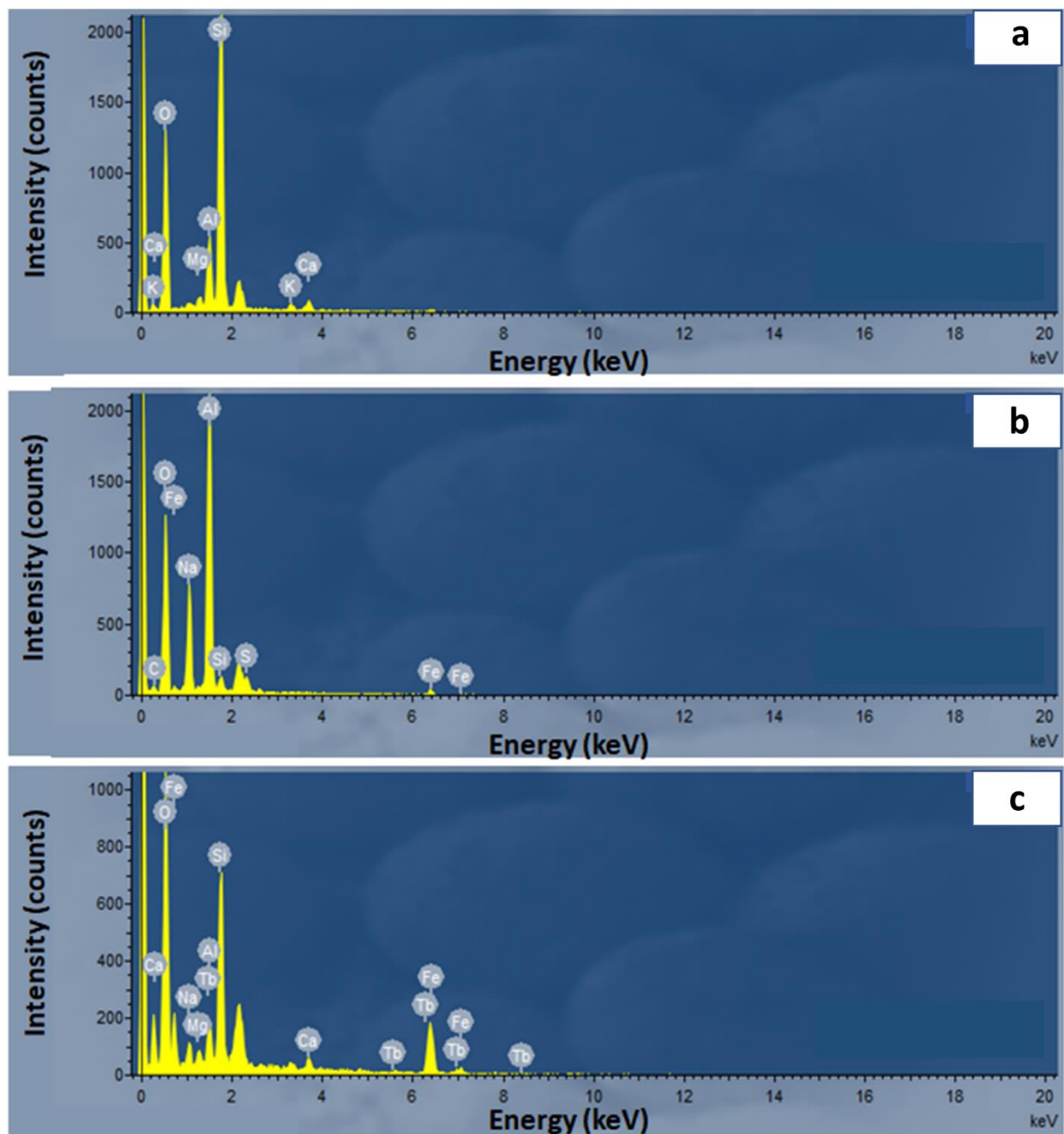
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651

652 **Fig. 1.** SEM analysis of natural zeolite (a and b), NZ-nZVI (c, d, e, and f), and spend NZ-nZVI (g
 653 and h) composites onto synthetic CI acid orange 52 dye removal.

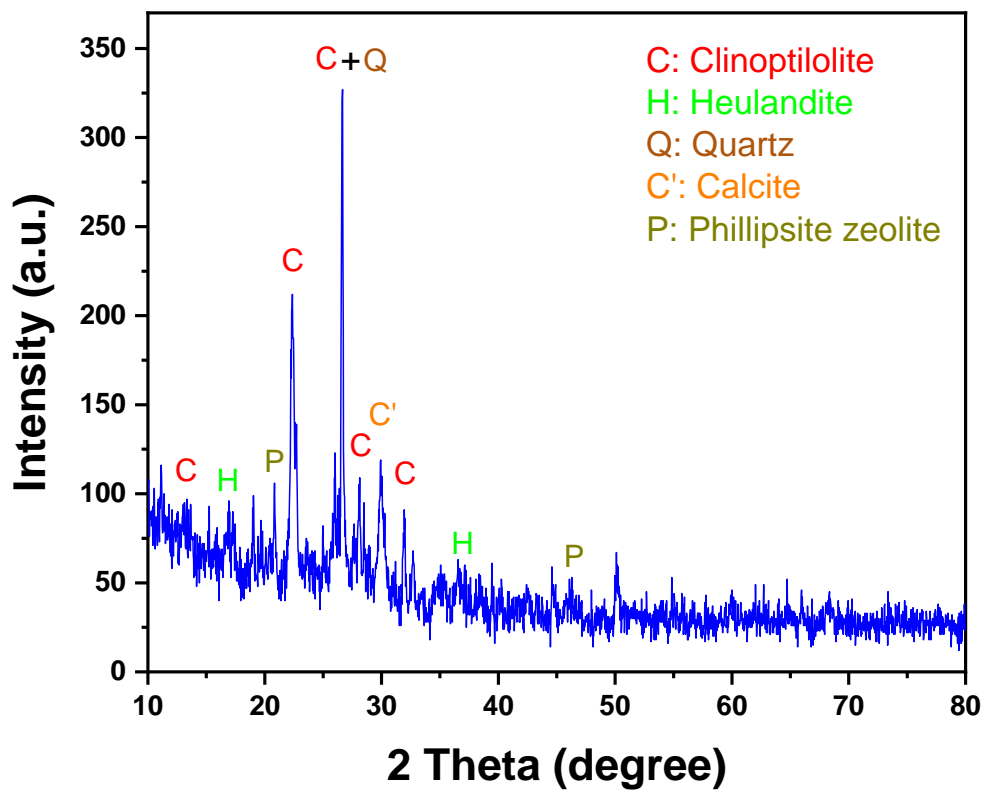
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655

656 **Fig. 2.** EDX spectrum of (a) natural zeolite, (b) NZ-nZVI, and (c) spent NZ-nZVI composites for
657 CI acid orange 52 dye removal.

658

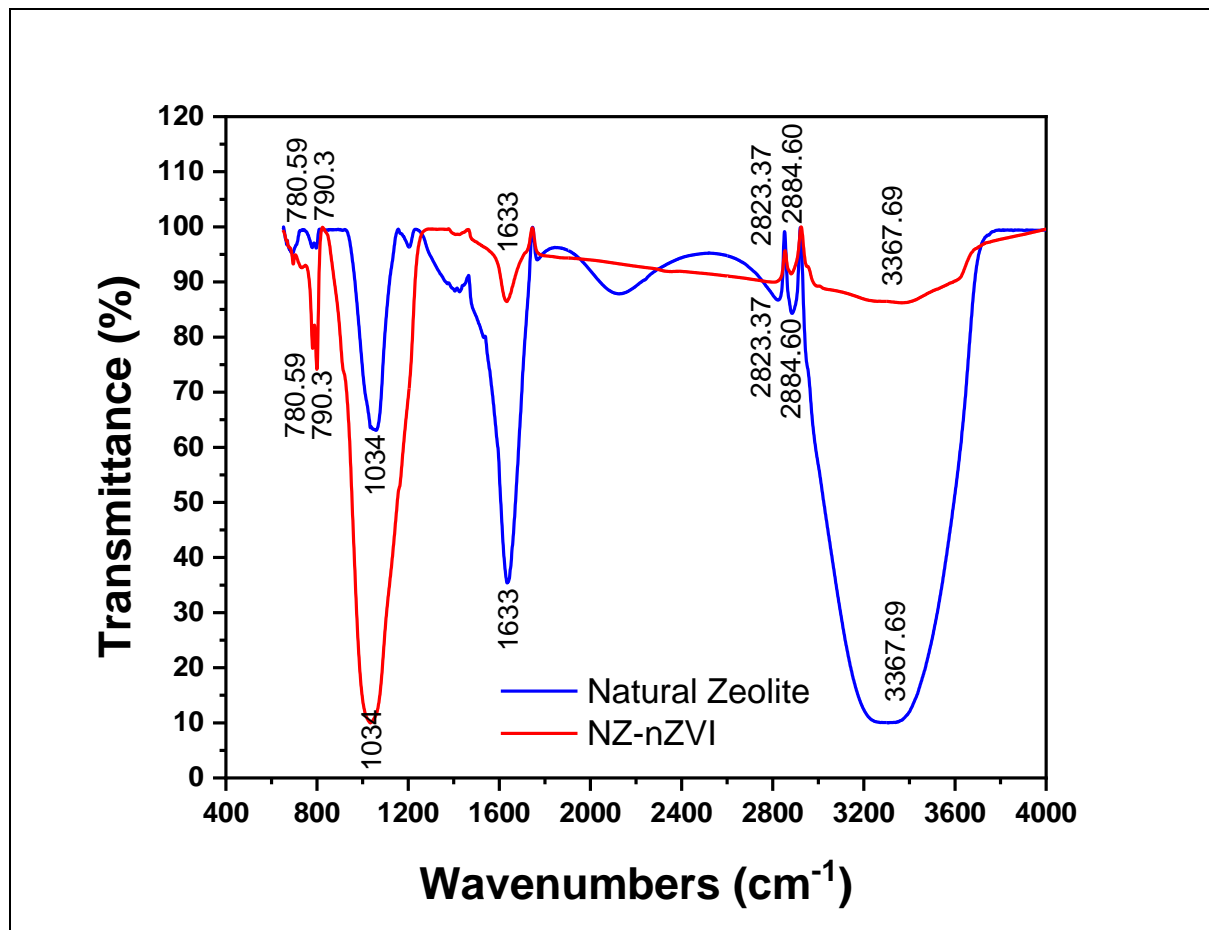


659
660 **Fig. 3.** XRD spectrum of natural zeolite for the determination of its composition as support
661 material of nZVI.
662

663

664

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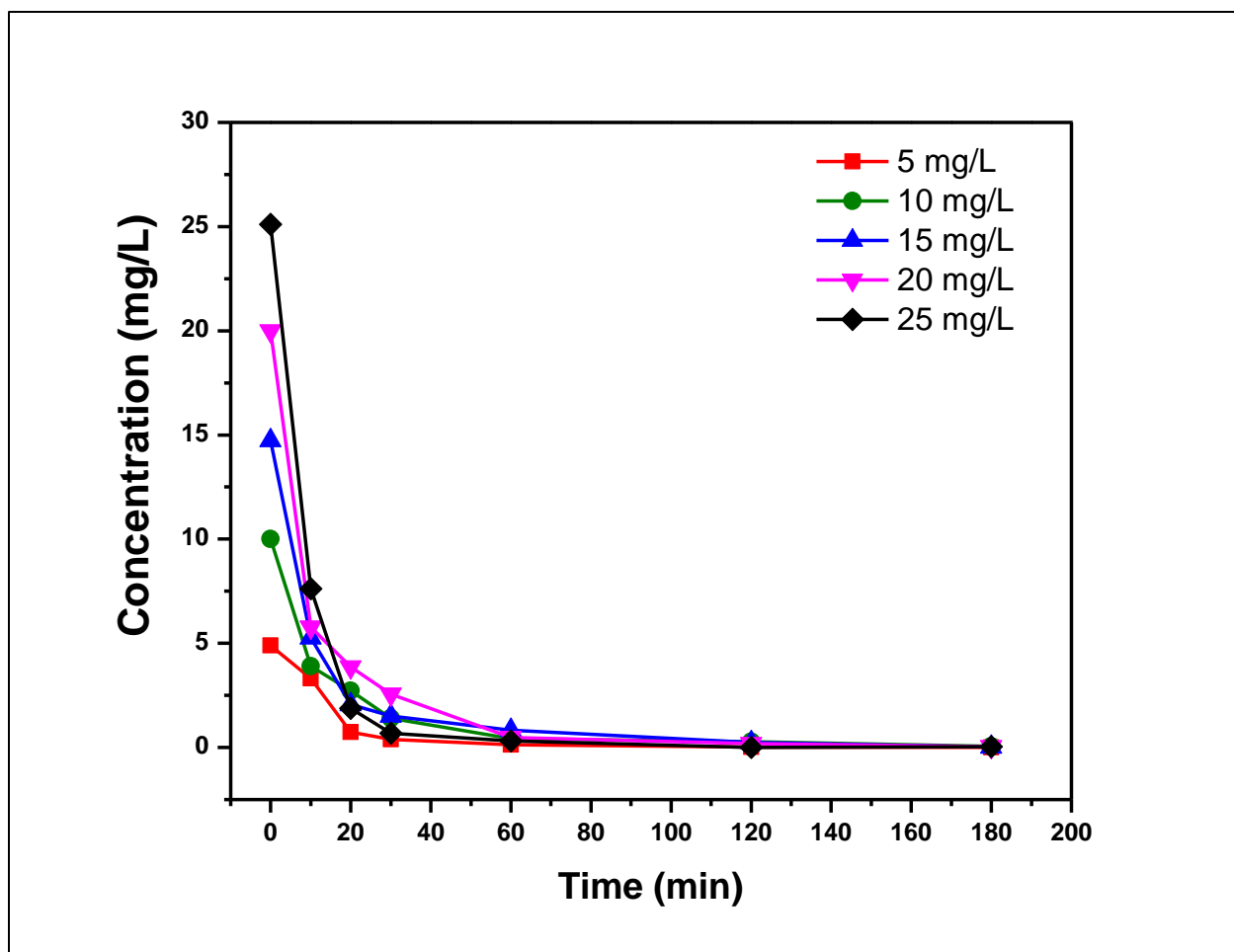


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667

668 **Fig. 4.** FTIR spectra of AO52 dye removal by natural zeolite and NZ-nZVI composites.

669

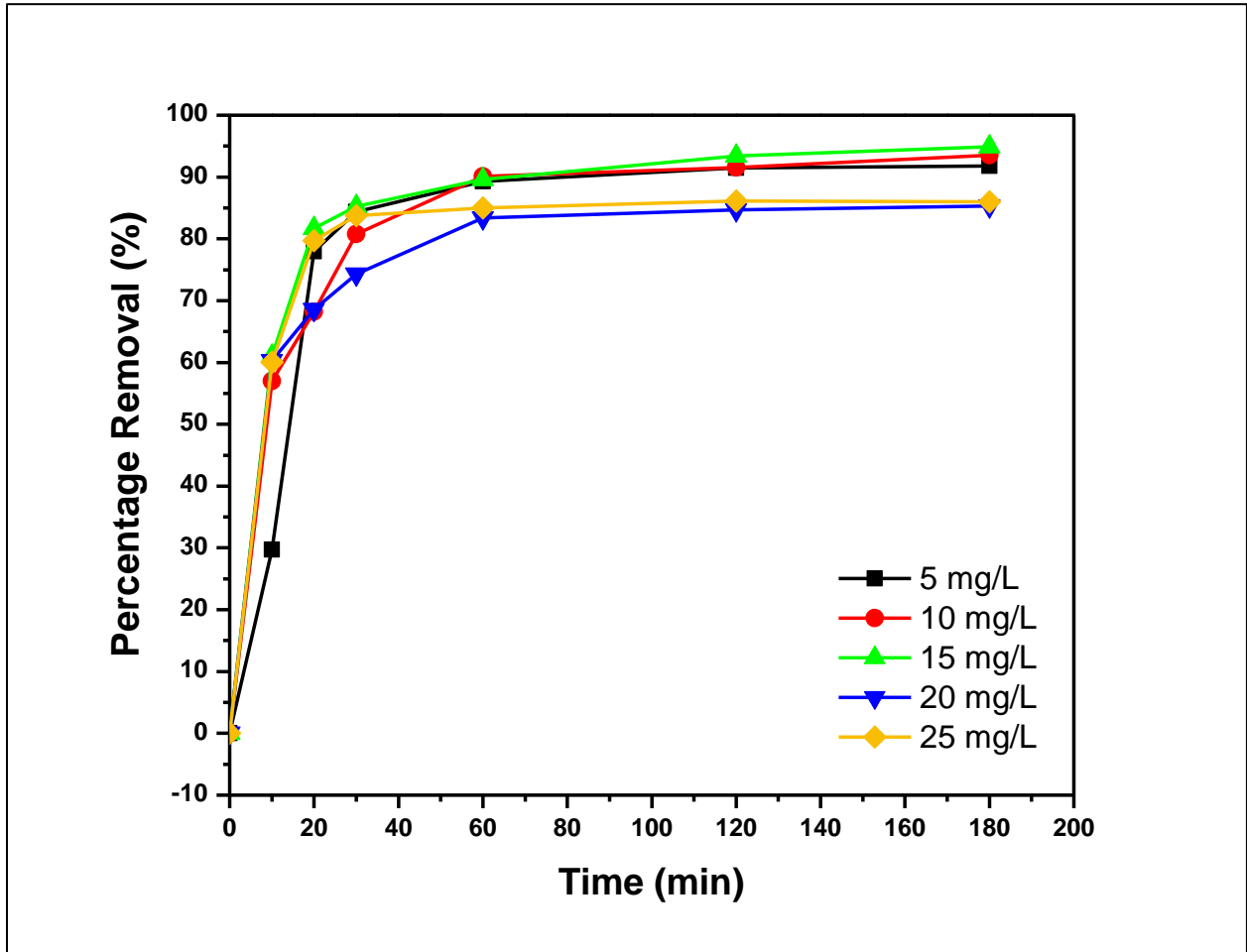


670

671 **Fig. 5.** The removal efficiency of OA52 dye by continuous NZ-nZVI treatment for 180 min at
672 different dye concentrations and neutral pH.

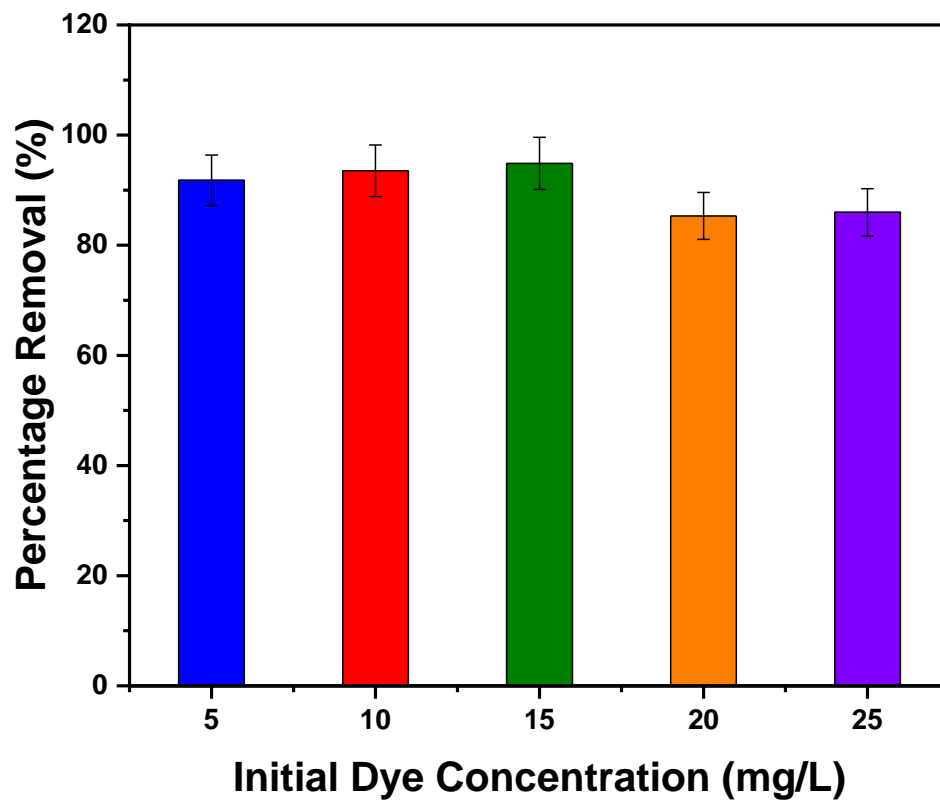
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675

676 **Fig. 6.** The effect of time on the percentage removal of synthetic CI acid orange 52 dye at neutral
677 pH after 180 min treatment.

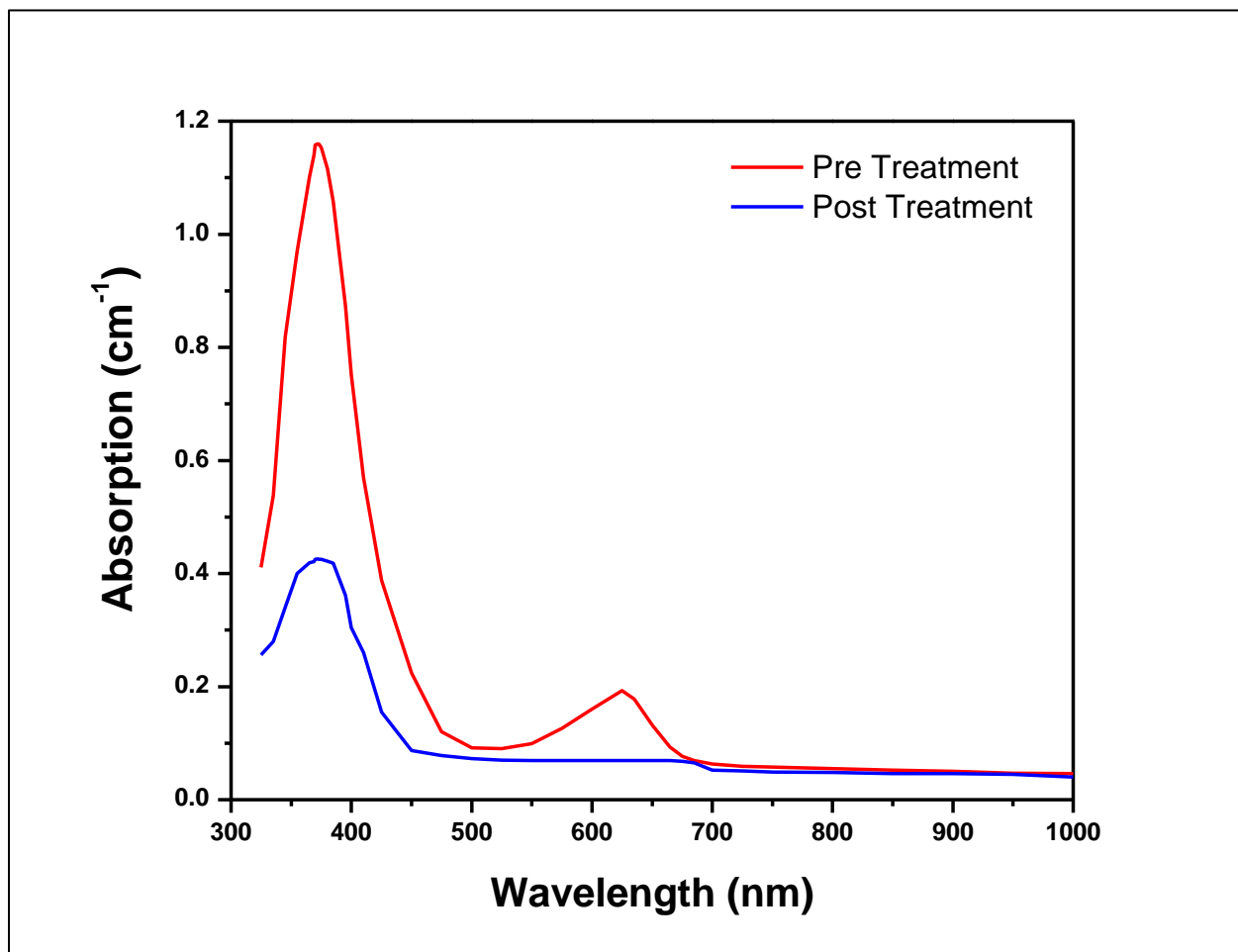


678

679 **Fig. 7.** Effect of initial dye concentration on percentage removal of synthetic CI acid orange 52
680 dye after 180 min treatment.

681

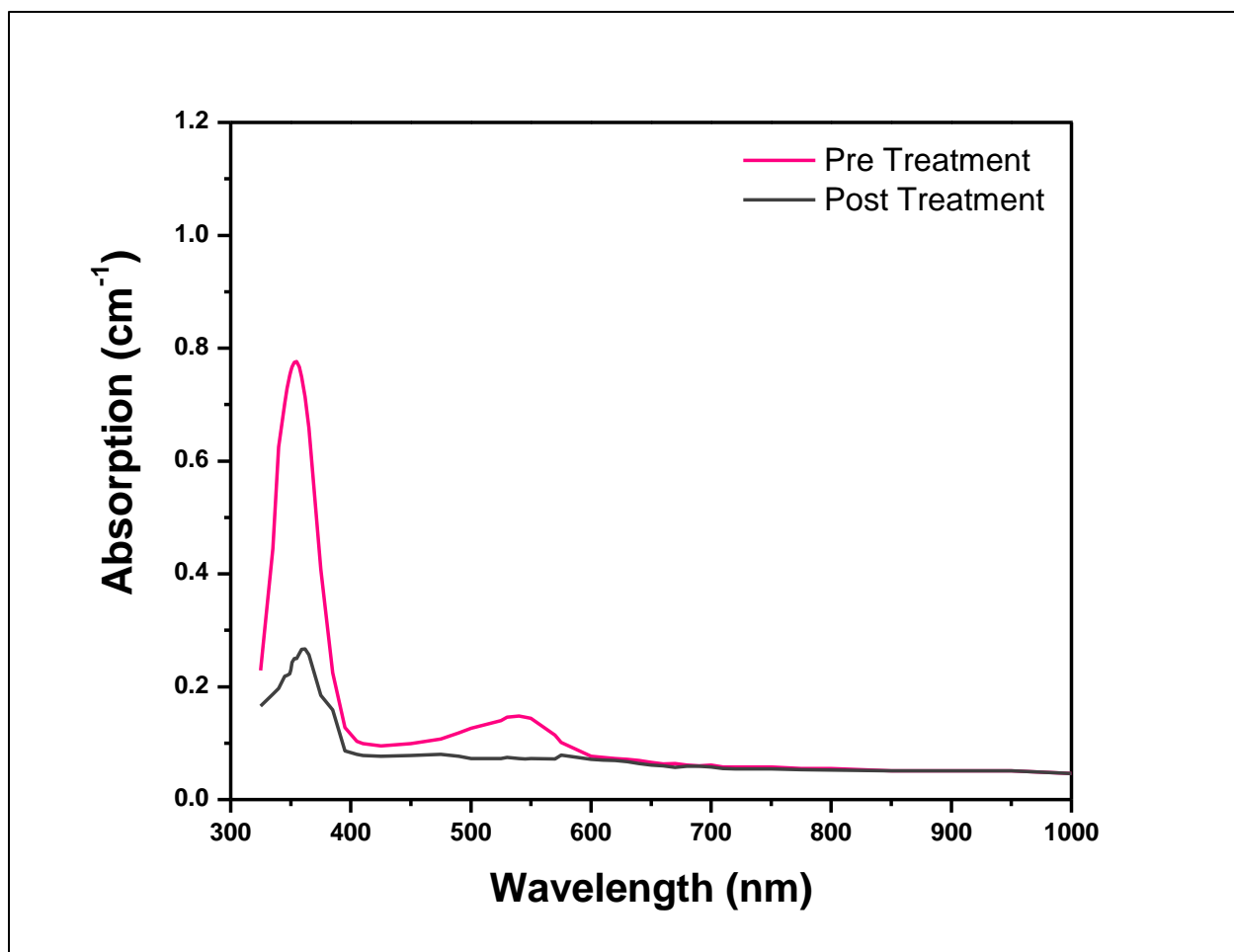
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683

684 **Fig. 8.** The pre and post-treatment of actual effluent green (AEG) colour by NZ-nZVI composite.

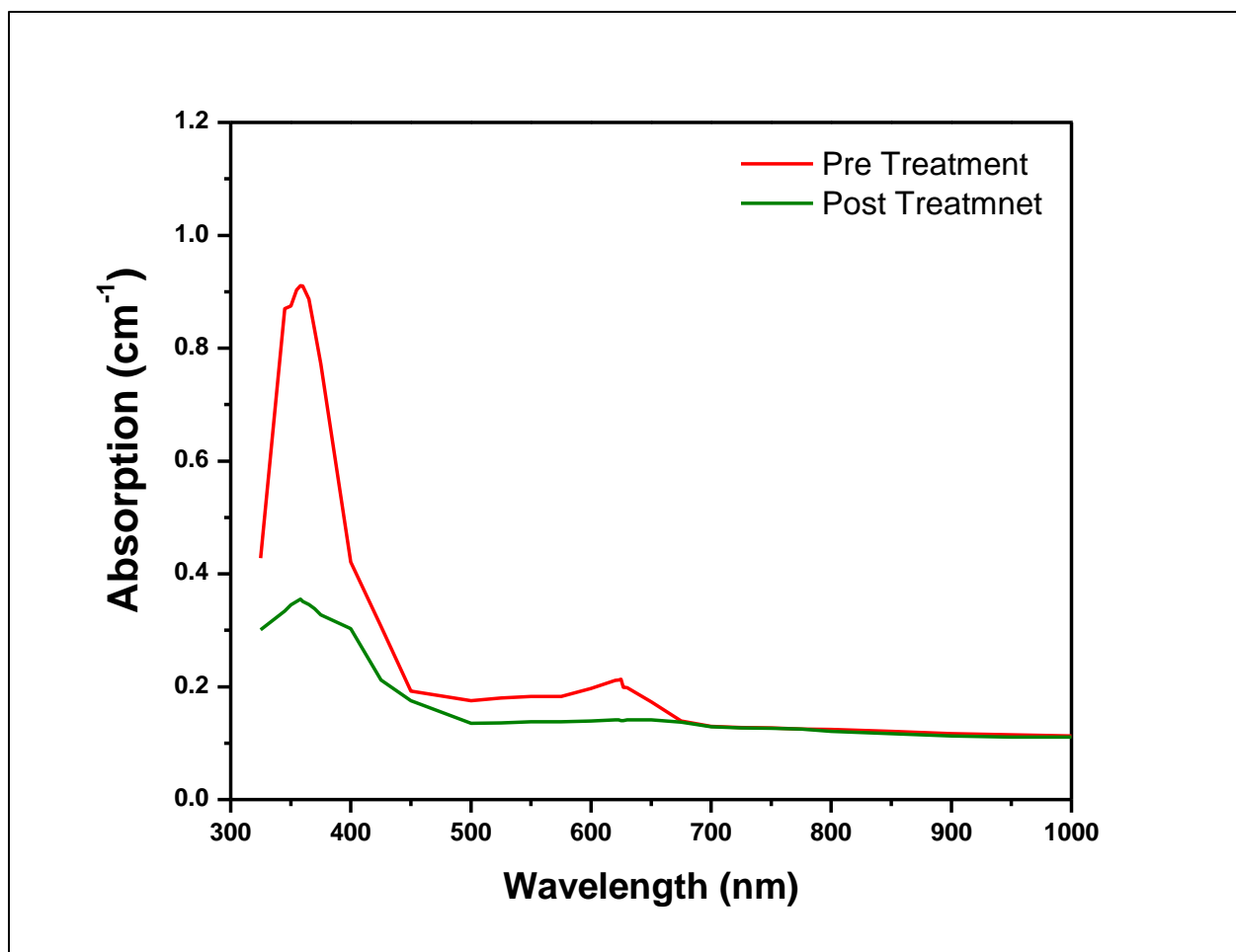
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687 **Fig. 9.** The effect of pre and post-treatment on the removal of actual effluent magenta (AEM)
688 colour by natural zeolite modified nZVI.

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691 **Fig. 10.** Spectrophotometer analysis of pre and post-treatment of AEB colour removal by natural
692 zeolite modified nZVI.

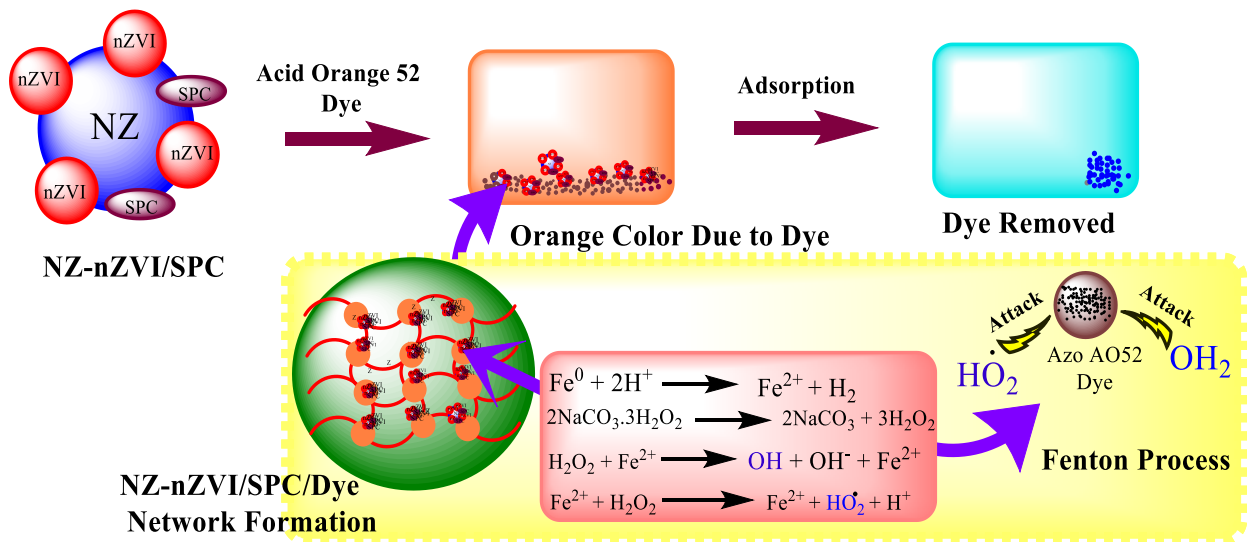
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Graphical Abstract

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