

Synergistic Effect of Pistachio Shell Powder and Nano-Zerovalent Copper for Chromium Remediation from Aqueous Solution

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1 **Synergistic Effect of Pistachio Shell Powder and Nano-Zerovalent Copper for**
2 **Chromium Remediation from Aqueous Solution**

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26 **Abstract**

27 Pistachio shell powder supported nano-zerovalent copper (**ZVC@PS**) material prepared by borohydride reduction,
28 was characterized using SEM, FTIR, XRD, TGA/DTA, BET, and XPS. SEM, XRD, and XPS revealed the nano-
29 zerovalent copper to consist of a core-shell structure with CuO shell and Cu(0) core with a particle size of 40-100
30 nm and spherical morphology aggregated on **PS** biomass. **ZVC@PS** was found out to contain 39% (w/w %) Cu
31 onto the pistachio shell biomass. Batch sorption of Cr(VI) from the aqueous using **ZVC@PS** were studied, and was
32 optimized for dose (0.1-0.5 g/L), initial Cr(VI) concentration(1-20 mg/L) and pH (2-12). Optimized conditions were
33 0.1 g/L doses of sorbent and pH=3 for Cr(VI) adsorption. Langmuir and Freundlich adsorption isotherm models
34 fitted well to the adsorption behavior of **ZVC@PS** for Cr(VI) with a pseudo-second-order kinetic behavior.
35 **ZVC@PS** (0.1g/L) exhibits q_{max} for Cr(VI) removal up to 111.1 mg/g. XPS and other spectroscopic evidence
36 suggest the adsorption of Cr(VI) by pistachio shell powder, coupled with reductive conversion of Cr(VI) to Cr(III)
37 by **ZVC** particles to produce a synergistic effect for the efficient remediation of Cr(VI) from aqueous medium.

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39 **Keywords:** Zerovalent copper, Pistachio, Biomass, Cr(VI), Adsorption, Kinetics, Synergistic effect.

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52 **1. Introduction**

53 Consumer demands of expanding population on the planet are met by our industries with production, which is a
54 threat to sustainable development. Herein, industries produce goods as per the demand of the consumer. Industries
55 meet these demands through time-efficient processes, which demand the use of chemicals that could be fossil-
56 oriented or mining-oriented (Carvalho 2017). These chemicals then enter into the biosphere through various
57 environmental pathways and food chains (Garvey 2019). Heavy metals are essential components of these chemicals
58 due to their desired redox, coordination, and physical attributes (Aigberua et al. 2018; Vardhan et al. 2019).
59 Chromium is considered as the 7th most abundant element on earth, existing in the core and mantle; and also ranked
60 21st in the earth crust with an average concentration of 185 mg kg⁻¹ (Sperling 2005). Chromium finds anthropogenic
61 use in leather tanning, manufacturing, electroplating, chemical refining, organic synthesis, etc. (Lunk 2015; Nigam
62 et al. 2015; Tadesse et al. 2017). The majority of the method for the treatment of chromium in wastewater involves
63 the use of chemical precipitation, coagulation, bioreduction, and electrocoagulation, etc. (GracePavithra et al. 2019;
64 Owwad et al. 2009; Peng and Guo 2020; Pradhan et al. 2017). In spite of these treatment techniques, chromium does
65 find its way into our environment, wherein it exists in two oxidation states [i.e. Cr(VI) and Cr (III)]. Trivalent
66 chromium is relatively stable and less toxic but poses health concerns at higher concentrations. However, hexavalent
67 chromium is very harmful even at lower concentrations due to its carcinogenicity, hemotoxicity, and genotoxicity
68 (Barceloux and Barceloux 1999; Burrows 2019). Based on the toxicity associated with chromium, the World Health
69 Organization (WHO) (WHO, 2003) and Bureau of Indian Standards (BIS 10500-2012) have set the permissible limit
70 of chromium at 50 µg/L in wastewater.

71 The treatment of chromium in wastewater by conventional methods like coagulation, electrocoagulation, (Khan et
72 al. 2019; Mahringer et al. 2020; Peng and Guo 2020) and chemical precipitation (Minas et al. 2017) are irreversible
73 processes, wherein extraction of chromium in the desired form may not be feasible from the waste/sludge generated.
74 Apart from this, conventional methods have the drawbacks of being time-consuming, require bulk wastewater, cost,
75 and manpower intensive, poor reproducibility under variable wastewater physicochemical characteristics (Crini and
76 Lichtfouse 2019; Hu et al. 2011; Sharma et al. 2009). More recently there have been studies on various emerging
77 technologies for the treatment of wastewater including ion exchange (Wang et al. 2020), membrane technologies
78 (Namdar et al. 2021), reverse osmosis (Zakmout et al. 2020), bioremediation (He et al. 2020a; Mohamed et al. 2020)
79 phytoremediation (Kullu et al. 2020) etc. Among these techniques, adsorption is a simple and cost-effective
80 technology. Adsorption is based upon the imbalance of intermolecular forces on the surface of solids leading the
81 way to interaction and removal of atoms, ions, or molecules from solution onto the surface of the solid phase (Artioli
82 2008). Thus, adsorption is a surface phenomenon, requiring more and more active surfaces on the solid phase for
83 efficient adsorption. Various surface-active adsorbents studied for chromium could be classified as lignocellulosic
84 biomass (Çelebi 2020), biochar (Qu et al. 2021), zeolites (He et al. 2020b), Chitosan (Lei et al. 2020), Graphene
85 oxide (Zhang et al. 2020), resin (Vilayatkar et al. 2020), clay (Ashour and Tony 2020), activated charcoal (Mahmudi
86 et al. 2020; Patel 2020) etc. Among lignocellulosic biomass, *Picea smithiana* cone (Mittal et al. 2016), pistachio
87 shell (Banerjee et al. 2018) etc. have been studied for chromium adsorption. These biomass have poor adsorption

88 and/or recovery for Cr(VI). On the other hand zeolites and activated charcoal show poor surface adsorption for
89 Cr(VI) oxoanions, due to the characteristic electrostatic surface negative charge (Jorfi et al. 2017; Puzskarewicz and
90 Kaleta 2019; Vaid et al. 2014).

91 Further, new classes of surface-active materials in the form of nanomaterials have shown promising activity.
92 Various nanomaterials studied for Cr(VI) remediation include nZVI (Sharma et al. 2009), MnO₂ (Dinh et al. 2020),
93 ZnO (Le et al. 2019), TiO₂ (Gopinath et al. 2020), Fe₂O₃ (Li et al. 2019), and their variants with other metal/metal
94 oxides and chalcogenides (Karimi-Maleh et al. 2020; Peng and Guo 2020; Zhao et al. 2019). Recently Cu/Cu₂O
95 nanoparticles have found application in electrochemical sensing (Devnani et al. 2019; Li et al. 2018) and adsorption
96 of heavy metal (Iqbal et al. 2019). Cu/Fe bimetallic nanocomposite materials have been found suitable for
97 remediation of Cr(VI) (Jia et al. 2019; Jiang et al. 2018; Qu et al. 2021; Zhu et al. 2016; Zhu et al. 2018), but very
98 few literature reports are known for utilization of zerovalent copper as Cr(VI) adsorbent (Li et al. 2015a; Wu et al.
99 2009).

100 However, CuNPs tend to agglomerate during synthesis and thus the surface area and the activity of the CuNPs is
101 reduced to a large extent (Huang et al. 2012; Li et al. 2015a; Li et al. 2015b). Thus, to prevent agglomeration,
102 stabilizers and immobilizers can be used in-situ during the preparation of the nanoparticles, to ensure dispersion of
103 the nanoparticles. The use of dispersing agents not only provides stable support to the nanoparticles, but also solves
104 the problem pertaining to agglomeration of nanoparticles resulting in pressure drop in the reactor bed and also to the
105 recyclability of nanoparticles (Wu et al., 2009). Supporting materials such as polymers (Sarawathi et al. 2019),
106 zeolites (Xu et al. 2018a), clay (Pandey and Saini 2019), graphene (Xu et al. 2018b), etc. has been widely utilized
107 for the synthesis of adhered nanoparticle scaffolds. Immobilizers have the added advantage of easy separation of the
108 material from the water/wastewater system. The selection of material to be used as an immobilizer becomes very
109 important. As the material must not themselves act as secondary pollutants after they have been employed for the
110 removal of primary pollutants. Many reports support the use of agricultural byproducts and wastes for the removal
111 of heavy metals from wastewater. These biodegradable adsorbent materials are significant in terms of their low cost,
112 abundant availability, easy disposal and use as green adsorbent without pre-treatments with chemicals (Afroze and
113 Sen 2018). Therefore, the use of biodegradable materials as immobilizers becomes very important for this field of
114 application (Guerra et al. 2018). Earlier one of the authors (Sharma et al. 2018; Sharma et al. 2015) has reported the
115 role of cellulose as an immobilizer and in nZVI reductive regenerative for enhanced adsorption of chromium. Thus,
116 lignocellulosic materials can stabilize metal nanoparticles and enhance the adsorption of Cr(VI). Therefore, this
117 study attempted to use pistachio shell powder, a biodegradable material known for its Cr(VI) removal tendencies
118 (Banerjee et al. 2018) as support for the synthesis of zero-valent copper nanoparticle dispersed nanocomposite
119 material using appropriate chemical reduction methods and investigate the synergistic effect of these two adsorbents
120 for their Cr(VI) removal efficacies.

121 **2. Materials and Methods**

122 **2.1 Preparation of pistachio shell (PS) powder**

123 Waste pistachio shells used for the studies were collected from the local market. The pistachio shells were washed
124 twice with distilled water before subjecting to air drying in an electric oven for the duration of 24 h at 100 °C
125 temperature. The dried shells were grounded using a common household grinder (Bajaj GX1) and sieved to get a
126 homogenous mesh of opening size 250 -350 µm.

127 **2.2 Reagents and material**

128 The chemical reagents used for the studies including CuSO₄.5H₂O, NaBH₄, K₂Cr₂O₇, diphenylcarbazide were
129 analytical reagent grade and purchased from Loba Chemie Laboratory Reagents, India. All reagents were prepared
130 in deionized water. Diphenylcarbazide was used for the determination of Cr(VI) concentrations (Lace et al. 2019).

131 **2.3 Preparation of ZVC@PS composite**

132 Pistachio shell powder (4.0 g) was suspended in 100 mL of distilled water at room temperature. CuSO₄.5H₂O (0.17
133 mol, 4.4 g) solution in 50 mL water was added to the reaction mixture with vigorous stirring. To this solution was
134 added dropwise a 20% aqueous NaBH₄ solution (100 mL) at a constant rate of 1 mL/min. After the completion of
135 the addition, the reaction mixture turned black and was subjected to stirring at room temperature for 30 min. The
136 black material was filtered, washed with an excess amount of distilled water followed by methanol, and dried under
137 inert conditions *in vacuo*.

138 **2.4 Physical Characterization of ZVC@PS**

139 FTIR analysis (Bruker, Model: Tensor 27) was performed to determine the characteristic bonds in **ZVC@PS**. X-ray
140 powder diffraction analysis (Bruker, Model: D8-Advance) was performed to evaluate the crystal structure and
141 crystal phase of the **ZVC@PS** composite at 2θ angles ranging from 5° to 80° with a scanning rate of 3° (2θ) per
142 minute at an accelerating voltage of 40 kV and emission current of 40 mA. The surface morphologies of the
143 **ZVC@PS** and pistachio shell powder were characterized by field emission scanning electron microscopy (FESEM,
144 Carl Zeiss, Model: Merlin Compact, Germany) with integrated energy dispersive X-ray (EDX) analyzer system. X-
145 ray Photo-electron spectroscopy (XPS, Physical Electronics, Model: PHI 5000 VersaProbe III, USA) was used to
146 determine the main element composition and valence state changes of the **ZVC@PS** composite. Pistachio shell
147 powder and **ZVC@PS** specific surface area were investigated in BET (Micromeritics, Model: ASAP 2010, France)
148 at -196 °C. Adsorbent degassing was performed under a nitrogen environment at 150 °C temperature for 4 h.
149 Thermogravimetric measurements were performed using Thermogravimetric/Differential Thermal Analyzer
150 (EXSTAR SII 6300, LabX, Canada) at a heating rate of 10 °C/min. UV-vis spectrophotometer (Shimadzu Japan,
151 Model: UV-2450) was used for determination of Cr(VI) concentration using diphenylcarbazide method.

152 **2.5 Experimental**

153 *2.5.1 Adsorption Equilibrium Study*

154 A stock solution (1.0 mM) of $K_2Cr_2O_7$ (294.0 mg) was prepared by dissolving it into deionized water (1000 mL) and
155 standard Cr(VI) concentrations of 2-20 mg/L obtained by serial dilution of the stock solution with deionized water,
156 were used for the adsorption study. **ZVC@PS** (100 mg/L) was added to individual Erlenmeyer flasks containing
157 100 mL solutions of Cr(VI) (2-20 mg/L), and the resulting mixtures were incubated at 25 ± 2 °C and 180 rpm for 24
158 h. The samples were subjected to filtration using Whatman 1 filter paper and analyzed for Cr(VI) concentration via
159 diphenylcarbazide method using UV-Vis spectrophotometer at a wavelength of 540 nm (Lace, Ryan et al. 2019).
160 The absorption efficiency (i.e. % Cr removal) and equilibrium adsorption capacity, q_e ($mg_{Cr(VI)}/g_{ZVC@PS}$) were
161 calculated using equation (1) and (2).

162
$$\text{Cr(VI) removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

163 Where, C_o and C_e ($mg \cdot L^{-1}$) are the initial and equilibrium Cr(VI) concentration in mg/L, respectively.

164
$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

165 Where V is the volume of the solution (in L) and W is the mass of adsorbent **ZVC@PS** taken.

166 Studies were performed by varying parameters like pH, adsorbent concentration, and initial dichromate
167 concentration to investigate the effect of different experimental parameters on the Cr(VI) adsorption and under
168 optimized conditions. The Cr(VI) concentration of 20 mg/L and **ZVC@PS** dose concentration of 1.0 g/L was
169 selected for pH optimization study. Cr(VI) solutions (100 mL) having different pH ranging from 2 to 10 were
170 prepared by adjusting the pH with 1N HCl and or NaOH solutions. The optimum dose determination experiment
171 was performed using 20 mg/L of Cr(VI) solution with varying amounts of **ZVC@PS** (0.05, 0.1, 0.15, and 0.2 g/L)
172 at optimum pH 3. All experiments were carried out in duplicate and average results are reported.

173 *2.5.2 Kinetic and isotherm experiments*

174 Adsorption of Cr(VI) using **ZVC@PS** was analyzed for its kinetics of adsorption and for optimization of
175 equilibration time. The procedure used to perform kinetic experiments was the same for the determination of
176 adsorption efficiency of **ZVC@PS**. To a 100 mL solution of Cr(VI) at a concentration of 20 mg/L was added 10 mg
177 of **ZVC@PS** and incubated at 25 ± 2 °C and 180 rpm for 24 h. A fixed volume of the reaction mixture was
178 withdrawn and diluted at regular intervals of time i.e. 0.5, 1, 2, 3, 4, 6, 8, 10, 12, and 24 hr to analyze the residual
179 Cr(VI) concentration. The data thus obtained for Cr(VI) adsorption onto **ZVC@PS** as a function of time and was
180 plotted to find the suitable fit to kinetic model.

181 *2.5.3 Adsorption isotherm study*

182 The adsorption equilibria were determined using Langmuir and Freundlich isotherms between **ZVC@PS** and Cr.
 183 In Langmuir adsorption isotherm, adsorption is assumed to be independent for each entity of adsorbate with the
 184 formation of a monolayer on the surface. Linearized form of the Langmuir equation (3) is:

$$185 \quad \frac{1}{q_e} = \frac{1}{q_{max}K_L C_e} + \frac{1}{q_{max}} \quad (3)$$

186 This model was used to draw a correlation between q_e (mg/g) i.e. the amount of Cr(VI) adsorbed at equilibrium, C_e
 187 (mg/L) i.e. equilibrium solute concentration, where q_{max} is the maximum saturation monolayer adsorption expressed
 188 in mg/g, and K_L is the Langmuir equilibrium constant.

189 The equilibrium parameter in Langmuir isotherm can be expressed in terms of a dimensionless constant (R_L , also
 190 called separation factor) by equation (4) as follows:

$$191 \quad R_L = 1/(1 + K_L C_0) \quad (4)$$

192 The value of R_L signifies the nature of isotherm i.e. unfavorable for $R_L > 1$; linear for $R_L = 1$; favorable for $0 < R_L$
 193 < 1 ; or irreversible for $R_L = 0$.

194 The Freundlich adsorption isotherm is applied to non-ideal sorption on heterogeneous surfaces as well as multilayer
 195 sorption and adsorption capacity is related to the Cr(VI) concentration at equilibrium. Linear form of Freundlich
 196 model is defined by equation (5) as:

$$197 \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

198 A straight-line graph is obtained upon plotting $\log q_e$ versus $\log C_e$ with a slope of $\left(\frac{1}{n}\right)$ and intercept $\log K_f$. The
 199 adsorption capacity and adsorption intensity are related to Freundlich constant K_f and $\left(\frac{1}{n}\right)$, respectively.

200

201 2.5.4 Removal Kinetics study

202 Adsorption kinetics depends upon various factors such as initial concentration, contact time, and temperature. The
 203 Cr(VI) adsorption kinetic studies are performed with 20 mg/L of Cr(VI) aqueous solution and 100 mg/L of
 204 adsorbent **ZVC@PS**.

205 The pseudo-first-order and pseudo-second-order kinetic models are used for the investigation of the mechanism of
 206 reduction, mass transport, and chemical reaction process involved in adsorption of Cr(VI) by **ZVC@PS**.

207

208 Linearized form of pseudo-first-order model is as given in eqn (6)

$$209 \quad \ln (q_e - q_t) = \ln q_e - K_t \quad (6)$$

210 where; q_e = amount of chromium adsorbed at an equilibrium in (mg/g)

211 q_t = amount of chromium adsorbed at time t

212 K = rate constant

213 Linearized form of pseudo-second-order is as given in eqn (6):

$$214 \quad \frac{t}{q_t} = \frac{1}{K_p q_e^2} + \frac{t}{q_e} \quad (6)$$

215 where, K_p is pseudo-second-order rate constant.

216 3. Result and discussion

217 **3.1 Characterizations of ZVC@PS**

218 *3.1.1 XRD Pattern Analysis*

219 X-ray powder diffraction patterns of **ZVC@PS** before and after Cr adsorption are shown in Fig. 1. XRD of
220 **ZVC@PS** contained peaks (2θ) at 22.1, 36.5, 43.2, 50.4, 61.3, and 74.1°. The peaks (2θ) at 43.2, 50.4, and 74.1° are
221 assigned to characteristic peaks of zerovalent copper (JCPDS 89-2838) (Ismail 2020). Two peaks (2θ) observed at
222 36.5 and 61.3° were ascribed to the presence of Cu_2O (JCPDS-05-0667) as a minor component along with $\text{Cu}(0)$
223 (Huang et al. 2012). The diffraction peak (2θ) at 22.1° in **ZVC@PS** is attributed to the typical reflection plane (002)
224 of the lignocellulose framework of pistachio shell powder used as support material (JCPDS card no. 03-0289)
225 (Cottayil et al. 2015). The XRD pattern adsorbent (**Cr-ZVC@PS**) exhibited the disappearance of peaks
226 characteristic of $\text{Cu}(0)$ nanoparticles at 43.2, 50.4, and 74.1° upon Cr(VI) adsorption at pH 3. This is ascribed to
227 oxidation of $\text{Cu}(0)$ to Cu(I or II) during reductive removal of Cr(VI) to Cr(III) .

228 *3.1.2 FTIR spectral Analysis*

229 Fourier Transform Infrared (FTIR) spectral analysis was employed for the determination of characteristic bonds in
230 the lignocellulosic biomass containing pistachio shell powder and immobilized zerovalent copper on pistachio shell
231 powder as a nanocomposite material. The pistachio shell powder with the presence of lignocellulose biomass was
232 characterized by FTIR. The IR of **PS** showed absorption bands at 3390, 2918, 1632, 1384, 1178, 1161, 1139, 1084,
233 and 877 cm^{-1} (**Fig. 2**). The bands that appeared at 1178, 1161, 1084, and 877 cm^{-1} , for the **PS**, were characteristic of
234 the monomer pyranose ring structure of cellulose. The broad peak at 3390 cm^{-1} was assigned to -OH stretching
235 vibrations of primary/secondary -OH groups of the glucopyranose of cellulose or phenolic -OH groups of lignin
236 present as a basic framework of biomass. The peak at 2917 cm^{-1} is attributed to aliphatic C-H stretching, which
237 confirmed the presence of CH_2/CH_3 groups, however, the band at 1380 cm^{-1} is characteristic of the bending of the
238 C-H group (Liu et al. 2006). The absorption band at 1632 cm^{-1} was attributed to the bending mode of the absorbed
239 water. The peaks at 1084 and 877 cm^{-1} , respectively, correspond to the C-O-C group of primary hydroxyl stretching
240 at C_6 and C_1 -H group deforming with ring vibration. This confirms the β -glycosidic linkage (Banerjee et al. 2018).
241 The surface chemical interaction of zerovalent copper with the functional groups of the lignocellulose framework of
242 pistachio biomass was evident from the significant shifts in all absorption peaks. The reductive adsorption of
243 chromium on **ZVC@PS** changes the chemical nature of **ZVC** particles on the surface and hence results in its
244 decreased interaction with the functional groups causing the shift of bands towards normal values as appeared in
245 FTIR of pistachio shell powder.

246 *3.1.3 FESEM and EDX Analysis*

247 The morphologies of the synthesized **ZVC@PS** nanocomposite material were analyzed using a field emission
248 scanning electron microscope (FESEM). The pistachio shell powder exhibited undefined morphologies with particle
249 sizes ranging from 10 to 100 μm as shown in **Fig. 3a**. FESEM of zero-valent copper (**ZVC**) particles (**Fig. 3b**),
250 synthesized by borohydride reduction, were found primarily in an agglomerated state but well dispersed on the

251 surface of the pistachio shell powder. The Cu⁰ nanoparticles were spherical in shape (**Fig. 3c**) and were formed with
252 an average size of 40 nm. The SEM-EDX spectrum analysis of **PS** contains peaks from carbon and oxygen. The
253 EDX spectrum of **ZVC@PS** exhibits peaks from copper along with carbon and oxygen, with no contamination from
254 any other metal. The adsorption of Cr(VI) on **ZVC@PS** was confirmed from the appearance of the characteristic
255 peak of Cr along with other elements (**Fig. 3d-f**).

256 3.1.4 BET Analysis

257 Brunauer-Emmett-Teller (BET) analysis of **ZVC@PS** was performed and compared with **PS** to determine the
258 surface area and contribution of immobilized nano-zerovalent copper (**ZVC**) towards the surface area of the
259 material. The specific surface area of **PS** was found to be 0.483 m²/g with an average BJH (Barrett-Joyner-Halenda)
260 pore size distribution of 5.7578 nm (Turan and Mesci 2011). The relatively lower surface area suggests the
261 microporous nature of the **PS**. Further, it characterized the poor adsorption capacity of **PS** for Cr(VI) up to 28 mg/g
262 (Banerjee et al. 2018). On the contrary, the specific surface area of the **ZVC@PS** was found to be 5.84 m²/g, which
263 was significantly higher than that of **PS**. The average BJH pore diameter of **ZVC@PS** was observed at 911 nm with
264 the satellite peak at 1374 nm (**Fig. 4b**). The substantial increase in specific surface area of **ZVC@PS** was attributed
265 to additional pores created by immobilized nano zerovalent copper (**ZVC**) on the surface of **PS**.

266 3.1.5 XPS Analysis

267 X-ray photoelectron spectroscopy (XPS) was used to determine the elemental compositions of surfaces of
268 **ZVC@PS** and Cr(VI) adsorbed **ZVC@PS**. The XPS survey scan of **ZVC@PS** and Cr(VI) adsorbed **ZVC@PS** is
269 depicted in **Fig. 5a**. Further, the deconvolution of the data was carried out with curve smoothing for Cu 2p and O1s
270 to find out the various source and oxidation states of these elements. The analysis of the survey scan of **ZVC@PS**
271 showed characteristic peaks in the range 529-536, 823, and 930-960 eV, which is characteristic of elements O, C,
272 and Cu, respectively in the sample surface.

273 The binding energy peaks for Cu 2p of **ZVC@PS** were observed at 932.1, 934.3, 942.5, and 953.4 eV (**Fig. 5b**).
274 These peaks were deconvoluted to find the contribution of various Cu species. The binding energy peak at 932.1 and
275 953.4 eV suggest the presence of Cu(0) whereas, the binding energy peak at 934.3 and 942.5 eV are characteristic of
276 Cu(II) present in **ZVC@PS** (Chang et al. 2019; Dong et al. 2014; Wu et al. 2009). The analysis of binding energy of
277 Cu in **ZVC@PS** indicates the presence of Cu in Cu(0), as well as Cu(II) on the surface, wherein surface-Cu(II),
278 could be attributed to the chemisorbed impurities of oxygen species. The **Fig. 5d** is the O1s XPS spectrum of
279 **ZVC@PS** that has three different peaks at 529.4, 531.1, and 532.4 eV, which are attributed to Cu(I) oxide, oxygen
280 in biomass polymer, and chemisorbed oxygen species like O, ⁻OH, etc., respectively (Wang et al. 2015).

281 The Cr(VI) adsorbed **ZVC@PS** showed peaks at 529-534, 570-590, 823, and 930-960 eV, are characteristic of
282 elements O, Cr, C, and Cu, respectively. Upon deconvolution of O1s spectral peak from 529-534 eV, showed the
283 presence of only two species in the sample characterized by the peak at 529.5 and 531.4 eV. The O1s peak at 532.4
284 is attributed to the C=O, C-O, of biomass as well as the Cu₂O due to sorption of Cr(VI). The characteristic

285 deconvoluted peak corresponding to O1s at 534.4 eV in **ZVC@PS** was missing in the Cr(VI) adsorbed sample and
286 could be attributed to the displacement of chemisorbed oxygen by the incoming Cr(III/VI) species on the surface of
287 **ZVC**. The weak Cr2p_{3/2} and Cr2p_{1/2} binding energy peaks observed at 574 and 585 eV, respectively, were
288 characteristic of Cr(III) oxide and Cr(OH)₃. Thus indicating reduction of Cr(VI) to Cr(III) under the adsorption
289 conditions using **ZVC@PS** as adsorbent. The binding energy peak of Cu in Cr(VI) adsorbed **ZVC@PS** showed four
290 deconvoluted peaks at 931, 933, 942.2, and 951.8 eV. The presence of CuO in Cr(VI) adsorbed **ZVC@PS** was
291 characterized by the Cu 2p_{3/2} and Cu 2p_{1/2} at 933.6 and 951.8 eV, respectively (Chang et al. 2019; Ji et al. 2018; Park
292 et al. 2006; Wang et al. 2015). The Cu 2p peaks after Cr(VI) adsorption showed a shift to lower binding energies as
293 it was attributed to the lower concentration of Cu(II) species after Cr(VI) adsorption.

294 *3.1.6 TGA Analysis*

295 Thermal stabilities of pistachio shell powder (**PS**), zerovalent copper loaded pistachio shell powder nanocomposite
296 before (**ZVC@PS**) and after chromium adsorption (**ZVC@PS-Cr**) were studied by TGA and DTA techniques. In
297 **Fig. 6a**, the **PS** decomposed completely in TGA analysis, as it consists of only organic matters. The TGA curve of
298 **ZVC@PS** showed mass loss up to 60% at the temperature 410 °C and retained the remaining mass up to 600
299 °C. The TGA curve of **ZVC@PS** after Cr adsorption showed higher mass loss up to 80% till 410 °C and no further
300 mass loss observed till 600 °C. This trend of TGA curves indicates the presence of non-oxidizable inorganic
301 substances in **ZVC@PS** and **ZVC@PS-Cr** materials that did not decompose till 600 °C. The DTA curves of **PS**,
302 **ZVC@PS**, and **ZVC@PS-Cr** are shown in **Fig. 6b**. All three materials exhibited thermal degradation in two stages.
303 The first stage or primary decomposition having a temperature range from 220-320 °C involves the weight loss of
304 65% with degradation of glycosyl units of hemicellulose and cellulose accompanied by the evolution of gases like
305 CO, CO₂, H₂O, etc. along with the formation of levoglucosan and charred residues (Shafizadeh 1982). The second
306 stage or secondary decomposition with a temperature range from 340-500 °C was assigned to degradation of
307 levoglucosan, decomposition of high energy bonds of lignin, and burning of char, resulting in loss of 30% of total
308 weight (Cheng et al. 2012). In **ZVC@PS** the thermal decomposition was observed in the temperature range of 200-
309 290 °C in the first stage and 310-400 °C in the second stage. The shift in the degradation curve towards the lower
310 temperature in **ZVC@PS** indicated the copper-mediated internal oxidative combustion of lignocellulosic biomass
311 resulting in its lower thermal stability in comparison to **PS**. There was no significant change observed in the
312 decomposition curve up to 600 °C, which indicates the complete oxidation of Cu(0) to Cu(II). The TG curve of the
313 chromium adsorbed sample exhibited a shift towards higher temperature in comparison to **ZVC@PS**, but with a
314 narrow decomposition temperature range between 270-300 °C in the first stage and 310-370 °C in the second stage.
315 The residual content was significantly higher than **PS** in before and after Cr(VI) adsorption samples of **ZVC@PS**,
316 which accounted for oxidation of copper and adsorption of Cr(VI).

317 The two thermal decomposition peaks at 320 °C and 480 °C were observed in the first derivative (DTA) curve of **PS**
318 pyrolysis. The two decomposition peaks were ascribed to the loss of two structural components of the lignocellulose
319 framework i.e. primary decomposition of relatively simpler cellulose structure and secondary decomposition of

320 highly complex lignin structure with high-energy bonds. In the case of copper-loaded **ZVC@PS**, two endothermic
321 peaks were observed at 285 and 380 °C, with significant lower temperature shifts of 35 K and 100 K, in the primary
322 and secondary decomposition curves, respectively in comparison to **PS**. The agglomeration of copper on the surface
323 of **PS** prevents the oxidation of cellulose and results in more heat gain in **ZVC@PS**. Further, the narrowing of heat
324 gain peaks in the case of **ZVC@PS** suggested the heat mediated conversion of copper to its oxide resulted in heat
325 loss, which reinforced the overall degradation process. However, in Cr(VI) adsorbed samples, the presence of oxides
326 of copper and chromium further prevents cellulose oxidation and results in a high-intensity endothermic peak with a
327 slight shift (15 K) of the primary decomposition curve towards the higher temperature in comparison to **ZVC@PS**.

328 **3.2 Adsorption Studies**

329 *3.2.1 Effect of pH on Cr (VI) adsorption*

330 The pH of a solution plays a regulatory role in the adsorption of oxoanion like Cr(VI). Therefore, the pH of the
331 solution was optimized for the adsorption of Cr(VI) onto **ZVC@PC**. The adsorption studies were performed in
332 varying pH conditions from 2 to 10 with **ZVC@PS** dose of 100 mg/L and Cr(VI) concentration of 20 mg/L. As the
333 pH increased from 2 to 10, the Cr(VI) uptake efficiency of **ZVC@PC** was decreased from 100 mg/g to 10 mg/g
334 (**Fig. 7**). The adsorption under pH 2 and 3 showed similar results, however, under highly acidic conditions of pH 2,
335 the solution turned yellowish due to dissolution of the oxidized Cu into the solution. Dissolution of Cu(I/II) from
336 **ZVC@PS** was restricted upon increasing the pH to 3 and above. The higher removal efficiency for Cr(VI) at lower
337 pH conditions is ascribed to: (a) surface protonation of **ZVC@PS** resulting in positively charged surface favoring
338 attractive interaction with Cr(VI) oxoanion; (b) protonation of Cr(VI) to reduce electrostatic repulsions with the
339 surface of **ZVC@PS** and thus facilitates the overall reductive removal of Cr(VI) ions. At higher pH, the proton
340 concentration is diminished and the negative charge on Cr(VI) is electrostatically less favored for adsorption on the
341 **ZVC@PS** surface.

342 *3.2.2 Effect of ZVC@PS dose on Cr(VI) adsorption*

343 Effect of adsorbent dose of **ZVC@PS** was investigated by changing the adsorbent dose from 50 to 200 mg/L with a
344 20 mg/L Cr(VI) solution maintained at pH 3. As the adsorbent dose of **ZVC@PC** increased from 50 to 200 mg/L,
345 the removal of Cr(VI) increased from 20 to 70% (**Fig. 8**). This may account for the increase in the number of
346 available adsorption sites on the nanocomposite adsorbent with the increase in adsorbent dose, resulting in the
347 significant adsorptive removal of Cr(VI) from the solution. As the dose of the adsorbent was increased from the
348 Cr(VI) adsorption (q_e) decreased from 73.22 mg/g to 58.13 mg/g. There was a marginal change in q_e from 100 mg/L
349 to 150 mg/g followed by a decrease in adsorption at 200 mg/g. dose of adsorbent can be attributed to the decrease in
350 the number of Cr(VI) ions available per unit mass of the adsorbent at higher adsorbent dose. Consequently, the
351 active sites on the adsorbent surface remained unsaturated in higher doses. Thus for the optimized conditions used
352 for further study is the adsorbent dose of 100 mg/L.

353 *3.2.3 Effect of Cr(VI) concentration on adsorption by ZVC@PS and Adsorption Isotherms*

354 Cr(VI) ion uptake equilibrium under varying initial concentration of Cr(VI) (1-20 mg/L) were studied. The Cr(VI)
355 uptake increased from 9.42 to 99.3 mg/g, upon increasing the concentration of an aqueous solution from 1 to 20
356 mg/L. However, the percentage removal decreased from 100% to 53.17% upon increasing the initial concentration
357 of Cr(VI). These results could be attributed to the increase in the number of Cr(VI) competing for the same amount
358 of adsorbent under increased initial concentration (**Fig. 9**).

359 The equilibrium data fitted to both Langmuir and Freundlich adsorption isotherm models and it confirmed the
360 monolayer adsorption behavior of **ZVC@PS** for Cr(VI) adsorption from aqueous solution (**Fig. 10**). The value of
361 q_{max} , adsorption energy (K_L), and dimensionless factor R_L determined from a linear fit diagram of Langmuir
362 adsorption isotherm models were 111.11 mg/g 1.5 L/mg, and 0.667, respectively (**Table 1**). As the value of R_L lies
363 between 0 and 1, indicates favorable adsorption of Cr(VI) on **ZVC@PS**.

364 **3.3 Kinetic equilibrium study**

365 The rate of Cr(VI) adsorption was slow with the removal of 77.50% of Cr(VI) during the first 120 minutes. The
366 Cr(VI) adsorption further increased from 77.50% up to 93.50% in 17 hrs. The initial increase in the adsorption
367 could be attributed to the free availability of adsorption sites on the surface of the adsorbent. Further, the slow
368 kinetics could be attributed to the diffusion of the anion to the surface of the **ZVC@PS** in the pores.

369 Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic models were applied to the data. The
370 linear fit diagram of pseudo-first order and pseudo-second-order adsorption kinetic plot are presented in **Fig. 11a-b**.
371 The kinetic plot shows a poor fit to pseudo-first-order kinetics with R^2 equal to 0.805, whereas a good fit with
372 pseudo-second-order kinetics with R^2 equal to 0.989 further verified with a significant chi-square value at a 95%
373 confidence level. The q_{max} and K_t for the adsorption under pseudo-second-order kinetic fit is 83.3 mg/g and $1.618 \times$
374 10^{-3} min^{-1} .

375 **4. Discussion**

376 The adsorption experiments showed that the Cr(VI) adsorption capacity (111.1 mg/g) of nano zerovalent copper
377 immobilized on to pistachio shell powder (**ZVC@PS**) was significantly higher than pistachio shell powder (27.95
378 mg/g) (Banerjee et al. 2018), polymer foam (PEI-PAA) immobilized zero-valent copper (3.77 mg/g) (Li et al.
379 2015a) and immobilized zerovalent Fe(0) (50 mg/g) used for the treatment of Cr(VI) from wastewater (Shi et al.
380 2011) (**Table 2**). This higher Cr(VI) adsorption efficiency of **ZVC@PS** may be ascribed to the formation of well-
381 dispersed **ZVC** nanoparticles on the surface of pistachio shell powder during synthesis, which otherwise gets
382 agglomerated in the absence of support. A synergistic effect was observed between the Cr(VI) adsorption tendency
383 of pistachio shell powder and reductive removal of Cr(VI) by zero-valent copper, which causes a significant increase
384 in Cr(VI) removal efficiencies of **ZVC@PS**. The optimum pH for the Cr(VI) adsorption studies with **ZVC@PS** was
385 in the acidic conditions, thus favoring its attractive interaction with Cr(VI) oxoanion. The removal of Cr(VI) was
386 improved with increasing the dose of **ZVC@PS**, which was ascribed to an increase in the available adsorption sites

387 in the nanocomposite. Langmuir and Freundlich adsorption isotherm models confirmed the monolayer adsorption
388 behavior of **ZVC@PS** for Cr(VI). **ZVC@PS** nanocomposite followed pseudo-second-order kinetic for the Cr(VI)
389 adsorption with a significant R^2 value of 0.989.

390 **Conclusion**

391 **ZVC@PS** an eco-efficient nanocomposite was synthesized, characterized, and used for the removal of Cr(VI) from
392 aqueous solution. Batch experiment studies demonstrated that Cr(VI) removal rate was increased with a decrease in
393 pH and initial Cr(VI) concentration, and increase in **ZVC@PS** dose. At optimum conditions, the Cr(VI) removal
394 capacity of **ZVC@PS** is observed as 111.1 mg/g, and the normalized adsorption efficiency of Cu for Cr(VI) in
395 **ZVC@PS** is 284.84 mg/g, which is quite significant. The mechanism of removal of Cr(VI) by **ZVC@PS** was
396 investigated as surface adsorption with concomitant reduction of Cr(VI) to Cr(III). In conclusion, the pistachio shell
397 powder immobilized zerovalent copper could be an efficient and promising material for Cr(VI) remediation from an
398 aqueous medium.

399

400

Abbreviations

401 PS: pistachio shell; ZVC: zerovalent copper; SEM: scanning electron microscopy; EDX: Energy Dispersive X-rays;
402 FTIR: Fourier-transform infrared; XRD: X-ray powder diffraction; TGA: thermo-gravimetric analysis; DTA:
403 differential thermal analysis; BET: Brunauer–Emmett–Teller; BJH: Barrett-Joyner-Halenda; XPS: X-ray
404 photoelectron spectroscopy.

405

406

Declarations

407 **Ethics approval and consent to participate:** Not applicable.

408 **Consent for publication:** All the data used for writing this manuscript has been cited with proper references.

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421 Amarjeet Dahiya: The author is research scholar in Department of Chemistry, Central University of Punjab and
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433 **References**

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Figures

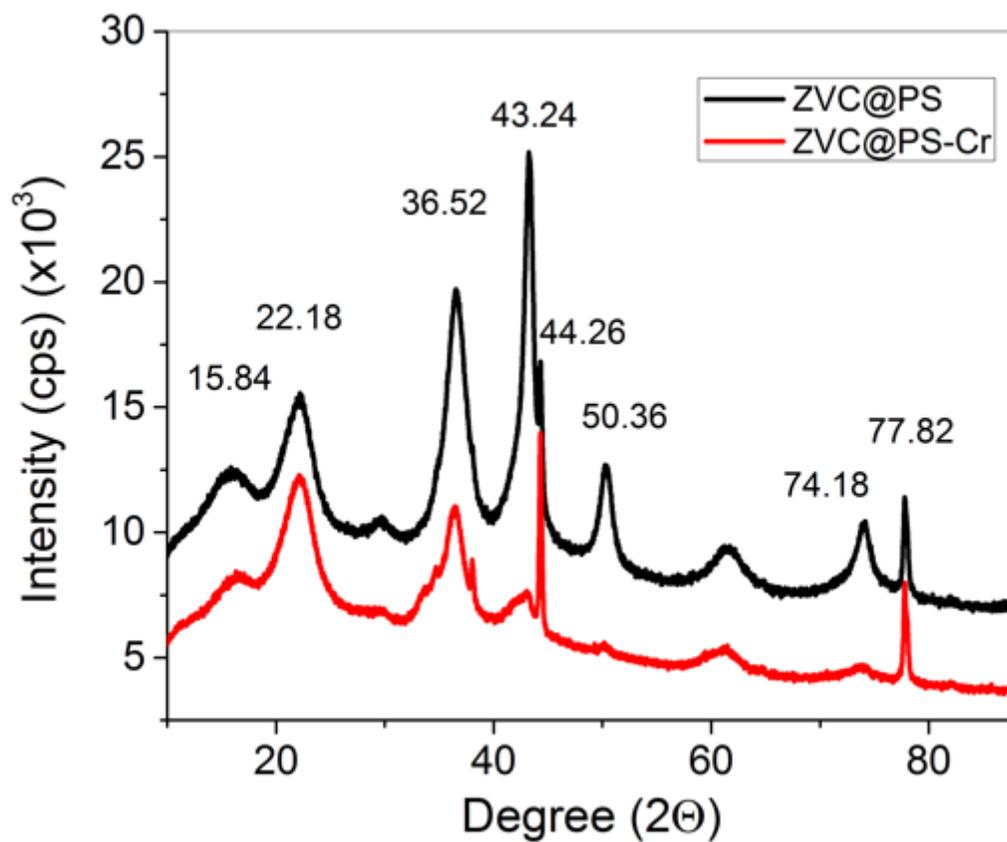


Figure 1

XRD pattern analysis of ZVC@PS and Cr(VI) adsorbed ZVC@PS samples

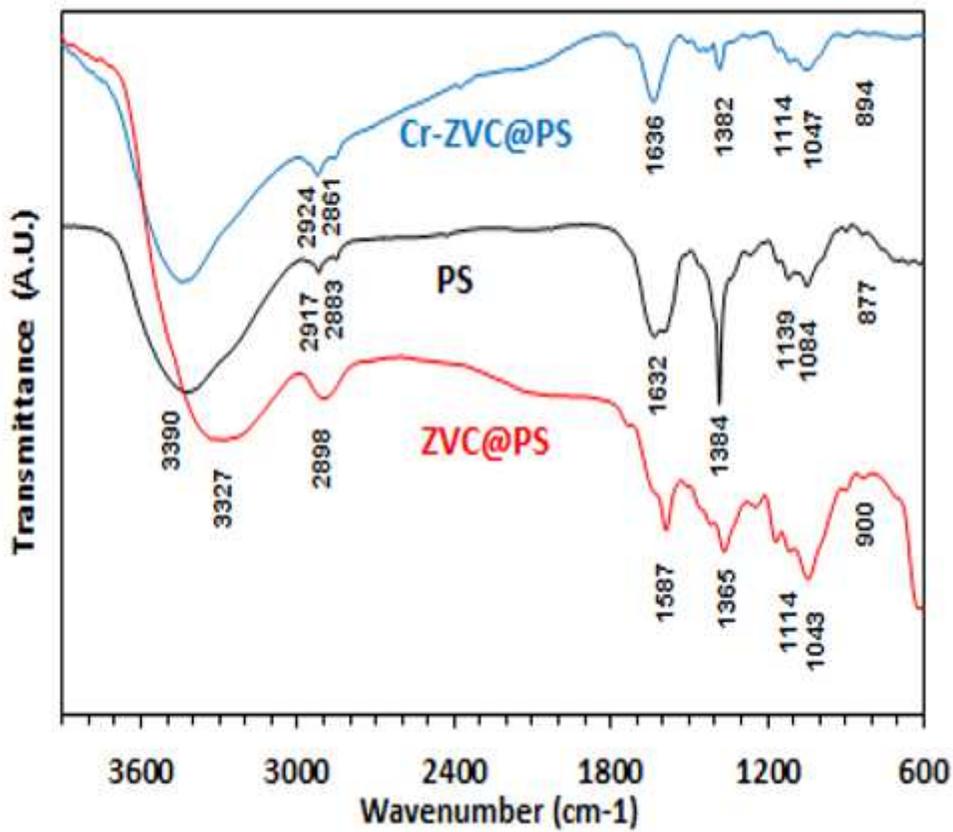


Figure 2

FTIR spectra of PS, ZVC@PS) and Cr(VI) adsorbed ZVC@PS samples

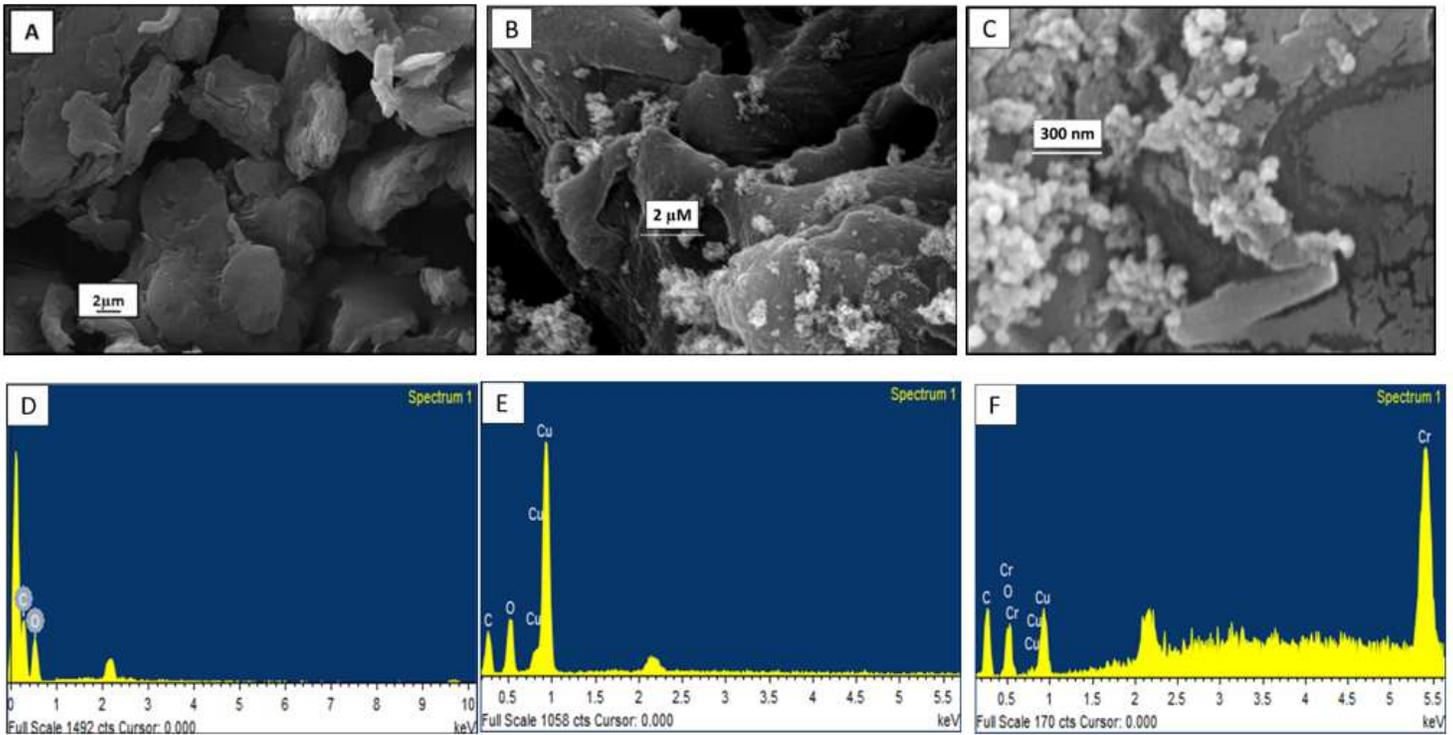


Figure 3

SEM images of (a) PS; (b) ZVC@PS; (c) ZVC@PS at increased magnification. EDX spectra of (d) PS; (e) ZVC@PS; and (f) Cr(VI) adsorbed ZVC@PS

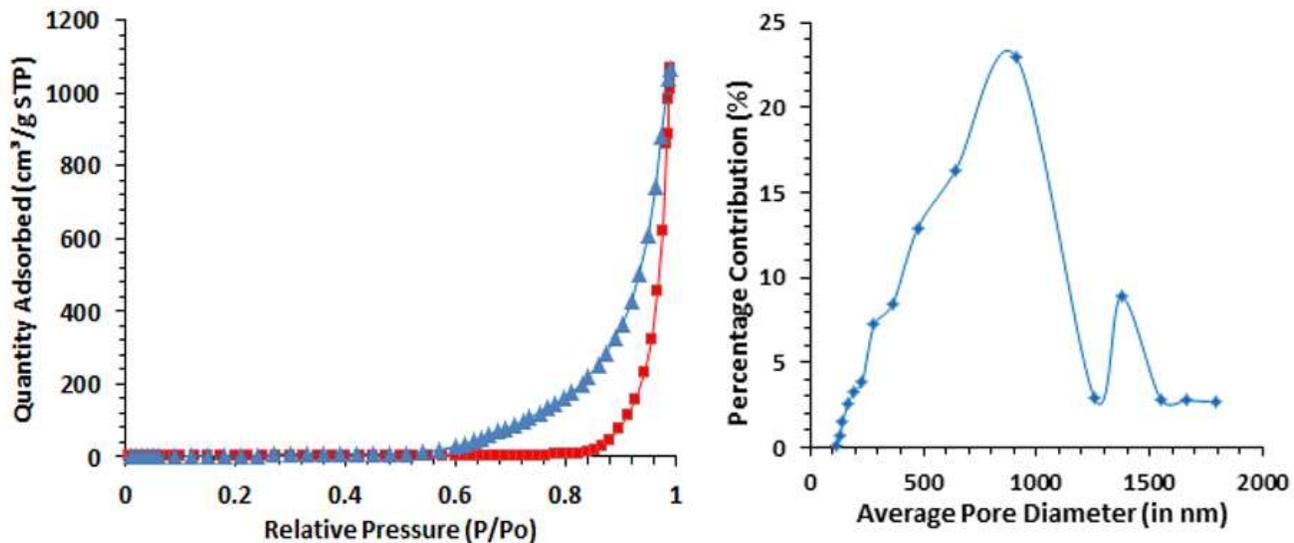


Figure 4

(a) Nitrogen adsorption-desorption isotherm for ZVC@PS; (b) average pore size distribution of ZVC@PS

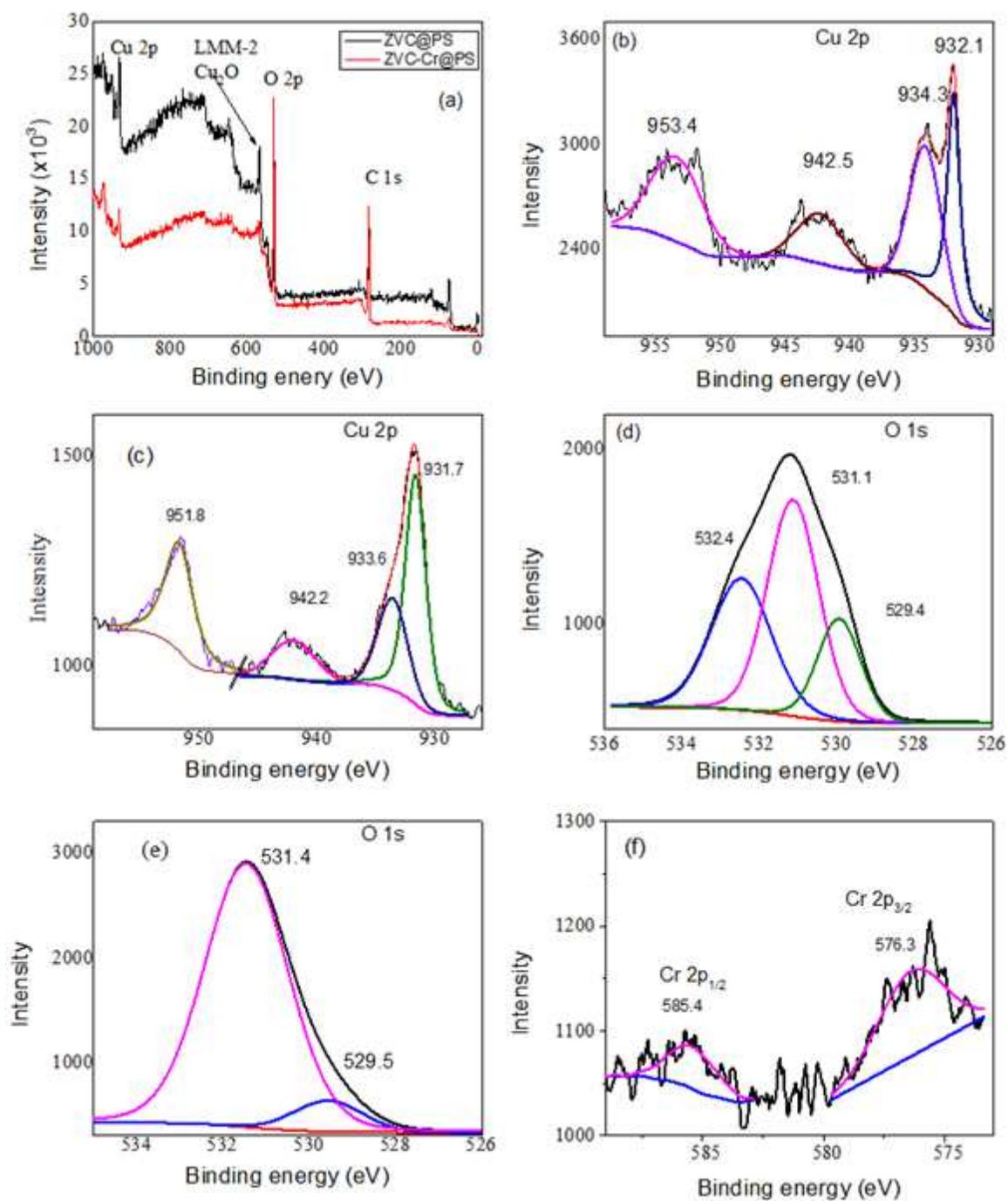


Figure 5

X-ray photoelectron spectroscopy spectra (a) survey scan of ZVC@PS; (b) Cu 2p before; and (c) Cu 2p after Cr(VI) adsorption on ZVC@PS; (d) O 1s before; and (e) O 1s after Cr(VI) adsorption on ZVC@PS

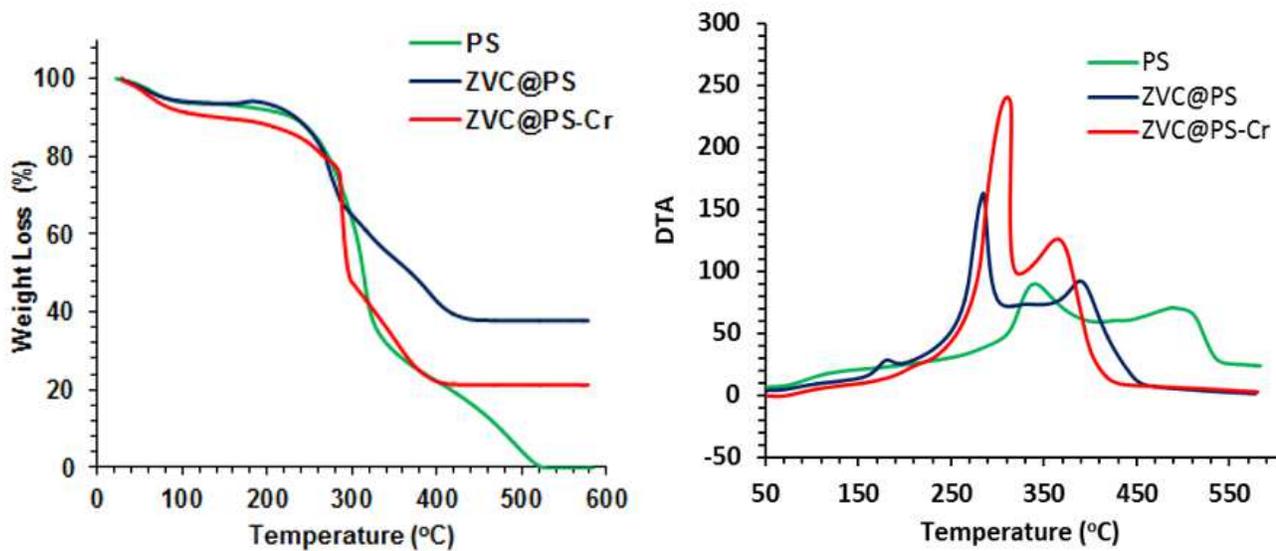


Figure 6

(a) TGA graphs; and (b) DTA curves of PS, ZVC@PS and ZVC@PS-Cr samples

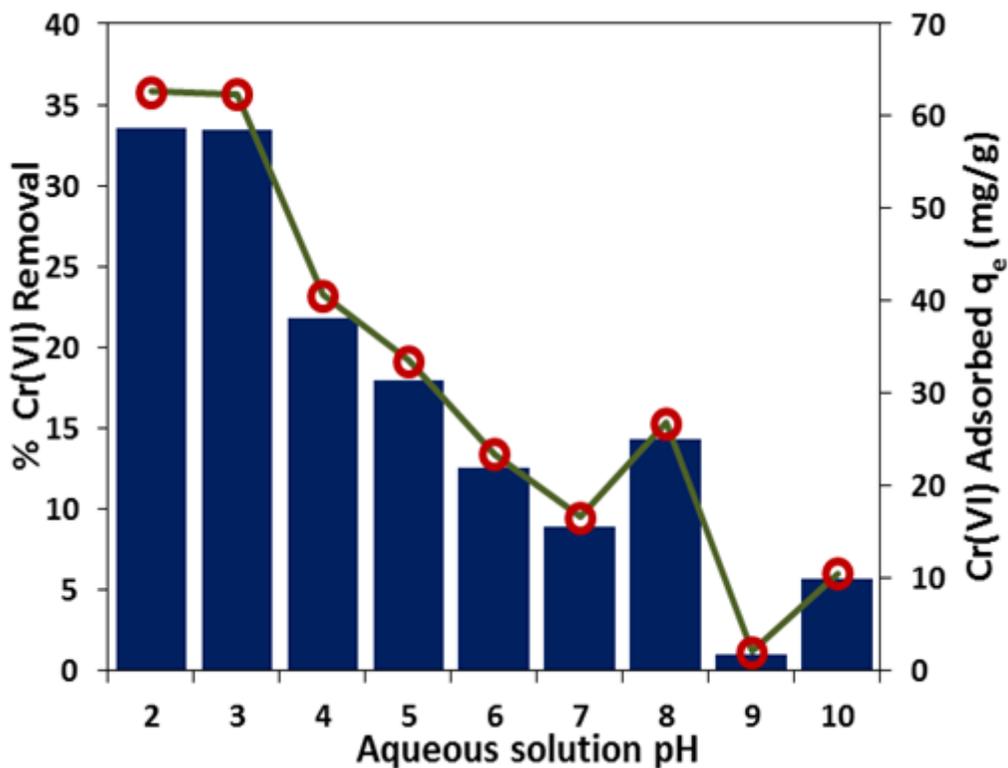


Figure 7

Effect of pH on Cr(VI) adsorption (q_e) and % Cr(VI) removal efficiency of ZVC@PS. [When ZVC@PS dose is 100 mg/L, Cr(VI) concentration is 20 mg/L, contact time is 24 hours, and shaking speed is 200 RPM]

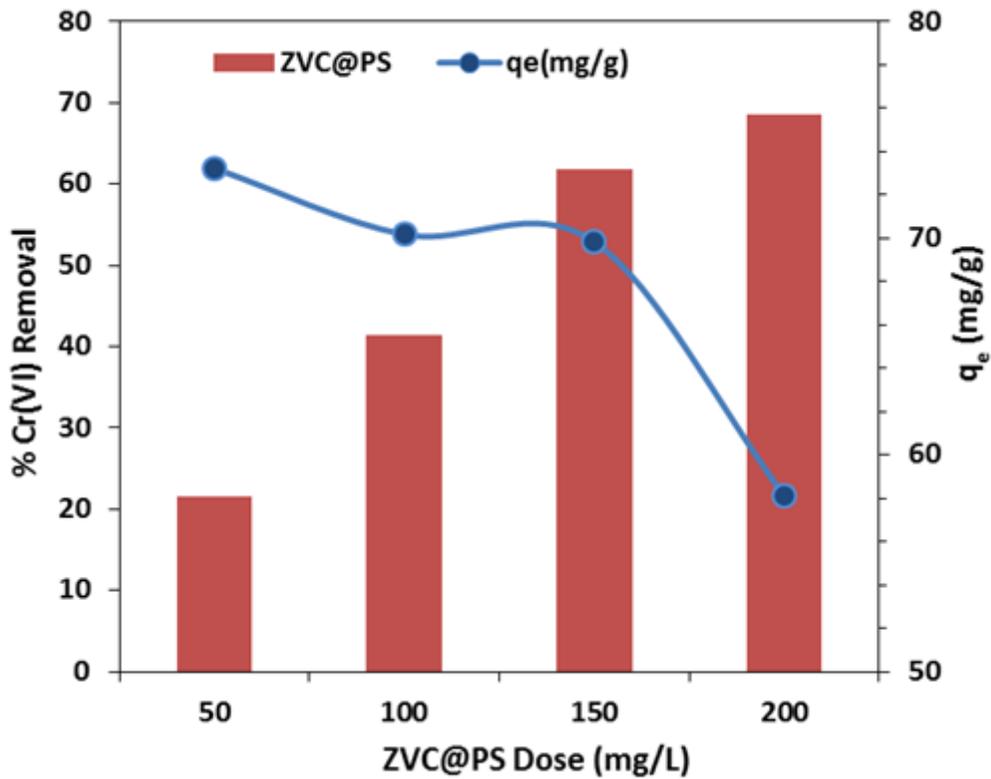


Figure 8

Effect of ZVC@PS dose concentration (50 to 200 mg/L) on Cr(VI) adsorption (q_e) and % Cr(VI) removal, upon treatment with 20 mg/L of Cr(VI) solution at pH 3

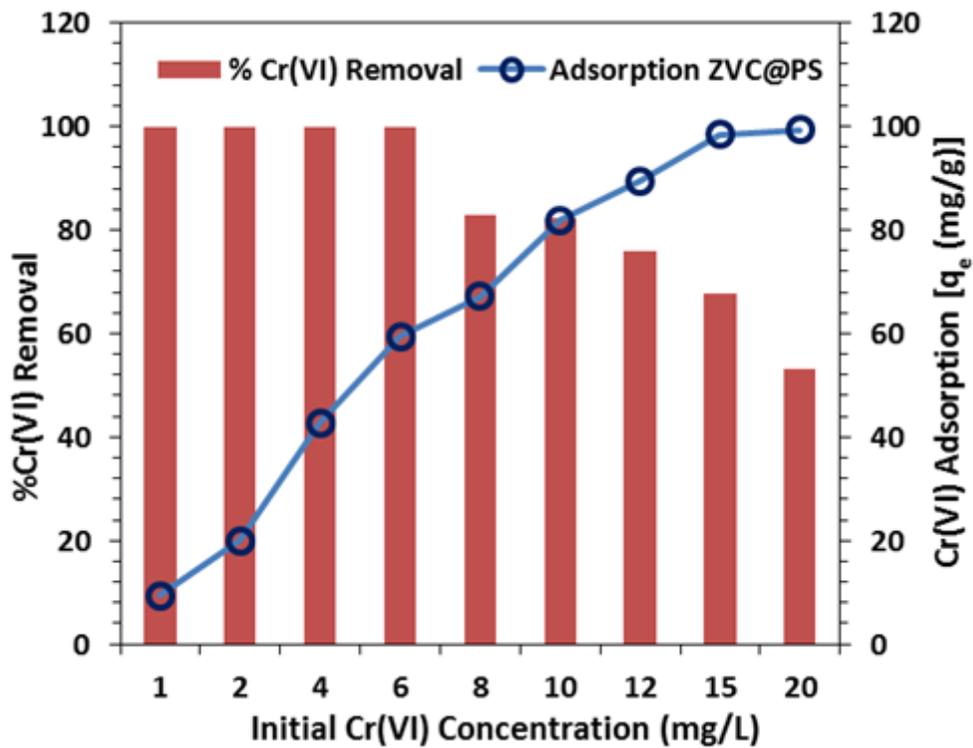


Figure 9

Effect of initial Cr(VI) concentration (1 to 20 mg/L) on Cr(VI) adsorption (q_e) and % Cr(VI) removal efficiency of ZVC@PS

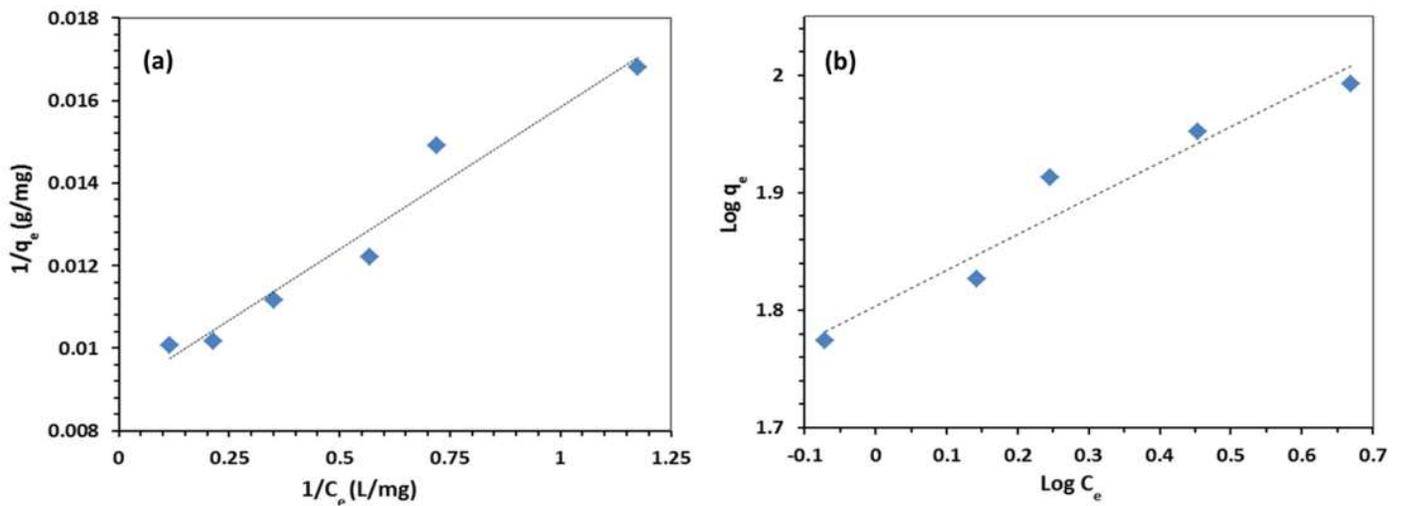


Figure 10

Langmuir adsorption isotherm (a); and Freundlich adsorption isotherm (b); for ZVC@PS for adsorption of Cr(VI)

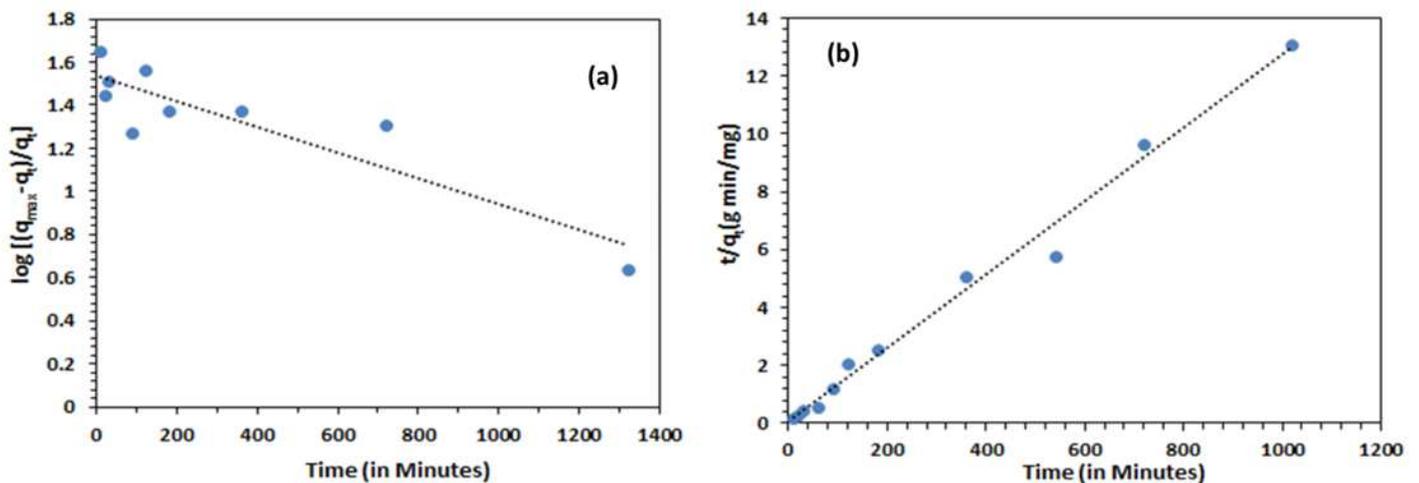


Figure 11

Linear fit plots of (a) pseudo first order and (b) pseudo second order adsorption kinetics

Supplementary Files

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