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Abdelaziz Imgharn, Lahoucine Anchoum, Abdelghani Hsini, Yassine Naciri, Mohamed Laabd, et al.. Effectiveness of a novel polyaniline@Fe-ZSM-5 hybrid composite for Orange G dye removal from aqueous media: Experimental study and advanced statistical physics insights. *Chemosphere*, 2022, 295, pp.133786. 10.1016/j.chemosphere.2022.133786 . hal-03561674

**HAL Id: hal-03561674**

**<https://hal.science/hal-03561674v1>**

Submitted on 7 Nov 2022

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# Journal Pre-proof

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PII: S0045-6535(22)00279-X

DOI: <https://doi.org/10.1016/j.chemosphere.2022.133786>

Reference: CHEM 133786

To appear in: *ECSN*

Received Date: 25 September 2021

Revised Date: 5 January 2022

Accepted Date: 27 January 2022

Please cite this article as: Imgharn, A., Anchoum, L., Hsini, A., Naciri, Y., Laabd, M., Mobarak, M., Aarab, N., Bouziani, A., Szunerits, S., Boukherroub, R., Lakhmiri, R., Albourine, A., Effectiveness of a novel polyaniline@Fe-ZSM-5 hybrid composite for Orange G dye removal from aqueous media: Experimental study and advanced statistical physics insights, *Chemosphere* (2022), doi: <https://doi.org/10.1016/j.chemosphere.2022.133786>.

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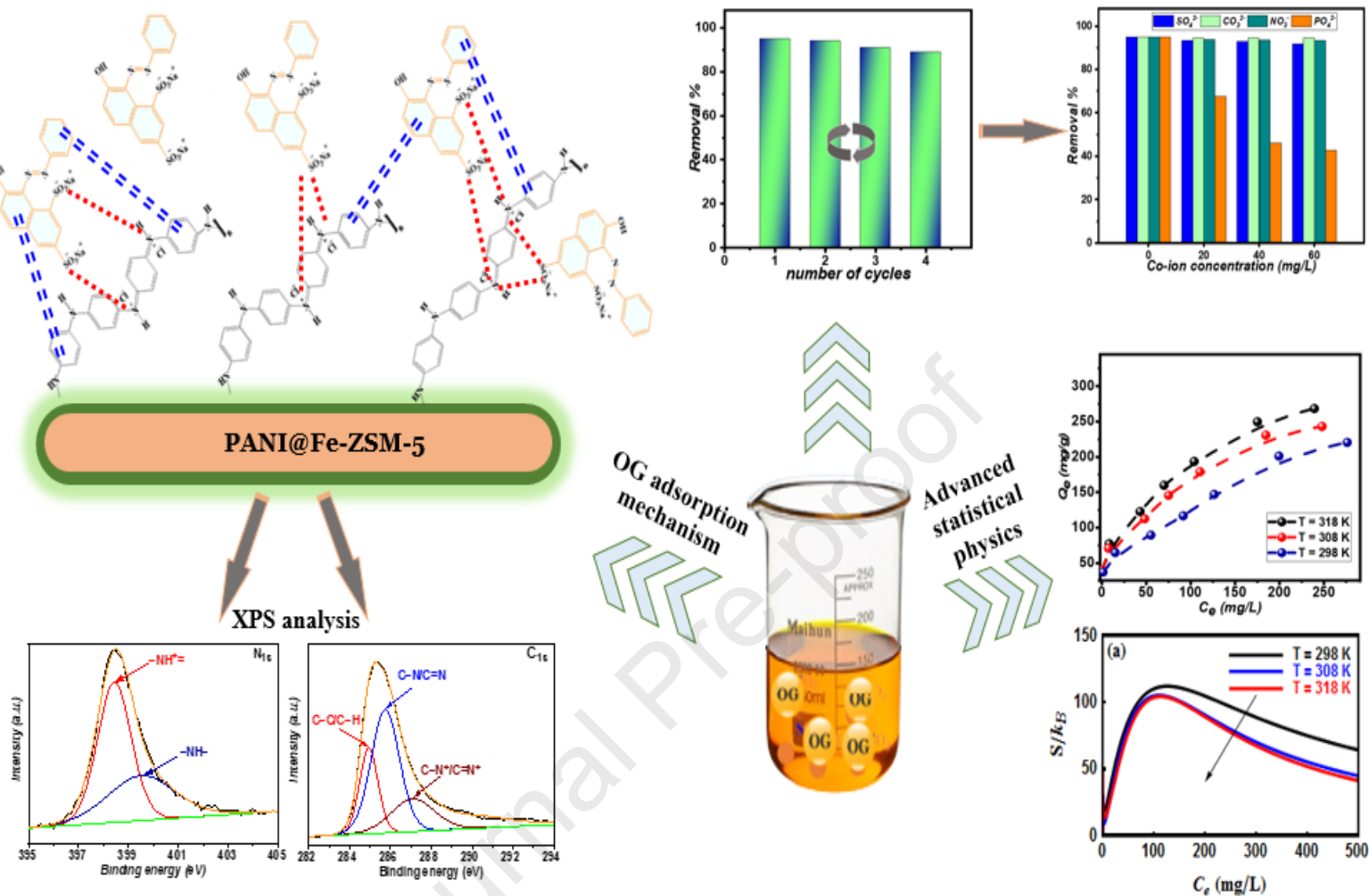
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## Author Contributions Statement

**Abdelaziz Imgharn:** Formal analysis, Data curation, Writing-original draft. **Lahoucine Anchoum:** Investigation. **Abdelghani Hsini:** Methodology, Formal analysis, Data curation, Writing-review & editing. **Yassine Naciri:** Methodology, Investigation, Writing-review & editing. **Mohamed Laabd:** Validation, Writing-review & editing. **Mohamed Mobarak:** Formal analysis, Data curation. **Nouh Aarab:** Investigation. **Asmae Bouziani:** Writing-review & editing. **Sabine Szunerits:** Investigation, Methodology. **Rabah Boukherroub:** Conceptualization, Validation, Writing-review & editing. **Rajae Lakhmiri:** revision, editing. **Abdallah Albourine:** Conceptualization, Validation, revision, editing, Supervision, Project administration.

## Graphical abstract



1 **Effectiveness of a novel polyaniline@Fe-ZSM-5 hybrid composite for Orange**  
2 **G dye removal from aqueous media: Experimental study and advanced**  
3 **statistical physics insights**

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**Abstract**

A polyaniline@Fe-ZSM-5 composite was synthesized *via* an *in situ* interfacial polymerization procedure. The morphology, crystallinity, and structural features of the as-developed PANI@Fe-ZSM-5 composite were assessed using scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The composite was efficiently employed for the first time as an adsorbent to adsorb Orange G (OG) dyestuff from water. The OG dye adsorption performance was investigated as a function of several operating conditions. The kinetic study demonstrated that a pseudo-second-order model was appropriate to anticipate the OG adsorption process. The maximum adsorption capacity was found to be 217 mg/g. The adsorption equilibrium data at different temperatures were calculated *via* advanced statistical physics formalism. The entropy function indicated that the disorder of OG molecules improved at low concentrations and lessened at high concentrations. The free enthalpy and internal energy functions suggested that the OG adsorption was a spontaneous process and physisorption in nature. Regeneration investigation showed that the PANI@Fe-ZSM-5 could be effectively reused up to five cycles. The main results of this work provided a deep insight on the experimental study supported by advanced statistical physics prediction for the adsorption of Orange G dye onto the novel polyaniline@Fe-ZSM-5 hybrid composite. Additionally, the experimental and advanced statistical physics findings stated in this study may arouse research interest in the field of wastewater treatment.

**Keywords:** Polyaniline; Fe-ZSM-5; Composite; Dye removal; Advanced statistical physics; Regeneration.

## 46 **1. Introduction**

47 Many industries use synthetic dyes to color their final product, including food, drugs,  
48 cosmetics, paper, leather, plastics, and textile (Abbasi, 2017). Dyes often exhibit  
49 persistence to biodegradation and significant toxic, carcinogenic, and mutagenic effects  
50 on aquatic organisms and humans, which has become a severe environmental problem in  
51 the world (Belbachir and Makhoukhi, 2017; Gottlieb et al., 2003). Therefore, the discharge  
52 of dyes in wastewater, even in a small amount, is unpleasant and should be removed  
53 before they enter the environment. In this context, several treatment processes, including  
54 coagulation-flocculation (Renault et al., 2009), photocatalysis (Akhsassi et al., 2021;  
55 Fahoul et al., 2022; Mimouni et al., 2021; Naciri et al., 2021), ion exchange (Hassan and  
56 Carr, 2018), membrane filtration, and adsorption (Amjlef et al., 2021; Imgharn et al.,  
57 2021; Njoya et al., 2020) have been implemented to clean up colored effluents. Adsorption  
58 is considered an effective, green, and low-cost approach used for dye elimination from  
59 aqueous solutions. Therefore, the last decades have witnessed a huge interest in the  
60 development of efficient adsorbent materials. The performance of adsorbents depends on  
61 their physicochemical characteristics like porosity, particle size, surface functional groups,  
62 and chemical stability (Benjelloun et al., 2021; Laabd et al., 2021).

63  $\pi$ -Conjugated polymers including polyaniline (PANI), polythiophene (PTh), and  
64 polypyrrole (PPy) have been widely employed in many fields like gas sensors, tissue  
65 engineering, photovoltaic cells, batteries, and wastewater purification (Liao et al., 2019).  
66 PANI is considered as the most promising conductive polymer among these polymers due  
67 to its particular characteristics: good redox reversibility, low-cost, environmental  
68 friendliness, excellent stability, good conductivity, and easy synthesis (Laabd et al., 2017;

69 Naciri et al., 2022). In addition, the uptake of organic dyes and heavy metal ions by PANI  
70 is high. The ion exchange property, porous structure as well as the presence of a large  
71 amount of protonated amine and imine groups on the surface of PANI are the reasons for  
72 its high adsorption capacity. However, the small particle size and poor physical  
73 (mechanical and thermal) properties of PANI seriously hinder its use in large scale  
74 wastewater purification systems (Sahu et al., 2019). In order to counterbalance these  
75 limitations, PANI-based composites using different reinforcing substrates like mineral  
76 clays (Zhou et al., 2017), natural lignocellulosic wastes (Kumar et al., 2008), activated  
77 carbon (Ansari et al., 2017) and zeolites (Abdellaoui et al., 2020; Shyaa et al., 2015) have  
78 been developed.

79 Zeolite has a tridimensional form of crystalline aluminosilicate, an open anionic  
80 framework consisting of tetrahedral oxygen-sharing  $TO_4$ , in which  $AlO_4$  and  $SiO_4$  are  
81 covalently linked to each other (Ba Mohammed et al., 2020; Shyaa et al., 2015). Besides,  
82 the zeolitic materials are microporous with a uniform pore distribution. As evidenced from  
83 the literature, the properties of zeolites can be enhanced by integrating different metals  
84 into their matrices. Incorporation of iron into adsorbents is highly preferred due to its  
85 economic, eco-friendly and semiconducting properties (Saifuddin et al., 2019). Several  
86 works focused on the optimization of the adsorption parameters and discussed the  
87 physical aspects of the process. However, only a restricted number of studies are available  
88 which decipher the main role of the active metal ions of the zeolite structure in the  
89 adsorption phenomenon.

90 Herein, we synthesized PANI@Fe-ZSM-5 zeolite hybrid composite through an oxidative  
91 polymerization route and characterized by SEM coupled with EDS, XRD, FTIR and XPS



92 analysis. The initial Orange G (OG) concentration, dosage of adsorbent, contact time,  
93 initial pH value of the solution and temperature were optimized to evaluate the  
94 effectiveness of the synthesized PANI@Fe-ZSM-5 composite for OG removal. The  
95 modeling of the equilibrium isotherms and adsorption kinetics of the OG dye on the  
96 composite was also evaluated. Furthermore, the theoretical predication of the OG  
97 molecules' binding on the surface of PANI@Fe-ZSM-5 was calculated using advanced  
98 statistical physics applied to the adsorption equilibrium. In addition, the effect of co-  
99 existing ions was assessed. Finally, the regeneration of PANI@Fe-ZSM-5 composite was  
100 performed to evaluate its reusability for OG dyestuff removal.

## 101 **2. Experimental**

### 102 **2.1. Chemicals**

103 Aniline monomer (Sigma-Aldrich) was used after distillation. Sodium persulfate  
104 ( $\text{Na}_2\text{S}_2\text{O}_8$ ), acetone, ethanol, tetrapropylammonium bromide ( $\text{C}_{12}\text{H}_{28}\text{NBr}$ , 98 %), iron  
105 (III) nitrate pentahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 99.95$  %), sulfuric acid ( $\text{H}_2\text{SO}_4$ ,  $\geq 95$  %),  
106 sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ,  $\geq 98$  %), hydrochloric acid (HCl, 37 %), sodium hydroxide  
107 (NaOH,  $\geq 97$  %), sodium chloride (NaCl,  $\geq 99$  %), and orange G (OG) dye were of analytical  
108 grade and purchased from Sigma-Aldrich. The dye solution was prepared by dissolving  
109 the accurately weighted dye in distilled water.

### 110 **2.2. Preparation of Fe-ZSM-5 zeolite**

111 The Fe-ZSM-5 zeolite synthesis was conducted using the procedure reported by Ba  
112 Mohammed et al. (Ba Mohammed et al., 2020). Briefly, 10 g of sodium metasilicate as a  
113 silicon precursor were dissolved in 25 mL of distilled water, and then 2 g of  
114 tetrapropylammonium bromide were added to the suspension under magnetic stirring

115 until the solution became uniform with a pH value of 10. The obtained solution was called  
116 first solution. A second solution was produced by dissolving 1 g of ferric nitrate  
117 pentahydrate in 10 mL of distilled water; then, the resulting solution was acidified using  
118 2 ml of H<sub>2</sub>SO<sub>4</sub> (0.01 M). This solution was poured dropwise into the first one and kept  
119 under stirring for 2 h. The formed gel was placed in a Teflon autoclave at 180 °C for 48 h.  
120 The resulting suspension was filtered and washed several times with acetone and distilled  
121 water. Finally, the as-prepared material was kept at 100 °C overnight to dry then calcined  
122 at 550 °C for 6 h.

### 123 **2.3. Elaboration of PANI@Fe-ZSM-5**

124 The PANI@Fe-ZSM-5 hybrid composite was prepared via an *in situ* oxidative  
125 polymerization of aniline with Fe-ZSM-5 particles in an acidic medium using Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as  
126 oxidant, according to the procedure in (Hsini et al., 2021b): 1g of Fe-ZSM-5 was dispersed  
127 in 100 mL of a hydrochloric acid solution (1M) under stirring for 6 h. Then, 0.5 mL of  
128 aniline was added to the suspension under stirring for 3 h. A 50 mL solution of HCl (1 M)  
129 containing sodium persulfate (with a 0.5 monomer/oxidant molar ratio) was added  
130 dropwise into the mixture under agitation. A green suspension was obtained after 12 h,  
131 indicating the formation of doped PANI on the Fe-ZSM-5 particles. The resulting  
132 precipitate was filtered and washed with distilled water and acetone. The PANI@Fe-ZSM-  
133 5 composite was dried at 70 °C overnight.

### 134 **2.4. Characterization of the adsorbent**

135 To check out the hybrid composite crystal structure, X-ray powder diffraction (XRD)  
136 analyses were carried out with a BRUKER D8 ADVANCE TWIN diffractometer. The Fe-  
137 ZSM-5 surface morphology before and after polymerization was systematically

138 characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-  
139 ray spectrometry (EDS) analysis (SEM, JEOL, JSM-IT200). X-ray photoelectron  
140 spectroscopy (XPS) analysis of the as-prepared PANI@Fe-ZSM5 composite was acquired  
141 using an ESCALAB 220 XL spectrometer equipped with a monochromatic Al K $\alpha$  X-ray  
142 radiation source at 1486.6 eV. The binding energies were calibrated to the C1s peak at  
143 284.6 eV. Fourier-transform infrared (FTIR) spectra of the obtained materials were  
144 acquired using KBr pellets using FTIR spectroscopy (ALPHA-Bruker Optics, Germany) in  
145 a wavenumber ranging from 400 to 4000 cm<sup>-1</sup>.

146 The zero charge point (PZC) of the PANI@Fe-ZSM-5 composite was determined via  
147 potentiometric titration method reported by Fiol and Villaescusa (Fiol and Villaescusa,  
148 2009). In short, 0.025 g of PANI@Fe-ZSM-5 was added to 50 mL of KNO<sub>3</sub> (0.03 M)  
149 solution and the pH of the solution was adjusted from 2 to 12 by adding HCl (0.1 M) or  
150 NaOH (0.1 M) aqueous solutions. The mixtures were stirred for 24 h at ambient  
151 temperature. The final pH<sub>f</sub> of each solution was assessed. Then, the PZC was identified as  
152 pH<sub>i</sub> when  $\Delta$ pH is zero.

## 153 **2.5. Adsorption experiments and regeneration**

154 The OG dye adsorption onto PANI@Fe-ZSM-5 hybrid composite was conducted in a batch  
155 reactor under various operational conditions. To evaluate the effect of adsorbent dose,  
156 various amounts of PANI@Fe-ZSM-5 composite (0.2-2 g/L) were introduced into 50 mL  
157 of OG dye solution at 20 mg/L initial concentration for 180 min at pH 6.0 and 25 °C. The  
158 influence of pH on the OG dye removal efficiency was studied by changing the solution pH  
159 from 2 to 12 with an adsorbent dose of 0.5 g/L. Under the same experimental conditions,  
160 the influence of initial concentration of OG dye (from 20 to 500 mg/L), contact time and

161 temperature was also assessed. After adsorption, the adsorbent was removed from  
162 adsorbate solution by filtration on Millipore filters (0.45  $\mu\text{m}$ ). The equilibrium  
163 concentration of OG dye was quantified by UV2300 spectrophotometer at 476 nm.

164 The **absorbed** percentage  $R(\%)$  and the adsorption capacity  $Q_e(\text{mg/g})$  were calculated by  
165 the following relations (Ait Haki et al., 2021; Brini et al., 2021b):

$$166 \quad R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$167 \quad Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

168 Where  $C_0$  (mg/L) is the initial OG concentration,  $C_e$  (mg/L) is the OG concentration at  
169 equilibrium,  $m$  (g) is the mass of the PANI@Fe-ZSM-5 composite, and  $V$  (L) is the volume  
170 of the solution.

171 In order to bring up the adsorption process more economically reliable and eco-friendly,  
172 the regeneration of PANI@Fe-ZSM-5 composite after the adsorption experiment is a very  
173 important aspect. For desorption/adsorption study, 0.3 g of PANI@Fe-ZSM-5 was  
174 introduced in 0.6 L of 20 mg/L OG dye solution. After 180 min of sorption, desorption  
175 experiment was performed using 0.5 M NaOH as eluent solution for 6 h. After that, the  
176 regenerated PANI@Fe-ZSM-5 composite was washed with distilled water, and then  
177 redoped with 1 M HCl solution. The fresh PANI@Fe-ZSM-5 composite was used for a  
178 subsequent OG adsorption cycle. In this work, five regeneration cycles were carried out.

## 179 **2.6. Theoretical background**

180 The statistical physics theory is an emerging effective approach to deeply illuminate the  
181 adsorption mechanisms at the liquid-solid interface (Mobarak et al., 2019b, 2019a;

182 Mohamed et al., 2020). The adsorption performance of OG dye on the PANI@Fe-ZSM-5  
 183 hybrid composite was examined by applying five statistical physics models to the  
 184 experimental equilibrium data.

185 ○ First model (**M1**): Monolayer model with similar receptor sites. This model assumes  
 186 that the adsorption process occurs by the formation of a monolayer on the adsorbent  
 187 surface with one type of adsorption sites (Mobarak et al., 2019b, 2019a). The  
 188 analytical expression of the M1 model is given by Eq. (3):

$$189 \quad Q_e = nN_o = \frac{nN_M}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n} = \frac{Q_{sat}}{1 + \left(\frac{C_{1/2}}{C_e}\right)^n} \quad (3)$$

190 where  $Q_e$  (mg/g) and  $C_e$  (mg/L) denote the equilibrium adsorbed amount and equilibrium  
 191 concentration, respectively;  $n$  represents the number of adsorbed molecules per binding  
 192 site;  $N_M$  (mg/g) is the active sites density;  $Q_{sat}$  (mg/g) is the adsorption capacity at  
 193 saturation;  $C_{1/2}$  (mg/L) is the adsorbate concentration at half-saturation.

194 ○ Second model (**M2**): Double-layer model with similar receptor sites. This model is  
 195 appropriate to describe the double-layer adsorption process over the adsorbent surface  
 196 with identical binding sites. The formalism of the M2 model is presented by Eq. (4):

$$197 \quad Q_e = nN_M \frac{\left(\frac{C_e}{C_{1/2}}\right)^n + 2\left(\frac{C_e}{C_{1/2}}\right)^{2n}}{1 + \left(\frac{C_e}{C_{1/2}}\right)^n + \left(\frac{C_e}{C_{1/2}}\right)^{2n}} \quad (4)$$

198 ○ Third model (**M3**): Monolayer model with two different energies. This model is  
 199 established on the hypothesis that the adsorption process is a monolayer coverage over  
 200 two kinds of adsorbent active sites (with different energies) (Mobarak et al., 2019b,  
 201 2019a).

$$202 \quad Q_e = \frac{n_1 N_{1M}}{1+(C_1/C_e)^{n_1}} + \frac{n_2 N_{2M}}{1+(C_2/C_e)^{n_2}} \quad (5)$$

203 where  $C_1$  and  $C_2$  (mg/L) are the half-saturation concentrations for the first and the second  
 204 adsorption sites, respectively;  $N_{1M}$  and  $N_{2M}$  (mg/g) are the receptor site densities of the  
 205 first and the second kinds of active sites, respectively;  $n_1$  and  $n_2$  are the number of  
 206 adsorbed molecules by each binding site for the first and the second kinds of active sites,  
 207 respectively.

208 ○ Fourth model (**M4**): Double-layer model with two different energies. This model is  
 209 suitable to predict the double-layer adsorption on the two different types of adsorbent  
 210 active sites. The equation of the M4 model is given as:

$$211 \quad Q_e = nN_M \frac{\left(\frac{C}{C_1}\right)^n + 2\left(\frac{C}{C_2}\right)^{2n}}{1 + \left(\frac{C}{C_1}\right)^n + \left(\frac{C}{C_2}\right)^{2n}} \quad (6)$$

212 where  $C$  (mg/L) denotes the equilibrium concentration;  $N_M$  (mg/g) refers to receptor  
 213 sites density;  $C_1$  and  $C_2$ (mg/L) correspond to the concentrations at half-saturation for  
 214 the first and the second type of active sites, respectively.

215 ○ Fifth model (**M5**): Finite multi-layer model. This model suggests the occurrence of  
 216 multilayer adsorption process. The formalism of the M5 model is expressed as follows:

$$217 \quad Q_e = nN_M \frac{\left(\frac{C}{C_1}\right)^n \left(1 - (N_\ell + 1) \left[\frac{C}{C_2}\right]^{nN_\ell} + N_\ell \left[\frac{C}{C_2}\right]^{n(N_\ell + 1)}\right)}{\left(1 - \left[\frac{C}{C_2}\right]^n\right) \left(1 - \left[\frac{C}{C_2}\right]^n + \left[\frac{C}{C_1}\right]^n - \left[\frac{C}{C_1}\right]^n \left[\frac{C}{C_2}\right]^{nN_\ell}\right)} \quad (7)$$

218 where  $(N_\ell + 1)$  represents the number of adsorption layers;  $n$  refers to the number of  
 219 ions per adsorption site;  $N_M$  (mg/g) refers to receptor sites density;  $C_1$  and  $C_2$ (mg/L)

220 correspond to the concentrations at half-saturation for the first and the second type of  
 221 active sites, respectively.

222 The equations of the above-presented statistical physics models were derived from the  
 223 corresponding grand-canonical partition functions in the statistical physics (Mobarak et  
 224 al., 2019b, 2019a). These models were fitted to the experimental results of OG dye  
 225 adsorption onto PANI@Fe-ZSM-5 composite using Mathematica 11 program. The  
 226 appropriateness of the selected models was evaluated based on the correlation coefficient  
 227 ( $R^2$ ) and root mean squared error (RMSE) values (Mobarak et al., 2019b).

$$228 \quad RMSE = \sqrt{\frac{\sum_{i=1}^m (Q_{i\text{ cal}} - Q_{i\text{ exp}})^2}{p - q}} \quad (8)$$

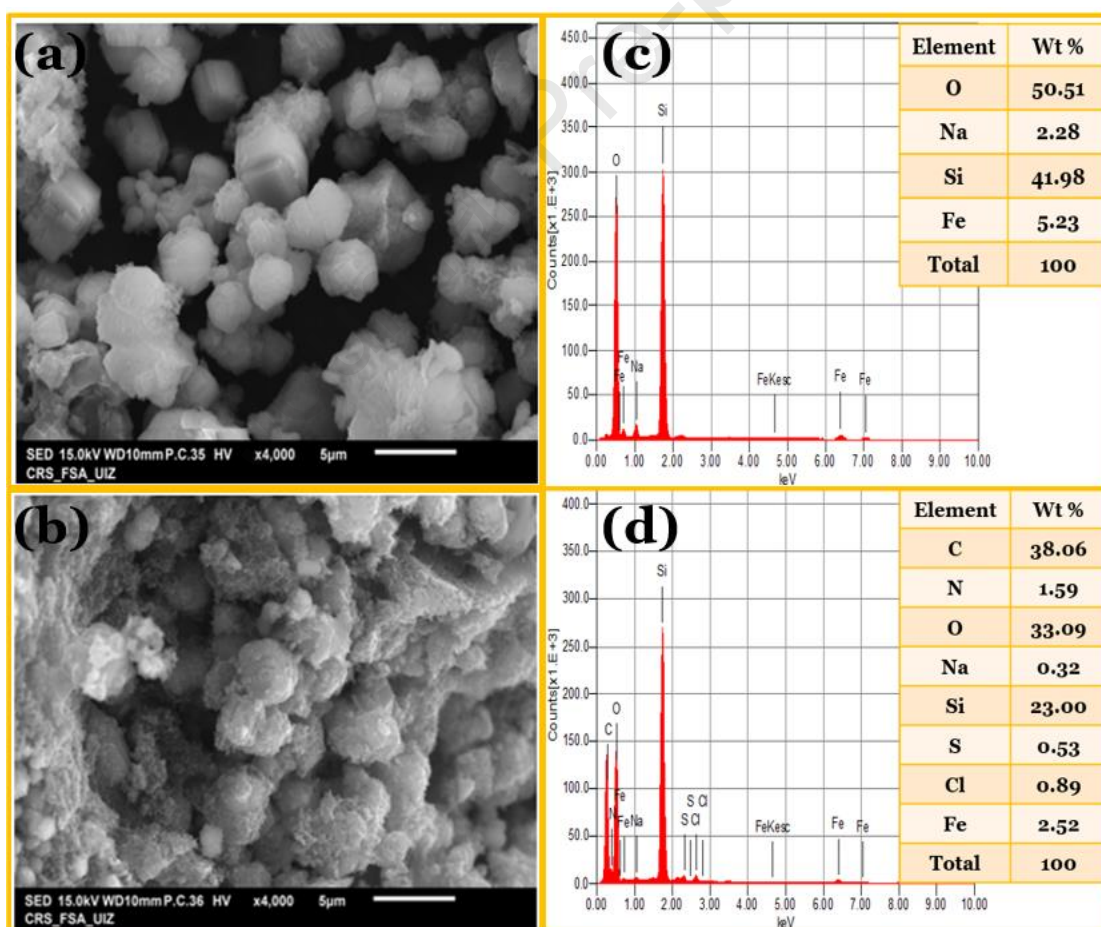
229 where  $p$  and  $q$  represent the number of actual data and adjustable parameters,  
 230 respectively.  $Q_{i\text{ cal}}$  and  $Q_{i\text{ exp}}$  denote the computed and the experimental OG dye uptake  
 231 capacities, respectively.

### 232 **3. Results and discussion**

#### 233 **3.1. Surface characterization and XRD analysis**

234 **Fig. 1** depicts the morphology and elemental analysis of Fe-ZSM-5 particles before and  
 235 after the polymerization of aniline. According to **Fig. 1(a)**, the SEM image of Fe-ZSM-5  
 236 features smooth agglomerated spheres with a size ranging from 1 to 5  $\mu\text{m}$ . **Fig. 1(b)**  
 237 confirms the deposition of polyaniline onto the Fe-ZSM-5 surface with a flake-like  
 238 structure. This surface morphology may constitute a good platform for the removal of  
 239 pollutants from aqueous media. In addition, the acquired textural information reveals  
 240 good adhesion of PANI onto the Fe-ZSM-5 surface. This may be due to interactions

241 (hydrogen bonds) between the amine groups of aniline and the hydroxyl groups (Si-OH)  
 242 of the Fe-ZSM-5 zeolite (Ba Mohammed et al., 2020). From **Figs. 1(c)** and **(d)**, the  
 243 elemental analysis of the Fe-ZSM-5 zeolite by EDS proves the existence of the following  
 244 elements: oxygen (50.51%), silicon (41.98%), iron (5.23%) and sodium (2.28%). This  
 245 result indicates that silicon oxide (SiO<sub>2</sub>) is the major phase of the Fe-ZSM-5 zeolite. After  
 246 the polymerization of aniline on the surface of Fe-ZSM-5 zeolite, the EDS spectrum shows  
 247 the appearance of carbon (38.06%). In addition, the EDS spectrum of PANI@Fe-ZSM-5  
 248 features other characteristic elements (N, Cl and S), which affirms that the surface of Fe-  
 249 ZSM-5 is well-coated by PANI.



250



251 **Fig. 1. (a)** SEM micrographs of Fe-ZSM-5, **(b)** PANI@Fe-ZSM-5 and **(c and d)** their  
252 respective EDS elemental spectra.

253 X-ray diffraction is an important technique used to identify the crystalline phases and  
254 structural properties of solid materials. Therefore, the as-prepared Fe-ZSM-5 zeolite and  
255 PANI@Fe-ZSM-5 composite were analyzed by this technique and the obtained XRD  
256 patterns are displayed in **Fig. 2(a)**. The synthesized Fe-ZSM-5 zeolite sample exhibited  
257 peaks at  $2\theta=7.95^\circ$ ,  $8.80^\circ$ ,  $23.10^\circ$ ,  $23.94^\circ$  and  $24.40^\circ$  associated with [0 1 1], [0 2 0], [0 5  
258 1], [0 3 3] and [3 1 3] planes, with corresponding d-spacing values of 1.11, 1.00, 0.38, 0.37  
259 and 0.36 nm, respectively. These values are in good agreement with the peaks of Fe-ZSM-  
260 5 zeolite (JCPDS no. 43-0321) with a well-resolved mordenite framework inverted (MFI)  
261 structure (Chemical formula:  $H_{0.32}Al_{0.32}Si_{95.68}O_{192}$ , Crystal system: Monoclinic and Space  
262 group: P21/n) (Narayanan et al., 2015). Moreover, the sharpness of the peaks of the  
263 diffraction peaks suggests that the as-prepared Fe-ZSM-5 sample has a more crystalline  
264 nature and no other peaks appeared, which discloses that the as-prepared Fe-ZSM-5  
265 material does not contain any impurities (Liu et al., 2011). Compared with bare Fe-ZSM-  
266 5 sample, the peak intensities of the [0 1 1] and [0 2 0] planes of PANI@Fe-ZSM-5  
267 composite were markedly decreased due to the PANI coating on the Fe-ZSM-5 surface,  
268 but their crystal framework structure was preserved. Moreover, no characteristic  
269 diffraction peaks of PANI were detected in PANI@ZSM-5 composite, because PANI was  
270 in amorphous phase. Furthermore, the absence of impurity phases in the XRD curves  
271 indicates the successful synthesis of PANI@Fe-ZSM-5 composite.

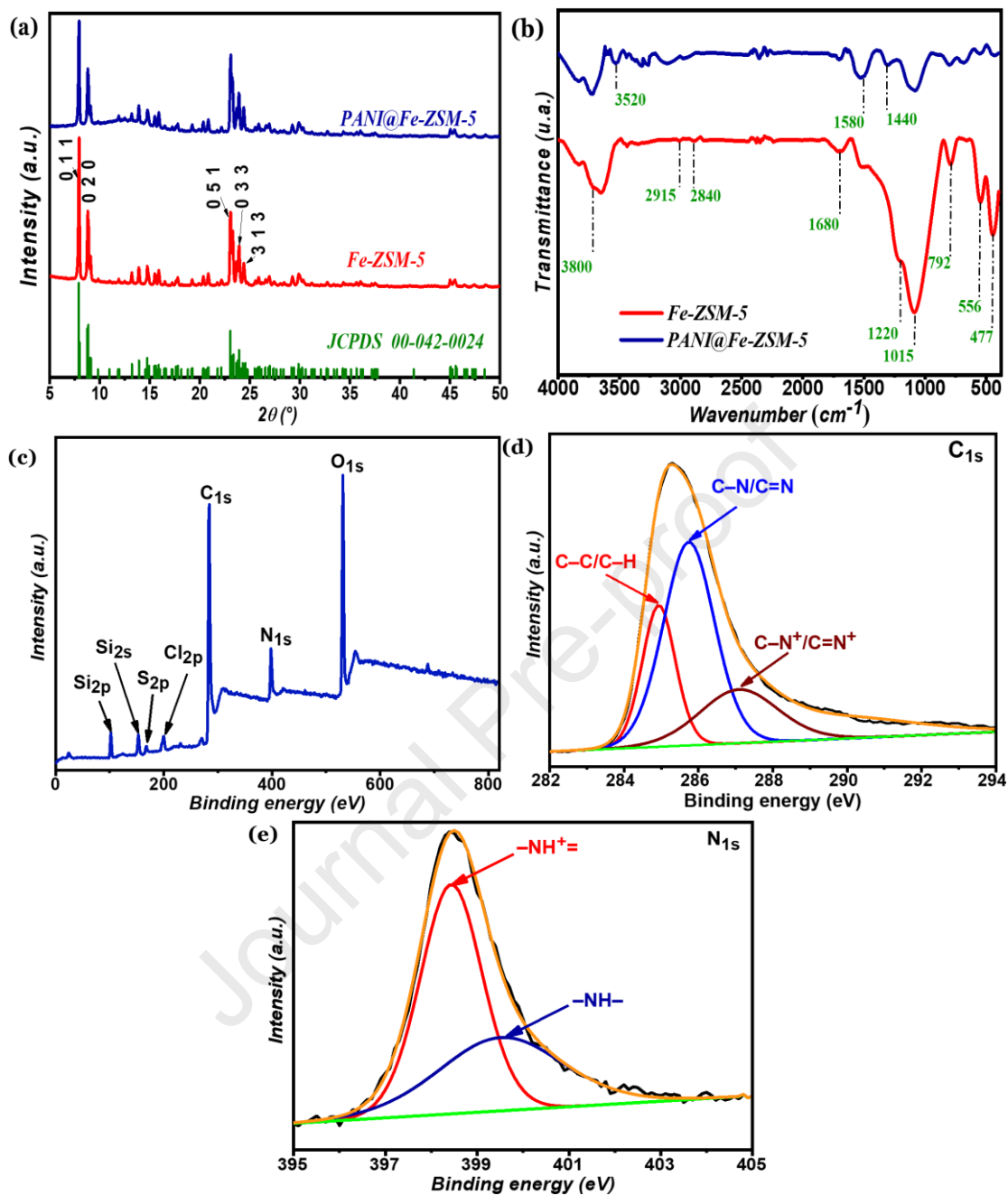
### 272 **3.2. FTIR data analysis**

273 The FTIR spectrum of Fe-ZSM-5 and PANI@Fe-ZSM-5 are depicted in **Fig. 2(b)**. The  
274 FTIR spectrum of Fe-ZSM-5 exhibits a characteristic peak at about  $3854\text{ cm}^{-1}$  ascribed to  
275 the silanol groups of Si-OH. The absorption bands at  $2915$  and  $2840\text{ cm}^{-1}$  can be assigned  
276 to the residual methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) vibrations of tetrapropylammonium  
277 bromide precursor (Kachangoon et al., 2020). The peak located at  $1631\text{ cm}^{-1}$  is ascribed  
278 to the stretching bending of adsorbed water molecules. The symmetric stretching of  
279 external linkages of the tetrahedron appears at around  $792\text{ cm}^{-1}$  (Liu et al., 2011). Also,  
280 the spectrum comprises a peak at  $556\text{ cm}^{-1}$  assigned to the stretching vibrations of Fe-O  
281 of  $\text{Fe}_2\text{O}_3$  (Suresh et al., 2014). The peaks at  $477$  and  $1220\text{ cm}^{-1}$  are attributed to the Si-O  
282 bending vibrations of  $\text{SiO}_4$  internal tetrahedral (Doula, 2007), (Niu et al., 2017). The FTIR  
283 spectrum of PANI@Fe-ZSM-5 reveals the appearance of a new peak at  $3520\text{ cm}^{-1}$  assigned  
284 to the N-H stretching vibration, indicating the existence of amine groups. Besides, the  
285 vibration bands at  $1580$  and  $1440\text{ cm}^{-1}$  are ascribed to the stretching vibration C=C in  
286 quinoid and benzenoid structure of doped PANI, respectively (Xu et al., 2014). These  
287 findings confirm that the PANI was well-incorporated onto the surface of Fe-ZSM-5  
288 particles.

### 289 **3.3. XPS analysis**

290 XPS analysis was performed to assess the chemical composition and chemical state of the  
291 PANI@Fe-ZSM5 surface. The full survey XPS survey of PANI@Fe-ZSM5 composite is  
292 depicted in **Fig. 2(c)**. The spectrum revealed the presence of  $\text{O}_{1s}$  ( $531.5\text{ eV}$ ),  $\text{N}_{1s}$  ( $397.9\text{ eV}$ )  
293 and  $\text{C}_{1s}$  ( $283.6\text{ eV}$ ) as the main components of the PANI@Fe-ZSM5 surface (Abdel Hamid  
294 et al., 2019). Besides, the presence of three weak peaks confirmed the occurrence of silicon  
295 ( $\text{Si}_{2p}$  and  $\text{Si}_{2s}$  at  $101.9$  and  $152.6\text{ eV}$ , respectively), sulfur ( $\text{S}_{2p}$  at  $168.1\text{ eV}$ ) and chlorine

296 (Cl<sub>2p</sub> at 199.4 eV) elements on the PANI@Fe-ZSM-5 surface (Abdel Hamid et al., 2019;  
297 Ravelo-Acuña et al., 2019; Zhang et al., 2016). The Si element is related to the silica in the  
298 ZSM-5 zeolite. The other elements (e.g., Fe and Al) of Fe-ZSM-5 zeolite were not detected,  
299 which eventually due to the formation of thick PANI layer on the surface of Fe-ZSM-5  
300 zeolite (penetration depth of the X-ray beam does not exceed 10 nm). The Cl and S  
301 elements are indicative of the existence of chloride anion doping (Cl<sup>-</sup>) and oxidizing agent  
302 (sodium persulfate) on the PANI@Fe-ZSM-5 surface. From **Fig. 2(d)**, the C<sub>1s</sub> high  
303 resolution spectrum was fitted with three peaks located at 284.9 (C–C/C–H), 285.7 (C–  
304 N/C=N) and 287.1 eV (C–N<sup>+</sup>/C=N<sup>+</sup>) (Chan et al., 1992; Wang et al., 2015). The positively  
305 charged N-containing functional groups indicated the doping of PANI chains by sulfate  
306 and chloride ions generated from the oxidant and HCl acid (Wang et al., 2005). **Fig. 2(e)**  
307 shows that the N<sub>1s</sub> spectrum which can be deconvoluted into two peaks at 398.4 and 399.6  
308 eV ascribed to amine (–NH–) and doped quinonoid imine (–NH<sup>+=</sup>) of benzenoid ring,  
309 respectively (Bhaumik et al., 2021). The XPS results demonstrated that the PANI  
310 Emeraldine salt (doped form) was successfully coated on the Fe-ZSM-5 zeolite.



311

312 **Fig.2. (a)** XRD patterns of Fe-ZSM-5 and PANI@Fe-ZSM-5 composite; **(b)** FTIR313 spectra of Fe-ZSM-5 zeolite and PANI@Fe-ZSM-5 composite; **(c)** XPS wide scan314 spectrum; **(d)**  $\text{C}_{1s}$  and **(e)**  $\text{N}_{1s}$  core level spectra of the PANI@Fe-ZSM-5 composite.

315

### 316 **3.4. Adsorption study**

#### 317 **3.4.1. Effects of adsorbent dosage and pH**

318 The influence of sorbent dosage on the OG dye adsorption was investigated in the 0.2 to  
319 2.0 g/L concentration range. **Fig. 3(a)** displays the removal efficiency and uptake  
320 capacity of OG onto PANI@Fe-ZSM-5 at different adsorbent doses. The adsorption  
321 percentage was increased up to 96.37 % with the increase of PANI@Fe-ZSM-5 dose from  
322 0.2 to 0.5 g/L. This might be due to the increment in the number of adsorbate binding  
323 sites available for OG dye removing (Hsini et al., 2020). Increasing the PANI@Fe-ZSM-5  
324 dosage beyond 0.5 g/L did not affect the OG dye adsorption efficiency. This trend may be  
325 due to the exhaustion of OG dye molecules. Besides, the uptake capacity was decreased,  
326 owing to the formation of adsorbent particles aggregates, which could minimize the  
327 availability of surface sites for OG dye adsorption (Hsini et al., 2021d; Tu et al., 2020).

328 It is widely-known that the solution pH is a key operating condition in adsorption  
329 processes (Hsini et al., 2021a). The surface charge of the PANI@Fe-ZSM-5 composite was  
330 investigated as a function of pH (inset of **Fig. 3(b)**). The PZC value of PANI@Fe-ZSM-5  
331 composite was found to be 3.75. This means that the as-prepared PANI@Fe-ZSM-5  
332 material surface is positively charged at pH below 3.75, while the surface becomes  
333 negatively charged at pH above 3.75. The influence of the solution pH on the adsorption  
334 process over the pH range 2–12 is displayed in **Fig. 3(b)**. As a result, the maximum  
335 removal percentage of OG dye was achieved at low pH values. That could be elucidated by  
336 the protonation of adsorbent sites (protonated silanol and amine groups), which results  
337 in the increment of the electrostatic interactions between anionic OG dye and positively  
338 charged PANI@Fe-ZSM-5 surface (Ba Mohammed et al., 2020). Whilst, at higher pH, the

339 OG dye adsorption efficiency decreased due to a decline of the number of positively  
340 charged sites. Therefore, we can conclude that the adsorption of OG dye on the as-  
341 prepared adsorbent surface is executed through electrostatic interactions (Yeamin et al.,  
342 2021), as well as the involvement of  $\pi$ - $\pi$  ones (Nasar and Mashkoo, 2019). Besides, under  
343 alkaline conditions, the competitive adsorption of  $\text{OH}^-$  ions with OG anions could be  
344 another reason to explain the observed downward trend of OG dye removal efficiency. In  
345 the next adsorption experiments, the pH value of OG solutions was maintained at 6.0 to  
346 minimize the costs related to the pH adjustment. It is worth highlighting the pivotal role  
347 of electrostatic and  $\pi$ - $\pi$  interactions in the OG dye adsorption mechanism. Based on the  
348 above discussion, a binding mechanism of OG dye on the PANI@Fe-ZSM-5 surface is  
349 proposed in **Fig. 6(d)**. To further confirm the adsorption of OG dye, the adsorbent surface  
350 after adsorption was analyzed by the FTIR technique. The FTIR spectra of PANI@Fe-  
351 ZSM-5 before and after OG dye removal are depicted in **Fig. 6(c)**. As a result, the FTIR  
352 data showed that there is no obvious shift in the bands of the functional groups on the  
353 PANI@Fe-ZSM-5 surface after adsorption, indicating that the molecular structure of the  
354 PANI@Fe-ZSM-5 composite remained unaltered after OG dye removal. Furthermore,  
355 no new peak was observed after OG adsorption, suggesting that there is no chemical  
356 interaction of OG molecules with PANI@Fe-ZSM-5. Therefore, it can be concluded that  
357 the binding of OG dye molecule on the PANI@Fe-ZSM-5 surface sites takes place via  
358 physical interactions (e.g., electrostatic forces and  $\pi$ - $\pi$  interactions). In light of the above  
359 presented discussion, a graphical illustration of the proposed adsorption mechanism is  
360 presented in **Fig. 6(d)**.

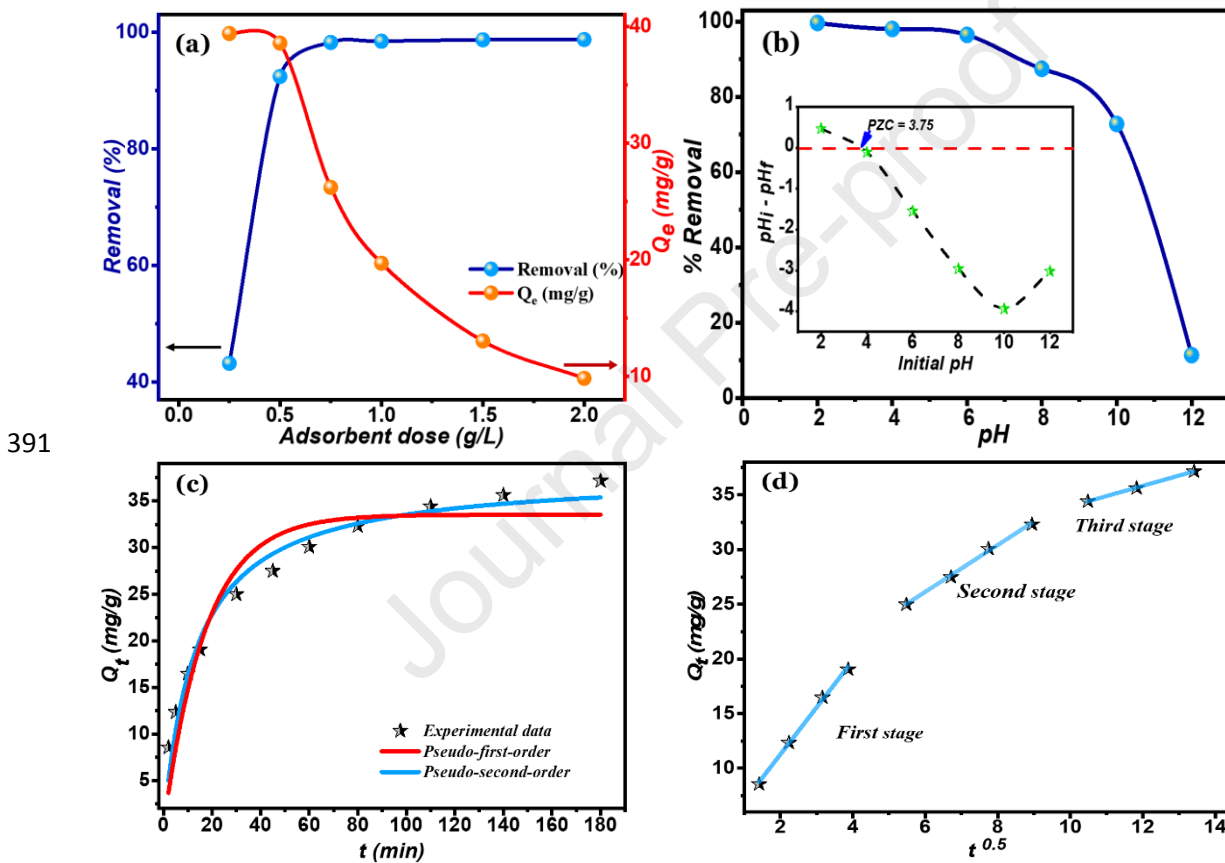
361

### 362 3.4.2. Adsorption kinetics

363 The result of adsorbent/adsorbate contact time on the removal of OG dye by PANI@Fe-  
364 ZSM-5 composite surface was investigated by plotting the adsorption capacity of OG dye  
365 versus contact time (from 2 to 180 min). The adsorbent dosage of 0.5 g/L was used in 100  
366 mL of OG solution with 20 mg/L initial concentration at pH 6 and 25 °C. From **Fig. 3(c)**,  
367 it can be seen that upon increasing the contact time, the OG dye uptake was improved. In  
368 the first 60 min, the increase was rapid then it became slow, and the equilibrium was  
369 reached after 120 min. Thus, the removal ability of PANI@Fe-ZSM-5 composite was  
370 related to the binding sites availability on the PANI@Fe-ZSM-5 surface for OG textile dye  
371 removal (Tu et al., 2020). The pseudo-first-order, pseudo-second-order, and intra-  
372 particle diffusion kinetic models were used to fit the kinetic data to evaluate the kinetic  
373 mechanism of OG adsorption on the PANI@Fe-ZSM-5 composite (Abbasi, 2017). The  
374 nonlinear equations and the corresponding fitting parameters of pseudo-first-order and  
375 pseudo-second-order kinetic models are summated in **Table S1** and **Fig. 3(c)**. As shown  
376 in **Fig. 3(c)**, the pseudo-second-order model with  $R^2$  of 0.97 is the model which had the  
377 highest correlation coefficient than the pseudo-first-order model (0.91). Furthermore, the  
378 adsorption capacity, calculated from pseudo-second-order model (37.99 mg/g), was  
379 found to be close to the experimentally-determined one (37.15 mg/g), confirming that the  
380 OG dye adsorption process was better described by this kinetic model.

381 In order to investigate the mass transfer mechanism that occurred during the adsorption  
382 process, the intraparticle diffusion model was applied to the actual removal data (Tang  
383 and Zhang, 2016). The fitting parameters are listed in **Table S1**. **Fig. 3(d)** illustrated that  
384 the removal of OG dye by the PANI@Fe-ZSM-5 composite consisted in three successive

385 stages. The first one was ascribed to the diffusion of OG dye molecules from the aqueous  
 386 phase to the external surface sites of as-prepared composite. The second stage implicates  
 387 the intra-particle diffusion as rate-controlling step. In the last stage the intraparticle  
 388 diffusion rate decreased, because of the extremely low concentration of OG (Tang and  
 389 Zhang, 2016). Besides, these results were supported by the reduction of rate constant  
 390 values when going from the first stage to the last one.



398 **Fig. 3. (a)** Effect of PANI@Fe-ZSM-5 dose on the OG dye adsorption efficiency  
 399 (Conditions: equilibrium time = 180 min; OG dye concentration = 20 mg/L;  
 400 temperature = 25 °C); **(b)** Adsorption efficiency of the OG dye onto PANI@Fe-ZSM-5 at  
 401 different pH values (inset: PZC determination of the PANI@Fe-ZSM-5 composite), **(c)**  
 402 Pseudo-first-order and pseudo-second-order kinetics models; **(d)** intraparticle diffusion  
 403 model.



404

### 405 **3.5. Advanced statistical physics interpretation**

406 The fitting of the considered statistical physics models to the experimental data for OG  
407 dye removal by the PANI@Fe-ZSM-5 composite was evaluated based on the  
408 determination of  $R^2$  coefficient and RMSE values. From **Table S2**, it is clear that the **M3**  
409 model (monolayer model with two different energies) demonstrated good correlation with  
410 OG dye adsorption data (high  $R^2$  values and low RMSE values) for all tested temperatures  
411 (**Fig. 4(a)**). Therefore, the **M3** model was chosen as the best fitting statistical physics  
412 model to elucidate the macroscopic and microscopic properties of the OG dye removal  
413 process by the PANI@Fe-ZSM-5 composite.

#### 414 **3.5.1. Statistical physics parameters**

415 To shed light on the orientation of OG dye molecules on the PANI@Fe-ZSM-5 surface, the  
416 values of the stoichiometric coefficient ( $n$ ) were calculated at different temperatures (**Fig.**  
417 **4(b) and Table S3**). On the one hand,  $n_1$  values (for the first type of active sites) are less  
418 than 1, indicating that the OG dye molecules adsorbed parallelly on the first type of active  
419 surface sites of PANI@Fe-ZSM-5 composite. In addition, each receptor site (first type) of  
420 PANI@Fe-ZSM-5 composite adsorbs more than one OG dye molecule, suggesting a multi-  
421 docking adsorption mechanism (Sellaoui et al., 2015). This adsorption behavior becomes  
422 more pronounced with increasing temperature ( $n_1$  values decreased). On the other hand,  
423 the  $n_2$  values (for the second type of active sites) are superior to unity, revealing that the  
424 OG dye molecules adsorbed perpendicularly *via* a multimolecular mechanism on the  
425 second type of active sites of PANI@Fe-ZSM-5 composite (Laabd et al., 2022). Moreover,  
426 it is worth noticing that the  $n_2$  values increased with the increase of temperature,

427 highlighting that the thermal agitation results in the decrease in the aggregation of the OG  
428 dye molecules in the liquid phase (Li et al., 2019).

429 The density of active sites ( $N_M$ ) is a crucial parameter governing the removal performance.

430 The temperature dependence of  $N_M$  parameter for OG dye removal by PANI@Fe-ZSM-5

431 composite surface is presented in **Fig. 4(c)**. It can be observed that the  $N_{1M}$  (for the first

432 type of active sites) and  $N_{2M}$  (for the second type of active sites) parameters follow an

433 inverse trend compared to  $n_1$  and  $n_2$  stoichiometric coefficients, respectively. This result

434 could be attributed to steric-hindrance effect of OG dye molecules during the adsorption

435 process onto the PANI@Fe-ZSM-5 surface (Sellaoui et al., 2017b). Indeed, as the number

436 of adsorbed OG dye molecules per active site ( $n$ ) decreases, the number of available

437 adsorption sites increases, thus leading to an increase in the density of active sites ( $N_M$ ),

438 and vice versa.

439 The saturation uptake capacity ( $Q_{sat}$  in mg/g) of the PANI@Fe-ZSM-5 composite for OG

440 dye adsorption depends on the stoichiometric coefficient ( $n$ ) and density of active sites

441 ( $Q_{sat} = nN_M$ ). From **Fig. 4(d)**, it is convenient to mention that the adsorbed amounts ( $Q_1$

442 and  $Q_2$ ) increased with raising the temperature (endothermic process), confirming that

443 the total OG dye adsorption capacity ( $Q_{sat}$ ) is predominantly affected by the density of

444 active sites ( $N_M$ ) rather than the stoichiometric coefficient ( $n$ ).

445 From an energetic point of view, the removal of OG dye by the PANI@Fe-ZSM-5

446 composite was assessed by calculating the adsorption energies  $E_1$  and  $E_2$  for the first and

447 second types of active sites, respectively. The values of  $E_1$  and  $E_2$  can be computed by the

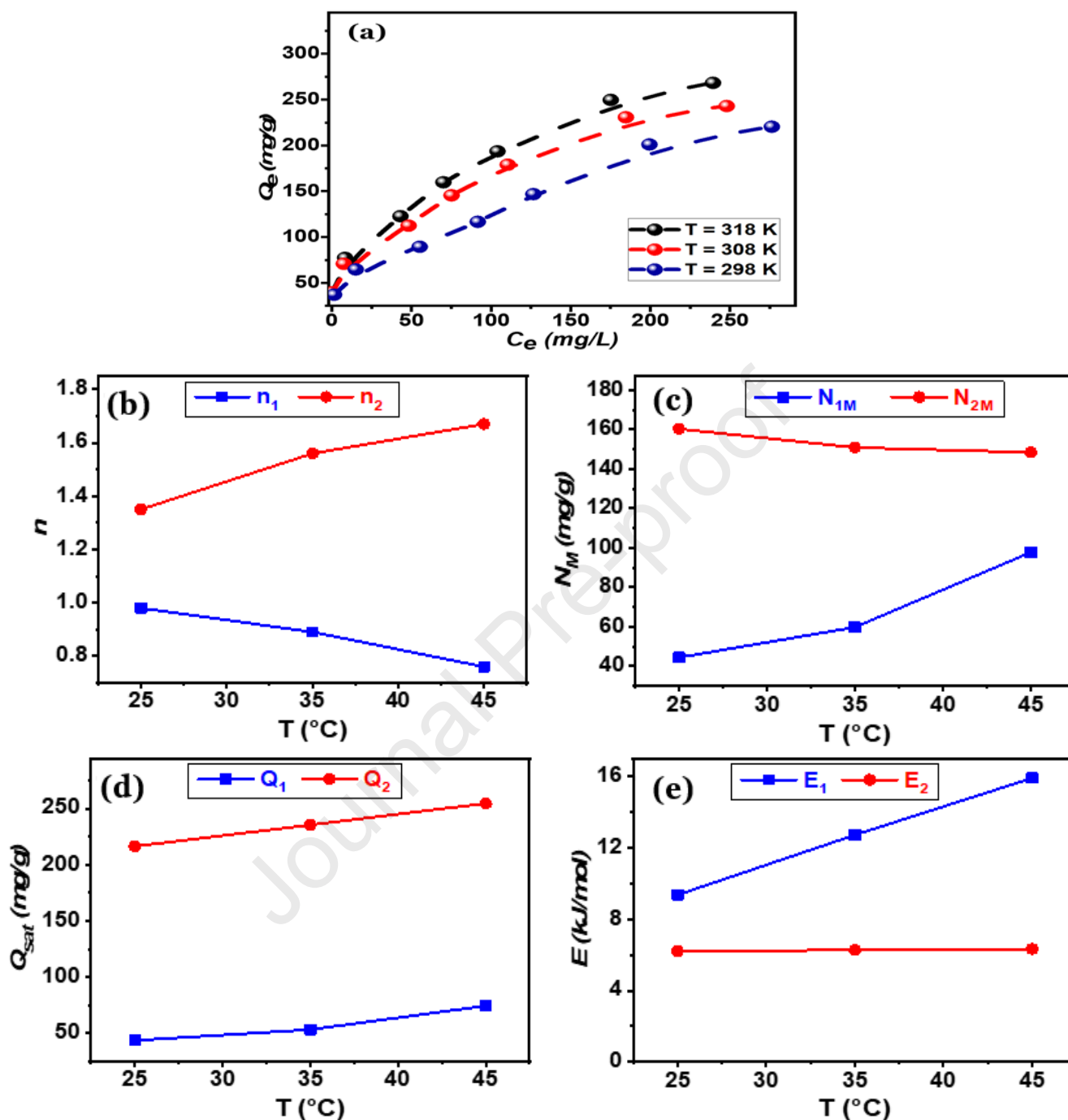
448 following Eqs.:

$$449 \quad E_1 = RT \ln \left( \frac{C_s}{C_1} \right) \quad (9)$$

$$450 \quad E_2 = RT \ln \left( \frac{C_s}{C_2} \right) \quad (10)$$

451 where  $C_s$  (mg/L) is the aqueous solubility of OG dye.  $C_1$  and  $C_2$  represent the half-  
452 saturation concentrations (mg/L) for the first and the second types of adsorption sites,  
453 respectively.  $R$  (8.314 J/mol K) is the universal gas constant and  $T$  is the temperature (K).

454 **Fig. 4(e)** shows the influence of temperature on the removal energy. It is noteworthy  
455 that the values of adsorption energies are positive and increased with temperature,  
456 proving that the OG dye removal by the PANI@Fe-ZSM-5 composite is an endothermic  
457 process. Therefore, the adsorption method is favorable at higher temperatures, which  
458 is in concordance with the saturation adsorption capacity. Moreover, the figure shows  
459 that  $E_1$  is higher than  $E_2$ , which confirm that PANI@Fe-ZSM-5 has a higher  
460 interaction with OG dye. From the calculated values of adsorption energies, we deduce  
461 that the adsorption was a physical process since these values are  $<40$  kJ/mol (Seliem  
462 and Mobarak, 2019). The adsorption ~~formed bonds could be a~~ hydrogen bonds or Van  
463 der Waals or dipole-dipole interactions (Wjihi et al., 2020, 2017), reinforcing that the  
464 OG dye adsorption is physisorption in nature (Sellaoui et al., 2016).



465

466 **Fig. 4. (a)** Fitting of actual equilibrium data of OG dye removal by the PANI@Fe-ZSM-5  
 467 composite to the M3 model (best fitted model); **(b)** The stoichiometric coefficient; **(c)**  
 468 the density of active sites; **(d)** the saturation uptake capacity and **(e)** the adsorption  
 469 energy for OG dye removal by the PANI@Fe-ZSM-5 composite at different  
 470 temperatures.

471 **3.5.2. Thermodynamic functions**

472 The thermodynamic functions (entropy, free enthalpy and internal energy) related to the  
 473 OG dye adsorption on the PANI@Fe-ZSM-5 composite were calculated using the  
 474 monolayer **layer** model with the different energy sites (**M3**). The entropy function is of  
 475 prime importance to predict the randomness of OG dye molecules at the solution-  
 476 adsorbent interface. This thermodynamic function was calculated according to the  
 477 following Eq. (Seliem and Mobarak, 2019):

$$478 \frac{s}{k_B} = \frac{-Q_{sat.1} \left[ \frac{c}{c_1} \right]^{n_1} \ln \left[ \frac{c}{c_1} \right] + Q_{sat.2} \left[ \frac{c}{c_2} \right]^{n_2} \ln \left[ \frac{c}{c_2} \right] + \left[ \frac{c}{c_1} \right]^{n_1} \left[ \frac{c}{c_2} \right]^{n_2} (Q_{sat.1} \ln \left[ \frac{c}{c_1} \right] + Q_{sat.2} \ln \left[ \frac{c}{c_2} \right])}{\left( 1 + \left[ \frac{c}{c_1} \right]^{n_1} \right) \left( 1 + \left[ \frac{c}{c_2} \right]^{n_2} \right) + \ln \left( \left( 1 + \left[ \frac{c}{c_1} \right]^{n_1} \right)^{N_{1M}} \left( 1 + \left[ \frac{c}{c_2} \right]^{n_2} \right)^{N_{2M}} \right)} \quad (11)$$

479 To evaluate the spontaneity of the OG dye adsorption system, the free enthalpy function  
 480 is computed as follows (Ayachi et al., 2019):

$$481 \frac{G}{k_B T} = \ln \left[ \frac{\mu}{Z_{tr}} \right] \left( \frac{Q_{sat.1}}{1 + \left[ \frac{c_1}{c} \right]^{n_1}} + \frac{Q_{sat.2}}{1 + \left[ \frac{c_2}{c} \right]^{n_2}} \right) \quad (12)$$

482 The internal energy ( $E_{int}$ ) represents the sum of energies in the adsorption system. This  
 483 thermodynamic function is written as follows (Seliem and Mobarak, 2019):

$$484 \frac{E_{int}}{k_B T} = \frac{-N_{1M} \left[ \frac{c}{c_1} \right]^{n_1} (n_1 \ln \left[ \frac{c}{c_1} \right] - \mu) + N_{2M} \left[ \frac{c}{c_2} \right]^{n_2} (n_2 \ln \left[ \frac{c}{c_2} \right] - \mu) + \left[ \frac{c}{c_1} \right]^{n_1} \left[ \frac{c}{c_2} \right]^{n_2} (N_{1M} (n_1 \ln \left[ \frac{c}{c_1} \right] - \mu) + N_{2M} (n_2 \ln \left[ \frac{c}{c_2} \right] - \mu))}{\left( 1 + \left[ \frac{c}{c_1} \right]^{n_1} \right) \left( 1 + \left[ \frac{c}{c_2} \right]^{n_2} \right)} \quad (13)$$

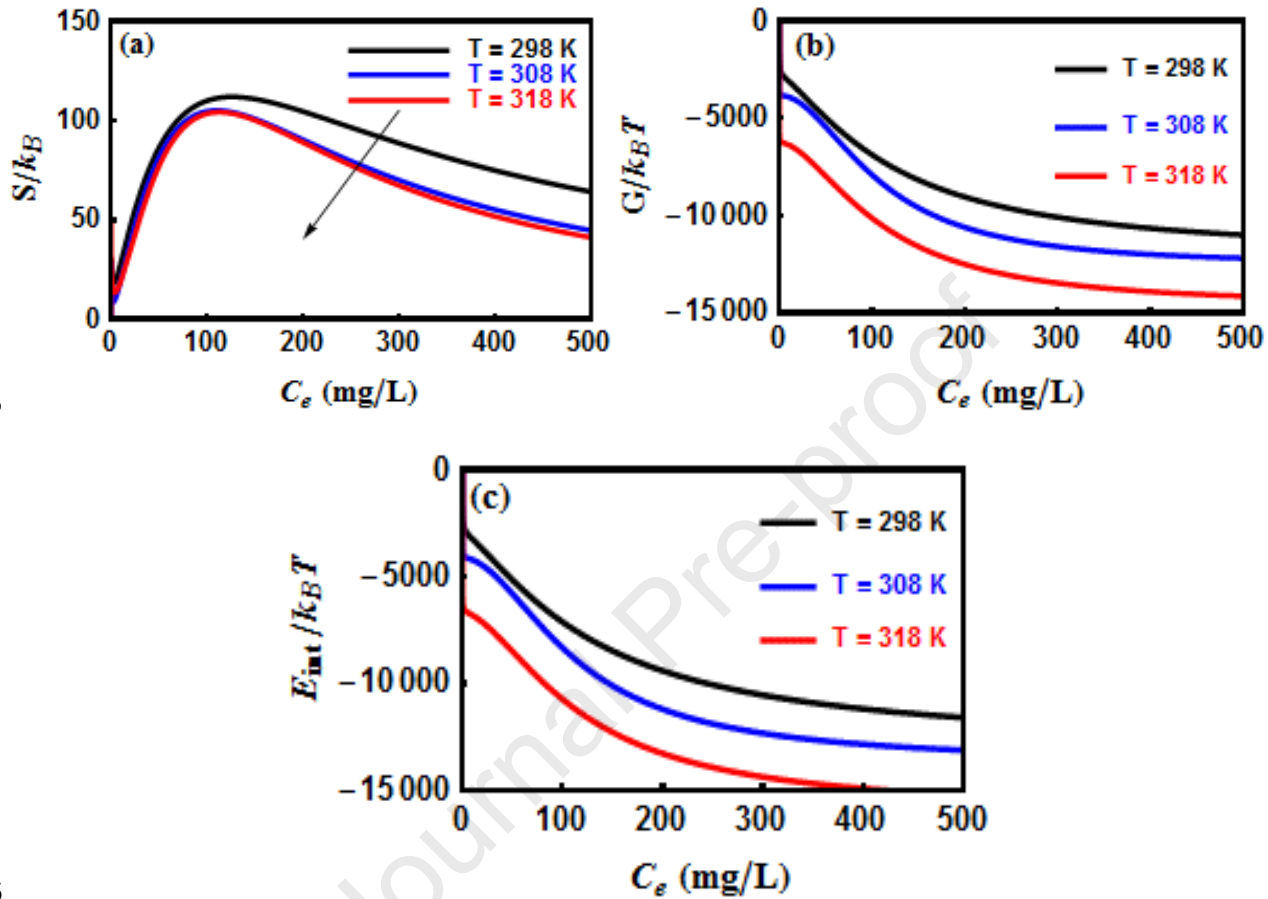
485 In Eqs. (11-13),  $k_B$ ,  $\mu$  and  $Z_{tr}$  are the Boltzmann constant, chemical potential and  
 486 translation partition function, respectively.

487 The evolution of the entropy function during the OG dye adsorption versus equilibrium  
 488 OG dye concentration at different temperatures (298, 308 and 318 K) is displayed in **Fig.**

489 **5(a)**. From this figure, the entropy function exhibited similar trend for all studied  
490 temperatures. In addition, we can see that, with increasing the equilibrium OG dye  
491 concentration, the entropy of OG dye removal system increased until a maximum at the  
492 half-saturation concentration and then decreased. At lower OG dye concentrations, the  
493 OG molecules possessed high probability to select an active site on the PANI@Fe-ZSM-5  
494 surface, resulting in an increase of disorder at the solution-adsorbent interface. At higher  
495 OG dye concentrations, the PANI@Fe-ZSM-5 surface tended to the saturation and the  
496 probability of OG molecules to find a vacant adsorption site was significantly decreased.  
497 Therefore, the entropy shifted towards lower values (decrease of disorder).

498 **Fig. 5(b)** represents the evolution of the free enthalpy as a function of OG dye  
499 concentration. As a result, the negative values of the free enthalpy function revealed that  
500 the OG adsorption on the PANI@Fe-ZSM-5 composite is a spontaneous process for all  
501 investigated temperatures (Sellaoui et al., 2016). Besides, it can be seen that the free  
502 enthalpy decreases with increasing temperature and OG dye concentration. Thus, we can  
503 conclude that the OG dye adsorption process is more favorable at higher temperatures  
504 (endothermic process) and higher OG dye concentrations (increase in the concentration  
505 gradient). **Fig. 5(c)** displays the variation of internal energy versus equilibrium OG  
506 concentration at different temperatures. The negative values of the internal energy during  
507 the OG dye adsorption on the PANI@Fe-ZSM-5 composite confirms its spontaneous  
508 nature (Sellaoui et al., 2017a), reflecting that the OG dye molecules exhibited good binding  
509 affinity with the PANI@Fe-ZSM-5 surface. Moreover, the internal energy tremendously  
510 decreases with OG concentration at low concentration range, which indicates that the OG  
511 dye molecules target the most active sites on the PANI@Fe-ZSM-5 surface. When the OG  
512 dye concentration is increased, the availability of PANI@Fe-ZSM-5 surface sites decreases

513 and the OG dye molecules interact with the less active sites, resulting in a slight  
 514 diminution in the internal energy (Khalfaoui et al., 2015).



515

516

517 **Fig. 5.** Thermodynamic functions: **(a)** entropy; **(b)** free enthalpy and **(c)** internal  
 518 energy for OG dye adsorption on the PANI@Fe-ZSM-5 composite.

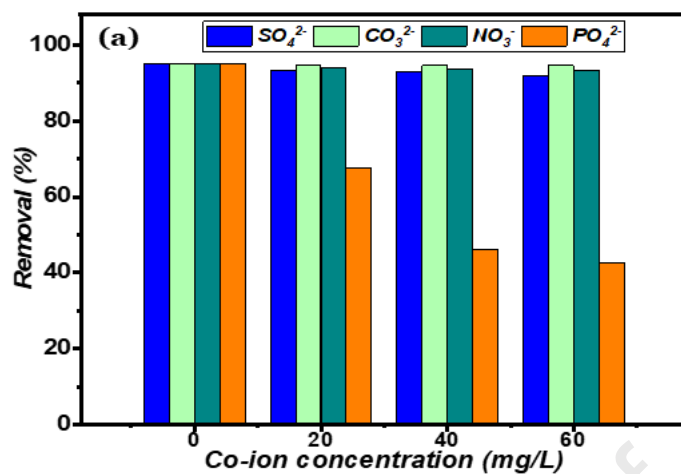
### 519 3.6. Effect of co-existing ions and Regeneration

520 It has been known that the wastewaters are polluted not only by dyes, but also by other  
 521 organic and inorganic pollutants (Ansari et al., 2017). Thus, it is necessary to assess the  
 522 influence of coexisting ions. For this goal, a series of adsorption tests were carried out by  
 523 keeping the concentration of OG dye constant at 20 mg/L while varying the concentration  
 524 of coexisting ions ( $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ ) from 20 to 60 mg/L. The operating

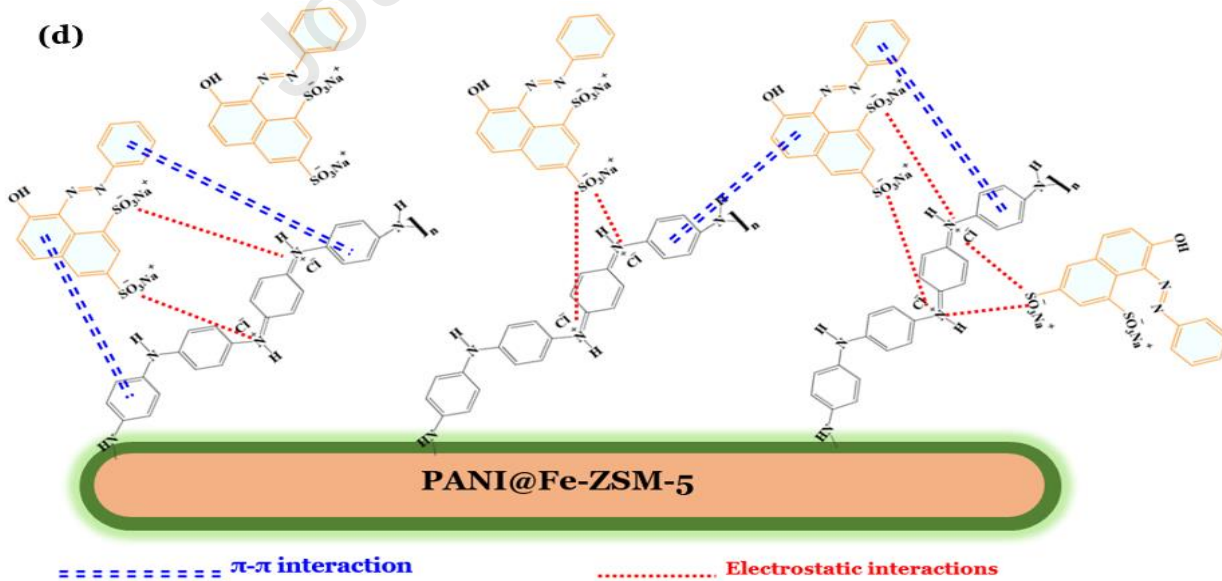
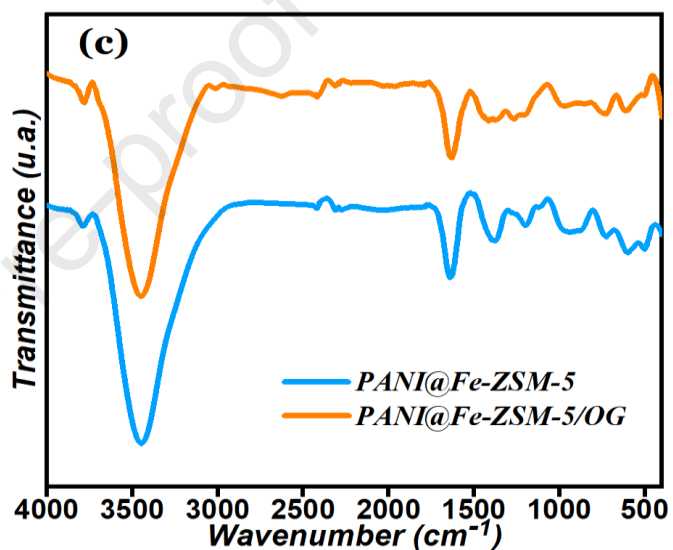
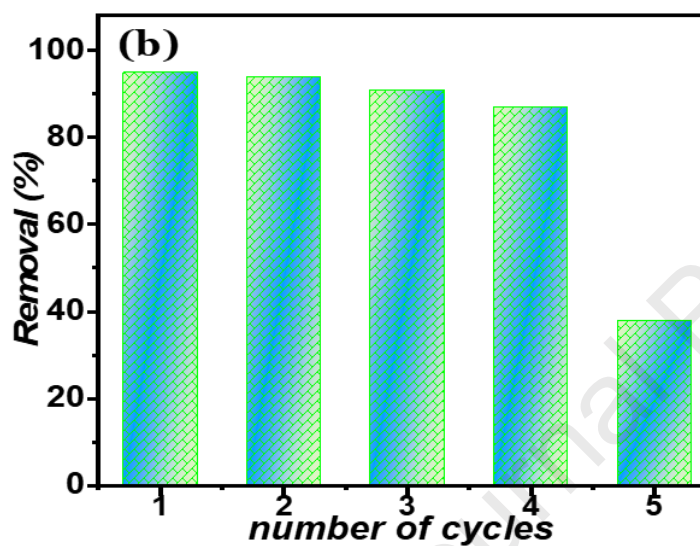
525 conditions were pH=6.0, adsorbent dose=0.5 g/L, contact time= 3 h and T = 25 °C. **Fig.**  
526 **6(a)** shows the effect of coexisting ions on the performance of OG dye removal by  
527 PANI@Fe-ZSM-5 composite (Laabd et al., 2021). The presence of  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$   
528 ions did not influence the OG removal and the adsorption capacity remained at 37.15  
529 mg/g. In contrast, the presence of  $\text{PO}_4^{3-}$  ions had a considerable effect on the performance  
530 of OG adsorption. The increase of concentration of  $\text{PO}_4^{2-}$  resulted in a decrease of the  
531 amount of OG adsorbed until 17.03 mg/g. This adsorption behavior could be ascribed to  
532 the affinity of PANI@Fe-ZSM-5 surface for  $\text{PO}_4^{3-}$  ions, and subsequently the competition  
533 between OG dye and  $\text{PO}_4^{2-}$  anions significantly inhibited the OG adsorption (Banerjee et  
534 al., 2019).

535 For regeneration and reuse of PANI@Fe-ZSM-5, NaOH (0.5 M) was used as a  
536 regenerating agent. Further, it was reported in the literature that NaOH is the best suitable  
537 agent for desorbing OG dye from the adsorbent surfaces (Brini et al., 2021a; Hsini et al.,  
538 2021c; Xu et al., 2020). In this study, the recyclability of PANI@Fe-ZSM-5 composite for  
539 OG dye removal efficiency was evaluated up to five adsorption-desorption cycles. **Fig.**  
540 **6(b)** depicts that the adsorption efficiency of OG dye from aqueous solutions was still  
541 above 86% in the first four desorption/adsorption cycles. However, in the fifth  
542 regeneration cycle, the OG dye removal performance (38%) decreases significantly owing  
543 to the possible accumulation of OG molecules on the PANI@Fe-ZSM-5 surface. Overall,  
544 the experimental results revealed that the PANI@Fe-ZSM-5 composite owns excellent  
545 reusability and could be reused as an efficient and inexpensive adsorbent to eliminate of  
546 OG dye from aqueous solutions.





547



548

549 **Fig. 6. (a)** Effect of coexisting ions on the removal of OG dye by PANI@Fe-ZSM-5:  
550 adsorbent dose = 0.5 g/L; pH= 6.0; 20 mg/L OG dye concentration; T=25°C; **(b)**  
551 Adsorption efficiency of OG dye by PANI@Fe-ZSM-5 composite for 5 regeneration  
552 cycles; **(c)** FT-IR spectral data of PANI@Fe-ZSM-5 before and after adsorption of OG  
553 dye, and **(d)** Schematic **presentation** of the proposed adsorption mechanism.

### 554 **3.7. Comparison with other adsorbents**

555 To evaluate the adsorption performance of PANI@Fe-ZSM-5, it is important to figure out  
556 its position compared with other adsorbents. From a literature survey, many studies  
557 reported the OG dye adsorption from water using different adsorbent materials. As shown  
558 in **Table 1**, it is evident that the PANI@Fe-ZSM-5 composite demonstrated an excellent  
559 maximum uptake capacity (217 mg/g) for OG dye removal compared with reported  
560 adsorbents. Thus, we conclude that the as-synthesized adsorbent may be a useful material  
561 for efficient OG dye removal. Finally, the as-developed PANI@Fe-ZSM-5 hybrid material  
562 can be recommended as a potential and inexpensive adsorbent to clean up OG dye from  
563 wastewaters.

564 **Table 1.** Comparison of the maximum uptake capacities of PANI@Fe-ZSM-5 for OG  
565 removal and other adsorbents addressed in the previously published studies.

566

567

568

Adsorbent	Q <sub>max</sub> (mg g <sup>-1</sup> )	Operating conditions			Reference
		Equilibrium time (min)	Dose (g L <sup>-1</sup> )	pH	
FSMD MNPs	109.1	60	1	3	(Zheng et al., 2019)
Alumina nanoparticles	93.3	45	1	2.5	(Banerjee et al., 2019)
Cts(x)-g-PNVP	63.7	175	10	3	(Sutirman et al., 2019)
Monoamine-modified silica	36.3	300	1	3	(Donia et al., 2009)
Prussian-Blue nanoparticles supported over alumina	44.4	100	6.5	3	(Doumic et al., 2015)
AC from coffee grounds	100	180	1	3	(Laksaci et al., 2019)
Modified montmorillonite nanoclay	39.4	60	2.5	8	(Salam et al., 2017)
PANI@Walnut shells	17.24	90	1	6	(Imgharn et al., 2021)
Bagasse fly ash	18.79	200	2	4	(Mall et al., 2006)
Kapok fiber oriented polyaniline	192.3	240	1	6	(Zheng et al., 2012)
H-MIL -53(Fe)	163.9	300	--	4	(Feng et al., 2020)

<b>PANI@AS biocomposite</b>	190.98	100	0.5	5	(Hsini et al., 2020)
<b>Cucumber peels</b>	37.8	60	0.5	6	(Stavrinou et al., 2018)
<b>PANI@Fe-ZSM-5 composite</b>	<b>217</b>	120	0.5	5	<b>Current study</b>

569

570 **Conclusion**

571 In this contribution, PANI@Fe-ZSM-5 composite was synthesized, characterized and used  
572 for OG dye removal from water. The adsorption study established that the PANI@Fe-  
573 ZSM-5 composite as an effective adsorbent for the removal of OG dye from aqueous  
574 solutions. Based on the results obtained for pH influence on the adsorption process and  
575 PZC of PANI@Fe-ZSM-5 composite, electrostatic interactions were likely the main forces  
576 governing the OG dye adsorption mechanism. The kinetic data for OG dye removal by the  
577 PANI@Fe-ZSM-5 composite was well-fitted by the pseudo-second-order model. The mass  
578 transfer process of OG dye from the solution to the PANI@Fe-ZSM-5 surface occurred via  
579 three consecutive stages: (i) external diffusion, (ii) intraparticle diffusion and (iii) final  
580 adsorption equilibrium. The OG dye binding mechanism and associated thermodynamic  
581 behavior were evaluated on the basis of advanced statistical physics theory. Among the  
582 fitted statistical physics models to the experimental findings, the **M3** model (monolayer  
583 layer model with the different energy sites) is the best one to describe the OG dye  
584 adsorption process. Based on this model, the macroscopic and microscopic aspects related  
585 to the adsorption system were assessed. The OG dye molecules were adsorbed in the  
586 perpendicular (multi-docking) and parallel (multimolecular) modes on the first ( $n_1 < 1$ )

587 and second ( $n_2 > 1$ ) types of active sites in the PANI@Fe-ZSM-5 surface. The  
 588 thermodynamic functions confirmed the feasibility of OG adsorption onto PANI@Fe-  
 589 ZSM-5 composite through physical interactions. The theoretical data are in satisfactory  
 590 concordance with experimental results. Finally, we can conclude that the as-developed  
 591 PANI@Fe-ZSM-5 material can be applied as an efficient and regenerable adsorbent for  
 592 treating the textile effluents.

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## Highlights

- ✓ A novel PANI@Fe-ZSM-5 hybrid composite was easily elaborated and fully characterized.
- ✓ The adsorption performance of PANI@Fe-ZSM-5 towards OG dye was investigated.
- ✓ The OG dye binding mechanism was assessed by advanced statistical physics modeling.
- ✓ Statistical physics parameters and thermodynamic functions of the adsorption system were studied.
- ✓ PANI@Fe-ZSM-5 composite has excellent adsorption ability and satisfactory reusability.

### **Declaration of Interest Statement**

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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