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#### Article

# Magnetic Metal–Organic Frameworks Embedded in a Reduced Graphene Oxide Hydrogel Network as a Promising Hybrid Nanocomposite for Cr(VI) and *p*-Nitrophenol Removal

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**ABSTRACT:** Reduced graphene oxide hydrogel-combined-magnetic metalorganic frameworks (nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads) with their multidiscipline advantages were efficiently fabricated with the aim of Cr(VI) and *p*nitrophenol (PNP) removal as inorganic and organic pollutants, respectively. The structural features of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were characterized by Fourier transform infrared, scanning electron microscopy, transmission electron microscopy, and BET surface area analyses. The nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads absorbed 65% water within only the first hour and then the maximum swelling equilibrium reached after about 3 h. In a separate adsorption process, the removal of Cr(VI) by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads reached 288.42 mg/g, while PNP reached 197.38 mg g<sup>-1</sup>. In a binary mixture, the removal values satisfied Cr(VI) (267.0 mg/g) and PNP (189.27 mg/g) to refer to the efficiency of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads in removing both inorganic and organic pollutants from water. The kinetic behavior and trend



for adsorption of Cr(VI) were best described by *pseudo*-second order, while PNP was fitted to *pseudo*-first order kinetic. The Langmuir isotherm model was characterized as the best fitting model for both Cr(VI) and PNP adsorption by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads. The thermodynamic study illustrated that a physisorption mechanism as the predominant in the PNP adsorption by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads ( $\Delta H = -12.07 \text{ kJ/mol}$ ), while a chemisorption process was characterized to control the adsorption of Cr(VI) ions onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH ( $\Delta H = -86.0 \text{ kJ/mol}$ ).

# 1. INTRODUCTION

Wastewater containing phenol compounds comes from various industries, such as medicine, plastics, rubber, and printing, which is considered to be the ultimate critical impendence to the human health and environment. As a result of chemical stability against the light and oxidation environment, these contaminants and even carcinogenic organic pollutants can be subsisted in the water for a long time and causes even adverse intrusion to the survival and reproduction of fish species.<sup>1</sup> *p*-Nitrophenol (PNP) is widely used in petrochemical synthesis.<sup>2</sup> PNP is identified as the priority pollutant by the U.S. Environmental Protection Agency.<sup>3</sup> On the other hand, chromium is excessively applied in the electroplating, photography, and leather tanning industries, and it has been reported to cause serious environmental problems.<sup>4</sup> According to drinking water quality guidelines prescribed by the World Health Organization, the concentration of Cr(VI) in drinking water should not exceed 0.05 mg/L.<sup>3</sup> It is important to control PNP and Cr(VI) pollutions due to their toxicities, and as such, the drinking water standards require new, highly effective treatment technologies. Therefore, the effective separation of these contaminants from wastewater is putting forward a major challenge. Considerable techniques have been utilized implicating coagulation, photocatalytic, sedimentation, membrane technology, ion exchange, and adsorption.<sup>6</sup> Among these approaches, the adsorption process is considered to be one of the most efficacious techniques for decontamination of pollutants in a fast and simple way.<sup>7,8</sup> Additionally, assorted adsorbents have been developed, like biochar, metal oxides, biosorbents, and zeolites.<sup>9,10</sup>

Compared with convention of porous materials, metal– organic frameworks (MOFs) have superior surface area, high porosity, functionalities, tunable structure, and flexibility to afford a great number of adsorbents for the removal of pollutants from water.<sup>11</sup> Generally, MOFs are mainly composed of two kinds of primary building units. The organic unit is possibly either a bridging ligand or linker as terephthalic acid, fumaric acid, and 2,2'-bipyridine-5,5'-dicarboxylic acid. On the other hand, the inorganic unit may be a metal ion or cluster of metal ions.<sup>12,13</sup> Incorporation of MOFs onto a 3D hydrogel network is

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#### Table 1. Specification of Used Chemicals

chemicals	IUPAC name	chemical formula	CAS number	molecular weight (g/mol)	purity (%)	source
graphite powder	carbon	С	7782-42-5, 14808-60-7	12.011	99.9	Nice Chemicals LTD, India
ascorbic acid	hexuronic acid	$C_6H_8O_6$	50-81-7	176.12	99.9	Sigma-Aldrich, USA
calcium chloride	calcium dichloride	CaCl <sub>2</sub>	10043-52-4	110.98	97.0	Sigma-Aldrich, USA
fumaric acid	(2E)-but-2-enedioic acid	НООССН= СНСООН	110-17-8	116.07	99.9	Sigma-Aldrich, USA
hydrochloric acid	hydrogen chloride	HCl	7647-01-0	36.46	37.0	BDH Chemicals Lt. England
sodium hydroxide	sodium hydroxide	NaOH	1310-73-2	39.99	97.0	BDH Chemicals Lt. England
ferric chloride	iron (III) chloride	FeCl <sub>3</sub>	7705-08-0	162.20	≥99.9	Sigma Aldrich, USA
sodium chloride	sodium chloride	NaCl	7647-14-5	58.44	99.9	BDH Chemicals Lt. England
potassium dichromate	dipotassium [(oxidodioxochromio)oxy] chromiumoylolate	$K_2Cr_2O_7$	7778-50-9	294.18	≥99.9	Sigma-Aldrich, USA
p-nitrophenol	4-nitrophenol	C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>	100-02-7	139.110	99.9	Sigma-Aldrich, USA

a promising candidate, which gaining great research interest for environmental applications. Diverse advantages may be obtained as increasing durability, adsorption capacity, and mechanical properties for the application in sorption and separation techniques.<sup>14</sup> Generally, Hydrogels are categorized as an important class of compounds with three-dimensional (3D) networks, high porosity, good flexibility, and excellent swelling in water, aqueous solutions, and other biological fluids. The reason for such a swelling property is mainly contributed by the presence of different hydrophilic functional groups such as hydroxyl, carboxyl, and amide.<sup>15,16</sup>

Graphene hydrogels in the form of 3D architectures have been characterized as highly porous nanomaterials with unique characteristics<sup>17</sup> to enable their applications in photocatalysis for hydrogen evolution, sensing and monitoring,<sup>18</sup> super-capacitance performance,<sup>19</sup> energy storage,<sup>20</sup> carriers for drug delivery,<sup>21</sup> drug removal,<sup>22,23</sup> and treatment of different pollutants. Commonly, graphene represents a very important class of two-dimensional (2D) carbon nanomaterials<sup>24,25</sup> with multidiscipline applications in different research and industrial activities.<sup>26,27</sup> The tremendous interests in these materials are directly focused on their remarkable chemical, electronic, thermal, and conductive characteristics, besides their excellent chemical stability, high mechanical strength, large specific surface area, and high mobility of charge carriers.<sup>28-30</sup> These materials and their based-composites have been recently found growing interests to successfully lead to the discovery of efficient nanosorbents for the removal of various inorganic and organic pollutants from water matrices.<sup>31,32</sup> Until now, various synthesis methods of the 3D graphene structure such as flow-directed assembly,<sup>33</sup> layer-by-layer deposition,<sup>34</sup> evaporation-induced self-assembly,<sup>35</sup> hydrothermal reduction,<sup>36</sup> chemical bonding via cross-linking agents,<sup>37</sup> and Langmuir–Blodgett technique<sup>3</sup> have been achieved and applied in the adsorption removal of oil,<sup>39</sup> dyes,<sup>37</sup> antibiotics,<sup>23</sup> and heavy metals,<sup>37</sup> etc. Excellent adsorption properties have been realized, making it a promising candidate for environmental applications such as sorption, filtration, and separation. Herein, we reported an efficient and environmentally friendly route for GH synthesis via one-step graphene oxide (GO) hydrothermal reduction with ascorbic.

The aim of this work is mainly focused on combining the advantages of reduced graphene oxide hydrogel (rGOH) and metal–organic frameworks (MOFs) with a nanomagnetite  $(nFe_3O_4)$  in a single novel multipurpose nanocomposite for the

removal of both chromium (VI), an example of a highly toxic metal ion, and *p*-nitrophenol (PNP), an example of organic contaminants, from an aqueous solution are also aimed to explore. The magnetic water stable MOFs (nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) used in this work was prepared by the reaction of a hard acid (FeCl<sub>3</sub>) with a hard base (fumaric acid) to produce Fe(FAC)) and further combined with the nanomagnetite to facilitate its removal from water by an external magnetic field.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials and Instruments.** The specification of used chemicals compiled in Table 1. The nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were characterized by FT-IR, SEM, TEM, and BET surface area analyses. The specifications of these instruments are compiled in the Supporting information, Table S1.

**2.2.** Synthesis. 2.2.1. Microwave-Assisted Synthesis of  $nFe_3O_4@Fe(FAC)$ . Microwave irradiation has been used to provide energy for the growth of MOFs. Microwave-assisted synthesis is based on the interaction between electromagnetic waves and mobile electric charges, such as polar-solvent molecules or ions in the solution. The advantages of this method include high efficiency, phase selectivity, particle size reduction, and morphology control.<sup>40</sup> In a typical procedure, 4.0 mmol of FeCl<sub>3</sub> and 2.0 mmol of fumaric acid (FAC) were dissolved in 100 mL of ethanol and stirred for 30 min. After that, the mixture was transferred to a microwave oven for 2 min at 200 W, followed by 15 min of constant irradiation at 80 W. The obtained MOFs molecules were dried at 70 °C for 12 h.

Doping magnetic iron oxide nanoparticles onto the Fe(FAC) frameworks was accomplished by the following steps. An amount of 1.0 g of Fe(FAC), iron (III) chloride (0.04 mol), and iron (II) chloride (0.02 mol) was dissolved in 20 mL of HCl (1.0 mol  $L^{-1}$ ), and the mixture was stirred for 1 h at 80 °C. Sodium hydroxide (1.0 mol  $L^{-1}$ ) was added dropwise (5 mL/min) and transferred to the microwave oven, heated for 2 min (800 W, 80 °C).

2.2.2. Synthesis of Reduced Graphene Oxide Hydrogel Beads (rGOH Beads). An amount of 1.0 g of graphite was mixed with 10 mL of potassium permanganate (0.5 mol  $L^{-1}$ ) as an oxidizing agent and 10 mL of sulfuric acid (2 N). The mixture was stirred for 15 min and transferred to a microwave oven for 2 min (800 W, temperature 80 °C). Afterward, 10 mL of hydrogen peroxide as a quenching agent for oxidation reaction was added dropwise with stirring for about 3 min. The mixture was

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centrifuged for 10 min, and the solid was washed with diluted HCl and deionized water several times. The obtained solid particles were dispersed in 50 mL of water and sonicated for 30 min, and the produced GO was dried overnight at 80  $^{\circ}$ C.<sup>41</sup>

In a typical procedure, the GO solution was mixed with ascorbic acid with a mass ratio of  $1:1.^{42}$  The coagulation bath was prepared by dissolving CaCl<sub>2</sub> in a mixture of deionized water and ethanol (4:1) to a final concentration of 2%. The GO hydrogel beads were produced by dropping the GO/ascorbic acid solution into the coagulation bath. The rGO hydrogel beads were kept in the coagulation bath for aging at room temperature for 4 h, and the resulting rGOH beads were kept at 60 °C for 4 h. The rGOH beads were obtained by fully washing the rGOH beads with deionized water and microwave drying (800 W, temperature 80 °C).

2.2.3. Synthesis of Magnetic MOFs@Reduced Graphene Oxide Hydrogel Beads (nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH Beads). An amount of 0.5 g of rGOH beads was added to 1.0 g of nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC) and sonicated in an ultrasound bath for 1 h. The mixture was heated in a microwave oven (800 W, temperature 80 °C) for 3 min as a reduction time without any interference. The obtained nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were washed with water and dried in a medium power microwave (Scheme 1).

**2.3. Adsorption Experiments.** The adsorptive removal of Cr(VI) or PNP from aqueous solutions by  $nFe_3O_4@Fe(FAC)@$ rGOH beads was performed via a batch technique. In general,  $nFe_3O_4@Fe(FAC)@rGOH$  beads (20 mg) were mixed with Cr(VI) or PNP solutions and shaken at room temperature for 30 min to enhance the adsorption of Cr(VI) or PNP onto the  $nFe_3O_4@Fe(FAC)@rGOH$  beads. The residual concentration of Cr(VI) or PNP in the solution was determined by UV–vis spectrophotometry at wavelengths  $\lambda_{max} = 540$  and 317 nm, respectively. The adsorption capacity at equilibrium,  $q_e$  (mg g<sup>-1</sup>), and percentage removal, R%, were determined according to the following eqs 1 and 2

$$q_{\rm e} = (C_{\rm e} - C_{\rm o})V/m \tag{1}$$

$$%R = (C_{\rm o} - C_{\rm e})/C_{\rm o} \times 100$$
 (2)

where  $C_{o}$  and  $C_{e}$  are the initial concentration and concentration at equilibrium (mg L<sup>-1</sup>), respectively, and *m* is the amount of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads (mg).

The effect of solution pH was monitored over the pH range 1-10, while other experimental factors were maintained as follows: the dosage = 20 mg; the initial Cr(VI) or PNP = 50 mg/L; contact time = 60 min; temperature = 25 °C.

The effect of ionic strength was investigated under a concentration range (0.01–1.0 mol/L) of sodium chloride. An amount of 50 mg/L Cr(VI) or PNP was added to 20 mg of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads and shaken for 30 min at room temperature under pHs 2 and 5 for Cr(VI) and PNP, respectively.

The kinetic study was monitored by applying the dosage of  $nFe_3O_4$ @Fe(FAC)@rGOH beads (20 mg), initial Cr(VI) or PNP (50 mg/L), pHs 2 and 5 for Cr(VI) and PNP, respectively, contact time (5–180 min), and temperature (25 °C).

The adsorption isotherm study was performed by monitoring the adsorbent dosage = 20 mg, the initial Cr(VI) or PNP concentration = 5–100 mg/L; pHs of 2 and 5 for Cr(VI) and PNP, respectively, contact time = 30 min; temperature = 25 °C.

The thermodynamic study was applied via adsorbent dosage = 20 mg, initial Cr(VI) or PNP concentration as 50 mg/L; pHs of 2 and 5 for Cr(VI) and PNP, respectively, contact time = 30 min; temperature in the range 25–55 °C. Moreover, Table 2 compiles the experimental conditions for the removal of Cr(VI) and PNP onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.

The zero point charge (pHpzc) of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads was monitored by the salt addition method including. An amount of 200 mg of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was added to 50 mL of KCl (0.01 mol/L). pH was adjusted to 2–10 by HCl (0.1 mol L<sup>-1</sup>) or NaOH (0.1 mol L<sup>-1</sup>), then shaken for 4 h at room temperature. After that, the final pHs (pH<sub>f</sub>) of suspensions were measured after equilibration. Finally, pHpzc of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was determined by plotting  $\Delta pH$  (pH<sub>f</sub> – pH<sub>i</sub>) against pH<sub>i</sub>.

**2.4. Single and Simultaneous Adsorption of Cr(VI) and PNP from Real Wastewater.** The efficiencies of  $nFe_3O_4@$ Fe(FAC), rGOH, and nFe3O4@Fe(FAC)@rGOH beads for the removal of PNP and Cr(VI) from wastewater were examined

Table 2. Parameters of Kinetics Models for Cr(VI) Ions and *p*-Nitrophenol Removal by  $nFe_3O_4@Fe(FAC)@rGOH$ Beads

	pollutant		
kinetic model	parameters	Cr(VI)	p-nitrophenol
pseudo-first order	$q_{\rm e}  {\rm mg}  {\rm g}^{-1}  ({\rm exp})$	288.36	197.28
	$q_{\rm e}  { m mg}  { m g}^{-1}  ({ m calc})$	223.94	192.60
	$K_1 (\min^{-1})$	0.06	0.89
	$R^2$	0.9761	0.9996
pseudo-second order	$q_{\rm e}  {\rm mg}  {\rm g}^{-1} \left( {\rm exp} \right)$	288.36	197.28
	$q_{\rm e}  {\rm mg}  {\rm g}^{-1}  ({\rm calc})$	285.07	148.39
	$K_2 (g mg^{-1} min^{-1})$	2.94	0.09
	$R^2$	0.9997	0.9695
pore film diffusion	K <sub>o</sub>	6.74	5.48
	α	0.35	0.32
	$R^2$	0.9799	0.9774
liquid film diffusion	$K_{ m fd}$	0.21	0.18
	intercept	0.48	0.35
	$R^2$	0.9711	0.9726

in this series of tests. Amounts of 50 mg of the adsorbent and 100 mg L<sup>-1</sup> Cr(VI) ions or 50 mg L<sup>-1</sup> PNP were added separately in the case of single removal. At a certain time interval, the suspension was withdrawn and centrifuge for 30 min. The removal efficiency (%) was calculated using eq 2. In addition, to investigate the mutual effect of the simultaneous Cr(VI) and PNP on their removal by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), rGOH, and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, a series of binary removal experiments were carried out at 293 K. Binary systems of PNP-Cr<sup>6+</sup> were prepared with initial concentrations of 50 mg/L for PNP and 100 mg/L for Cr<sup>6+</sup>.

**2.5.** Swelling Behavior of  $nFe_3O_4@Fe(FAC)@rGOH$ Beads. An amount of 200 mg of the  $nFe_3O_4@Fe(FAC)@$ rGOH beads was incubated for (10–300 min) in deionized water at 25 °C. After a while, the  $nFe_3O_4@Fe(FAC)@rGOH$ beads were wiped and weighted after the removal of the excess water from the  $nFe_3O_4@Fe(FAC)@rGOH$  beads surface. Similarly, the water retention can be obtained by incubating the swelling equilibrium  $nFe_3O_4@Fe(FAC)@rGOH$  beads at 60 °C. The swelling ratio (SR) and water retention (%WR) were calculated according to the following eqs 3 and 4

$$SR = (W_t - W_d) / W_d \times 100\%$$
 (3)

where  $W_t$  and  $W_d$  represent the weights of swollen hydrogels at a predetermined time interval and the weights of dried hydrogels, respectively.

WRR = 
$$((W_{\rm s} - W_{\rm d})/W_{\rm d} \times 100\%)/\text{SR}$$
 (4)

where  $W_s$  is the weight of hydrogels in an oven at different temperatures with a predetermined time interval and  $W_d$  is the weight of dried hydrogels, respectively.

**2.6. Regeneration of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH Beads.** To monitor the reusability of the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, 100 mg of hydrogel beads was added to 10 mL of either Cr(VI) ions or PNP (100 mg/L) at room temperature and the solutions were adjusted to pH 6. Then, the adsorbed Cr(VI) ions or PNP onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were eluted with convenient HCl solution (0.1 mol/L) and the residual mass of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was washed with distilled water and dried for further use. The regenerated hydrogel beads were used for another adsorption cycle.

# 3. RESULT AND DISCUSSION

3.1. Synthesis and Characterization. Previous studies have proved that the formation of 3D structured graphene hydrogels is mainly due to the coalescing and partial overlapping of reduced GO nanosheets via  $\pi - \pi$  stacking, hydrogen bonding, coordination, and electrostatic interaction. It is well known that GO is hydrophilic and is able to be uniformly dispersed in water with a state of a stable suspension on account to the ample functional groups and electrostatic repulsion between GO sheets as a result of the ionized carboxyl groups. Therefore, acidification of GO dispersion by ascorbic acid is an efficient way to enhance the hydrogen bonding force via protonation and weaken the electrostatic repulsion, which would result in the aggregation of GO sheets. Moreover, the reduction process by ascorbic acid removed oxygen-containing groups, leading to recovery of the conjugated structure and the formation of hydrophobic graphene.<sup>43</sup> On the other hand, Ca<sup>2+</sup> was crosslinked and solidified with the oxygen-containing functional groups on the GO sheets, which was removed after reduction was completed.

The optimum mass ratio between  $nFe_3O_4@Fe(FAC)$  and rGOH was examined in presence of various mass ratios as 0.5,

Table 3. Isotherm Parameters	of Cr(V	I) and	<i>p</i> -Nitropheno	l Removal b	y nFe <sub>3</sub> O <sub>4</sub> @Fe	(FAC	)@rGOH Bead	ls
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		pollutant								
			Cr(VI)				<i>p</i> -nitro	phenol		
isotherm models	parameters	25 °C	35 °C	45 °C	55 °C	25 °C	35 °C	45 °C	55 °C	
Langmuir	$q_{\rm max} ({\rm mg}~{\rm g}^{-1})$	288.36	297.30	312.94	328.36	197.28	204.69	230.16	242.91	
	K <sub>L</sub>	1.73	1.73	1.82	1.85	1.62	1.75	1.83	1.89	
	$R^2$	0.9993	0.9991	0.9991	0.9996	0.9998	0.9996	0.9998	0.9998	
Freundlich	$K_{\rm f} \left( {\rm L \ mg^{-1}} \right)$	0.45	0.48	0.48	0.49	0.04	0.05	0.07	0.08	
	n	1.18	1.19	1.19	1.22	0.92	0.94	0.95	0.95	
	$R^2$	0.9588	0.9586	0.9586	0.9583	0.9573	0.9559	0.9581	0.9581	
Temkin	$a_{\rm T}  ({\rm L}  {\rm g}^{-1})$	1.07	1.07	1.09	1.12	0.95	0.96	0.98	0.98	
	В	18.90	18.93	19.82	19.82	8.93	9.06	9.14	9.18	
	$b_{\mathrm{T}}$	12.85	12.93	13.05	13.18	0.16	0.18	0.19	0.19	
	$R^2$	0.9591	0.9589	0.9588	0.9566	0.9618	0.9605	0.9616	0.9608	
R-P	Α	1.09	1.09	1.12	1.27	0.95	0.96	0.98	0.98	
	β	0.75	0.83	0.85	0.92	0.38	0.42	0.46	0.46	
	$R^2$	0.9689	0.9661	0.9664	0.9661	0.9771	0.9763	0.9758	0.9746	



Figure 1. SEM images of (a) Fe(FAC), (b)  $nFe_3O_4@Fe(FAC)$ , (c) GO, (d)  $nFe_3O_4@Fe(FAC)@rGOH$  beads, (e)  $nFe_3O_4@Fe(FAC)@rGOH$  bead-loaded Cr(VI), and (f)  $nFe_3O_4@Fe(FAC)@rGOH$  bead-loaded *p*-nitrophenol.

1.0, 1.5, and 2.0% (w/w) of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) into rGOH by comparing the removal ratios for Cr(VI) ions and PNP. The recognized data confirmed that the increase in the nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC) percentage into the prepared hydrogel caused a positive increase in the removal efficiency of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) @rGOH beads toward Cr(VI) ions and PNP. This behavior may be related to the presence of more active functional groups. The adsorption capacities of Cr(VI) (157.39, 188.39, 210.85, and 288.36 mg g<sup>-1</sup>) and PNP (108.15, 122.69, 148.64, and 197.28 mg g<sup>-1</sup>) were characterized at 0.5, 1, 1.5, and 2% (w/w), respectively, of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) to rGOH. Finally, the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) percentage (2.0%) was selected as the optimum value to prepare the aimed nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads.

3.1.1. Surface Morphology. The morphologies of Fe(FAC), GO nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were monitored via SEM and TEM analyses. Figure 1a illustrates the rod-like structure of Fe(FAC). On the other hand, the morphology of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was monitored via SEM (Figure 1d), which confirmed the deposition of nFe<sub>3</sub>O<sub>4</sub> on the surface of Fe(FAC), with a particle size about 100 nm. Furthermore, the plate form of GO is demonstrated in Figure 1c, with a particle size about 0.5  $\mu$ m. The SEM image showed a cross-linked network of the formed nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads in the range of micrometer. There are an obvious difference between the morphology of nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads before and after adsorption of Cr(VI) (Figure 1e) and PNP (Figure 1f) to confirm to the successful adsorption process.<sup>44</sup> As shown, the adsorption of Cr(VI) and PNP did not only affect the morphology of MGH but also the particle size, while the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads before adsorption were in the range of 2–4  $\mu$ m and after Cr(VI) and PNP adsorption became in the range of 20–25 nm and 30–50 nm, respectively. Otherwise, the TEM images of Fe(FAC), GO nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads are illustrated in Figure 2.

The EDX analysis discloses that the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads were composed from (56.09% carbon, 23.05% oxygen, 20.86% iron) and is shown in the Supporting information, Figure S1 the iron content related to the magnetic iron oxide nanoparticles, behind the metal ion of MOFs. Otherwise, the EDX spectrum of the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads after Cr(VI) adsorption comprised of 27.10% carbon, 24.23% oxygen, 25.07% iron, and 23.60% Cr(VI) and is illustrated in the Supporting information, Figure S1, to confirm the successful adsorption of Cr(VI) onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads.

The purities of the prepared nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) and GO were confirmed by XRD analysis. The XRD pattern of Fe(FAC) revealed a set of narrow well-defined reflections  $(2\theta = 10-32^{\circ})$ to refer to a highly crystalline structure, Supporting information, Figure S2. In addition, the positions of all peaks of the MIL-88A(Fe) sample were in good agreement with the previously synthesized iron-based MOFs.<sup>44</sup> On the other hand, In the case of pure graphite, a strong XRD peak at  $2\theta = 26.5^{\circ}$  and a slight peak at  $2\theta = 54.5^{\circ}$ . The XRD pattern of graphene oxide shows a peak at  $2\theta = 9.9^{\circ}$ , and peak at  $2\theta = 42.0^{\circ}$  according, confirming the successful GO synthesis.<sup>45</sup>



Figure 2. TEM images of (a) Fe(FAC), (b)  $nFe_3O_4@Fe(FAC)$ , (c) GO, and (d)  $nFe_3O_4@Fe(FAC)@rGOH$  beads.

3.1.2. Surface Area Analysis. Figure 3 demonstrates the BET adsorption–desorption of  $nFe_3O_4@Fe(FAC)@rGOH$  beads. The BET surface area of  $nFe_3O_4@Fe(FAC)@rGOH$  beads was found 309.64 m<sup>2</sup>/g. Commonly, the high surface area of hydrogel beads improves the adsorption of investigated pollutants. Besides the surface area, the pore volume is also known to have a major contribution in the adsorption process. The pore volume of  $nFe_3O_4@Fe(FAC)@rGOH$  beads (8.65 cm<sup>3</sup>/g) confirmed the pore filling mechanism facilitated by the hydrogel formation.

3.1.3. FT-IR Spectroscopy. Figure 4 illustrates the FT-IR spectra of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), GO, and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@



Figure 3. BET adsorption–desorption of  $nFe_3O_4@Fe(FAC)@rGOH$  beads.





rGOH beads. For the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), four characteristic peaks appear. The peak at 3400 cm<sup>-1</sup> is related to O–H (COOH) stretching of fumaric acid. The peaks at 1609 and 1400 cm<sup>-1</sup> are due to C=O and –OH bend, respectively. Additionally, the peak at 1300 cm<sup>-1</sup> is manifested from C–O stretch. In addition, the peak at 570 cm<sup>-1</sup> represents the Fe–O bond to certify the doping of iron oxide nanoparticles into Fe(FAC).<sup>46</sup> Moreover, the characteristic spectral peaks of GO are identified at 3380 cm<sup>-1</sup> (O=C–O carboxyl), and 1200 cm<sup>-1</sup> (C=C aromatic), 1390 cm<sup>-1</sup> (O=C–O carboxyl), and 1200 cm<sup>-1</sup> (C–O–C epoxy). The peak at 1050 cm<sup>-1</sup> is related to C–O alkoxy.<sup>47</sup> On the other hand, the spectra of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads demonstrate a weak peak at 3400 cm<sup>-1</sup> compared with that in the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) and GO spectra. As observed, the red shifts in the peaks of C=C and –OH stretching aromatics confirm the  $\pi$ - $\pi$  interaction and H-bonding in the reduced graphene oxide.

**3.2.** Sorption Study of Cr(VI) and PNP by  $nFe_3O_4@$ Fe(FAC)@rGOH Beads. 3.2.1. pH Contribution. The pH value is known as a significant factor in the adsorption efficiency of heavy metals and organic pollutants onto a hydrogel adsorbent. At low pH, Cr(VI) mostly is present as  $Cr_2O_7^{2-}$  and  $HCrO_4^-$ , which can be combined with the positively charged  $nFe_3O_4@$ Fe(FAC)@rGOH beads. A large amount of H<sup>+</sup> promotes the electrostatic attraction of the adsorbent to Cr(VI) ions. As shown in Figure 5, the maximum adsorbed amount of Cr(VI)



Figure 5. Effect of pH on Cr(VI) and PNP removal by nFe $_3O_4@$  Fe(FAC)@rGOH beads.

was 288.42 mg  $g^{-1}$  at pH = 1.0. As the pH increased, the OHconcentration increased and Cr(VI) was as  $CrO_4^{2-}$ . At the same time, the surface of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads became negatively charged, which promoted the repulsive interaction between Cr(VI) and OH-, and the adsorption decreased.<sup>48</sup> Moreover, the pHpzc of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads determined by the salt-addition method was 3.0. When the solution pH was less than pHpzc, protonation occurred on the surface of the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads and resulted in a positive charge on the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, which enhanced adsorption of hexavalent chromium on its surface. On the other hand, at low pH, the surface of  $nFe_3O_4$ Fe(FAC)@rGOH beads is positively charged and the PNP is in the molecular form, while at higher pH, the PNP molecules gradually changed to the anionic form. It is known that the adsorption of phenolic materials may be decreased in alkali media, at pH > pHpzc as the net charge of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads becomes negative and the PNP is present as an anion to enhance the electrostatic repulsion between  $nFe_3O_4$ Fe(FAC)@rGOH beads and PNP.49

To consider the chemical stability, XRD of  $nFe_3O_4@$ Fe(FAC)@rGOH beads in different pHs was compared. To estimate the influence of pH on  $nFe_3O_4@Fe(FAC)@rGOH$ beads, samples were exposed to different pH aqueous solutions at room temperature up to 3 days. In the Supporting information, Figure S3 displays the XRD pattern of  $nFe_3O_4@$ Fe(FAC)@rGOH beads to study the framework structure stability after dispersing in different pHs. As shown, no significant changes were observed in peak positions for the  $nFe_3O_4@Fe(FAC)@rGOH$  beads. This reveals that  $nFe_3O_4@$ Fe(FAC)@rGOH beads are stable in different pHs at room temperature.

3.2.2. Ionic Strength Contribution. It is well known that the industrial wastewater contains not only organic contaminant species but also different types of salts, which affect the efficiency

of pollutant removal. The influence of background electrolytes on the removal of Cr(VI) or PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads was investigated using NaCl with different concentrations from 0.01 to 1.0 mol/L.<sup>49</sup> The adsorption capacity of Cr(VI) showed an slight decrease from 288.42 to 258.94 mg g<sup>-1</sup> as the electrolyte concentration increased from 0.01 to 1.0 mol L<sup>-1</sup>, and the same behavior was also observed in the case of the PNP adsorption process (Figure 6). The presence



Figure 6. Effect of ionic strength on Cr(VI) and PNP removal by  $nFe_3O_4@Fe(FAC)@rGOH$  beads.

of electrolyte solution causes the weakness of the electrostatic interaction between Cr(VI)/PNP and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads. The recognized data from this study illustrate that the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads can be categorized as an efficient hydrogel for PNP and Cr(VI) decontamination in the presence of solution with high electrolyte concentrations.

3.2.3. Reaction Time Contribution and Kinetic Study. Contact time between Cr(VI) ions or PNP and  $nFe_3O_4(a)$ Fe(FAC)@rGOH beads is the major parameter in the study of different kinetic models. The highest adsorption capacity values of Cr(VI) and PNP were 288.36 and 197.28 mg g<sup>-1</sup>, respectively, after 180 min of contact time. This phenomenon might be related to increase the adsorption process with time, and after a certain time, saturation takes place when all active sites of the adsorbent surface were occupied with adsorbate molecules.<sup>50</sup>

Adsorption is a physicochemical process that includes three major steps; (i) film diffusion: transport of adsorbate, Cr(VI) or PNP, from the bulk to the external adsorbent surface, and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, (ii) pore diffusion: transport of adsorbate into the adsorbent pores, and (iii) surface reaction: attachment of the adsorbate to the internal surface of the adsorbent.<sup>51</sup> On the other hand, the kinetics study is mainly investigated to examine the rate of adsorption reaction by the target hydrogel adsorbent. Study of chemical kinetics includes careful monitoring of the experimental conditions, which influence the speed of a chemical reaction and, hence, help to attain equilibrium in a reasonable length of time. Such studies yield information about the possible mechanism of adsorption and the different transition states on the way to the formation of the final adsorbate-adsorbent complex and help develop appropriate mathematical models to describe the interactions.

The *pseudo*-first order equation<sup>52</sup> supposes the adsorption of Cr(VI) ions or PNP onto one adsorption sites of  $nFe_3O_4(\emptyset)$  Fe(FAC)@rGOH beads

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$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where  $q_e$  is the amounts of Cr(VI) or PNP adsorbed at equilibrium (mg/g),  $q_t$  is the amounts of Cr(VI) or PNP adsorbed at time *t* (mg/g), and  $k_1$  is the rate constants (min<sup>-1</sup>).

The pseudo-second model<sup>53</sup> supposes the adsorption of Cr(VI) or PNP onto two adsorption sites of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) @rGOH beads. In addition, the uptake rate is second order with respect to the available surface sites

$$t/q_{\rm t} = 1/(k_2 q_{\rm e}^2) + (1/q_{\rm e}) t \tag{6}$$

The liquid-film diffusion<sup>54</sup> suggests the flow of desired heavy metals through the surrounded liquid film of the hydrogels, and this step is known as the slowest step, namely, the rate determining step

$$\ln(-F) = -k_{\rm fd}t\tag{7}$$

where *F* is the fractional attainment of equilibrium  $(q_t/q_e)$  and  $k_{\rm fd}$  (min<sup>-1</sup>) is the film diffusion rate coefficient. The linear plot of this model graphed between  $-\ln(1 - F)$  and t. The case of no intercept indicates that the kinetics of this adsorption process was monitored by diffusion of the solute (metal ions) through the liquid-surrounded adsorbent (solid surface).

On the other hand, pore film diffusion 54 is generally assuming that an irreversible adsorption process between the pores of hydrogels and heavy metal ions or organic phenolic compounds.

$$\log(C_{\rm o}/(C_{\rm o} - q_{\rm t}m)) = \log(K/2.303 \,\rm V)\alpha \,\log(t)$$
(8)

Table 4 lists out the good correlation co-efficient (>0.9), indicating that kinetics confirmed to the Bangham's equation,

#### Table 4. Thermodynamic Parameters of Cr(VI) and p-Nitrophenol Adsorption onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH Beads

		adsorption thermodynamic parameters					
pollutant	temperature	$\Delta G^{\circ}$ (KJ mol <sup>-1</sup> )	$\Delta H^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\circ}$ (J mol <sup>-1</sup> K <sup>-1</sup> )			
Cr(VI)	298	-160.5	-86.0	0.25			
	303	-161.75					
	308	-163.0					
	313	-164.25					
	318	-165.5					
	323	-166.75					
	328	-168.0					
р-	298	-68.69	-12.07	0.19			
nitrophenol	303	-69.64					
	308	-70.59					
	313	-71.54					
	318	-72.49					
	323	-73.44					
	328	-74.39					

and therefore, the adsorption of Cr(VI) or PNP onto NFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads was pore diffusion controlled.

Based on the calculated  $R^2$  values of these kinetic models (Table 4) and the difference between the theoretical  $(q_{calc} =$ 192.60 mg/g) and practical capacity ( $q_{exp} = 197.28 \text{ mg/g}$ ), the pseudo-first model is the most suitable model to explain the PNP adsorption onto NFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads ( $R^2$  = 0.9996) and is shown in Figure 7a. On the other hand, adsorption of Cr(VI) was well fitted by the *pseudo*-second order kinetic model ( $R^2 = 0.9997$ ) and is represented in Figure 7b. The



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Figure 7. (a) Pseudo-second-order kinetic for Cr(VI) ion removal and (b) pseudo-first order kinetic for PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.

outlined results refer to physical adsorption between PNP and  $NFe_3O_4@Fe(FAC)@rGOH$  beads, while a chemical adsorption reaction was concluded between Cr(VI) and NFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads.

3.2.4. Isotherm Study. The effect of concentration on the removal efficiency of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was monitored to evaluate the adsorption isotherm equilibrium models. The removal capacity of Cr(VI) or PNP increased with increasing the initial concentration up to 50 mg  $L^{-1}$ , and then it kept roughly constant. The maximum capacities of Cr(VI) and PNP were 291.07 and 202.38 mg  $g^{-1}$ , respectively as obtained at 100 mg  $L^{-1}$ . It is predicted that the increase in the initial concentration of Cr(VI) or PNP causes the increase in the concentration gradient, which results in the increase of the driving force of adsorption.53

Isotherm models describe the relationship between the adsorbed metal ions and remained amount under equilibrium condition, at constant temperature. Langmuir,<sup>53</sup> Freundlich,<sup>54</sup> Temkin,<sup>15</sup> and R-P<sup>55</sup> models were investigated to examine the adsorptive removal of Cr(VI) and PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads, at 25, 35, 45, and 55 °C.

3.2.4.1. Langmuir Isotherm. The Langmuir model depends on the assumption that the adsorption of Cr(VI) and PNP onto the monolayer surface of the adsorbent,<sup>53</sup> nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads. The maximum monolayer adsorption capacity of the Langmuir model 291.07 and 202.38 mg  $g^{-1}$  were relatively equal to the experimental adsorption capacity values 288.36 and  $197.28 \text{ mg g}^{-1}$ 

$$q_{\rm e} = q_{\rm max} b C_{\rm e} / 1 + b C_{\rm e} \tag{9}$$

Table 5. Comparison of the Maximum Adsorption Capacity (	$q_e$ : mg g <sup>-1</sup> ) of Cr(VI) and PNP onto nFe <sub>3</sub> O <sub>4</sub> @Fe(FAC)@rGOH
Beads with Other Reported Literature	

	conditions					
adsorbent	pollutant	$q_{\rm e}~({\rm mg~g^{-1}})$	pН	time (min)	fitted model	reference
biochar from sweet lime peel	Cr(VI)	100.0	2	60	Pseudo-second, Langmuir	60
pineapple peel derived biochars		41.67	2	30	Pseudo-second, Langmuir	61
functionalized biochars from fruit waste		14.0	4	60	Pseudo-second, Langmuir	62
carboxymethyl cellulose hydrogel		100.99	2	120	Pseudo-second, Langmuir	63
GO-CS@MOF [Zn(BDC)(DMF)]		206.84	2	60	Pseudo-second, Freundlich	64
nFe3O4@Fe(FAC)@rGOH beads		288.36	2	30	Pseudo-second, Langmuir	this work
magnetic activated carbon	PNP	23.40	5	40	Pseudo-second, Langmuir	65
montmorillonite-grapheneoxide		28.02	4	60	Pseudo-first, Langmuir	66
activated carbon		39.06	6	60	Pseudo-second, DR	67
nFe <sub>3</sub> O <sub>4</sub> @Fe(FAC)@rGOH beads		197.28	6	30	Pseudo-first, Langmuir	this work

Hall et al.  $(1966)^{53}$  noted that the essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $R_{L}$ , which is defined by

$$R_{\rm L} = 1/(1 + K_{\rm L}C_{\rm o}) \tag{10}$$

where  $C_o (\text{mg/L})$  is the initial dye concentration and  $K_L (L/\text{mg})$  is the Langmuir constant related to the energy of adsorption. This parameter indicates the shape of the isotherm as follows: (i)  $R_L = 0$  for irreversible adsorption as  $K_L$  is very large, which means that adsorption is too strong; (ii)  $0 < R_L < 1$  for favorable adsorption process; (iii)  $R_L = 1$  for the linear isotherm and this can occur only if  $K_L = 0$ , and (vi)  $R_L > 1$  for the unfavorable isotherm. In this study, the determined  $R_L$  values of Cr(VI) (0.79, 0.68, 0.62, 0.59, 0.55, 0.53, 0.44, 0.41, 0.38, and 0.36) and PNP (0.68, 0.66, 0.52, 0.43, 0.32, 0.28, 0.26, 0.25, 0.23, and 0.22) at 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg L<sup>-1</sup> confirm the favorable isotherm for the adsorption process of Cr(VI) and PNP onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.

3.2.4.2. Freundlich Isotherm. The Freundlich model is an empirical adsorption isotherm to assume the adsorption of targeted heavy metal ions and organic molecules onto the multilayer surface of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads<sup>54</sup>

$$q_{\rm e} = K_{\rm F} C^{1/n} \tag{11}$$

The failure of the Freundlich model to discuss Cr(VI) or PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads (Table 3) is probably due to the decrease in the adsorption efficiency after first layer adsorption of Cr(VI) or PNP onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads. So as previously reported, the Freundlich model can only describe the experimental data at low pollutant concentration.

*3.2.4.3. Temkin Isotherm.* The Temkin isotherm model contains a factor that explicitly takes into the account of adsorbing species adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage.<sup>15</sup> As implied in the equations, its derivation is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The nonlinear Temkin isotherm model is represented by the following equation

$$q_{\rm e} = RT/b_{\rm T} \ln ATC_{\rm e} \tag{12}$$

where *b* is the variation of the adsorption energy. Typical bonding energy range for ion exchange mechanism is reported to be in the range of 8-16 kJ/mol, while physisorption processes

are reported to have adsorption energies less than -40 kJ/mol. Very low values of b (0.06 kJ/mol) obtained in the present study indicates rather weak ionic interaction between the sorbate and present sorbent, and the dye removal seems to involve physisorption. The listed value of *B* compiled in Table 3 confirms the chemical adsorption between Cr(VI) and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, while the physical adsorption controlled the PNP adsorption by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.

3.2.4.4. Redlich–Peterson Isotherm. Finally, the adsorption of Cr(VI) or PNP onto  $nFe_3O_4@Fe(FAC)@rGOH$  beads was discussed by the empirical Redlich–Peterson isotherm, which is based on the combination of Langmuir–Freundlich into one equation. This model is defined by the following expression<sup>55</sup>

$$q_{\rm e} = AC_{\rm e}/1 + BC_{\rm e}^{\ \beta} \tag{13}$$

where A is Redlich–Peterson isotherm constant (L g<sup>-1</sup>), B is constant (L mg<sup>-1</sup>),  $\beta$  is exponent that lies between 0 and 1,  $C_e$  is equilibrium liquid-phase concentration of the adsorbent (mg L<sup>-1</sup>), and  $q_e$  is the equilibrium adsorbate loading on the adsorbent (mg g<sup>-1</sup>).

At high liquid-phase concentrations of the adsorbate, eq 14 reduces to the Freundlich equation

$$I_e = A/BC_e 1 - \beta \tag{14}$$

where  $A / B = K_F$  and  $(1 - \beta) = 1/n$  of the Freundlich isotherm model.when  $\beta = 1$ , it reduces to Langmuir equation with b = B(Langmuir adsorption constant (L mg<sup>-1</sup>)), which is related to the energy of adsorption; when  $\beta = 0$ , it reduces to the Henry's equation.

The adsorption process of Cr(VI) ( $R^2 = 0.9993$ , 0.9991, 0.9991, and 0.9996) or PNP ( $R^2 = 0.9998$ , 0.9996, 0.9998, and 0.9998) at 25, 35, 45, and 55 °C by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads can be clearly discussed based on the assumption of the Langmuir model according to the data represented in Table 3 and Figure 8.

3.2.5. Thermodynamic Study. The effect of temperature on the removal efficiency of Cr(VI) or PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) @rGOH beads was optimized under temperature range 25–55 °C to investigate the standard thermodynamic parameters as Gibbs free energy  $\Delta G^{\circ}$ , enthalpy change  $\Delta H^{\circ}$ , and entropy change  $\Delta S^{\circ}$ . The removal capacity values of Cr(VI) by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were found to increase from 245.93 mg g<sup>-1</sup> at 25 °C to 288.36 mg g<sup>-1</sup> at 55 °C. On the other hand, the maximum adsorption capacity of PNP was 197.28 mg g<sup>-1</sup> at 55 °C. With increasing temperature, the



Figure 8. Langmuir, Freundlich, Temkin, and R-P isotherm models for Cr(VI) and PNP removal by  $nFe_3O_4@Fe(FAC)@rGOH$  beads at 25, 35, 45, and 55 °C.

motion of ions or molecules increased in the solvent, resulting in their increased kinetic energy. Therefore, the movement rate of pollutants to the surface of the adsorbent accelerated to increase the adsorption capacity. On the other hand, the increased temperature enhanced the activities of oxygen-containing groups on the surface of the adsorbent. As a result, the contact probability of pollutants with groups on the surface of the adsorbent improved to increase the adsorption capacity.<sup>56</sup> The values of  $\Delta G$  were calculated using eq 15.

$$\Delta G^{\circ} = -RT \ln K_{ads} \tag{15}$$

where  $K_{ads}$  is the equilibrium constant. There are significant differences in the calculations of the thermodynamic equilibrium constant for different types of contaminants. For a neutral or weak charged adsorbate, the equilibrium constant of PNP is calculated from eq 16<sup>57</sup>

$$K_{\rm ads} = (10^3 \, K_{\rm L} \cdot {\rm M} \cdot [{\rm adsorbate}]) / \gamma \tag{16}$$

where  $K_{\rm L}$  is the Langmuir constant in L mg<sup>-1</sup> (fitted isotherm model),  $\gamma$  is the activity coefficient, and M is the molecular weight of the Cr(VI) or PNP (g mol<sup>-1</sup>). On the other hand, for strong charged pollutant like Cr(VI), the calculation formula of the equilibrium constant for Cr(VI) is described by eq 17

$$q = q_{\text{max}} \left( k_{\text{ads}} \cdot C_{\text{e}}^{n} / 1 + k_{\text{ads}} \cdot C_{\text{e}}^{n} \right)$$
<sup>(17)</sup>

The negative values of  $\Delta G^{\circ}$  (Table 6) confirm spontaneous reaction. Furthermore, the enthalpy change  $\Delta H^{\circ}$  and entropy change  $\Delta S^{\circ}$  was calculated using eq 18

$$\ln K_{\rm ads} = \Delta S^{\circ}/R - \Delta H/RT \tag{18}$$

 $\Delta H^{\circ}$  values were found -86.0 and -12.07 kJ/mol for Cr(VI) and PNP, respectively. Generally, the values of  $\Delta H$  (80–200 kJ/ mol) correspond to chemical adsorption. The chemical adsorption controls the Cr(VI) ion adsorption by nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads, while PNP controlled by physical adsorption. However, the negative value of  $\Delta H^{\circ}$  < 0 proposed that Cr(VI) or PNP adsorption onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@ rGOH beads was exothermic.  $\Delta S^{\circ}$  values were 0.25 and 0.19 J/ mol K for Cr(VI) and PNP, respectively (Table 6). The positive value of  $\Delta S^{\circ}$  indicated the increased randomness at the solid/ solution interface in the adsorption process of Cr(VI) or PNP.<sup>58</sup>

The removal of inorganic/organic pollutants such as Cr(VI) and PNP onto porous materials as hydrogel beads may involve different binding mechanisms. These may include hydrogen bonding, van der Waals force, electrostatic attraction, porefilling,  $\pi - \pi$  interaction, redox reaction, cation/anion exchange, and complex formation.<sup>15</sup> Generally, the adsorption mechanisms of inorganic/organic pollutants are strongly dependent on the experimental conditions (i.e., pH, contact time, adsorbent dose, concentration, and temperature) and characteristics properties of the adsorbate (i.e., molecular size, solubility, pzc, and electron distribution). Based on the obtained results from this work, one can conclude that the binding interaction between Cr(VI) ions and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads may be established by the electrostatic attraction, redox reaction, and anion– $\Pi$  interaction. On the other hand, the removal of PNP onto  $nFe_3O_4@Fe(FAC)@rGOH$  beads may be based on physical adsorption as the  $\pi - \pi$  interaction ( $\Pi$  stacking) and Hbonding, Supporting information, Scheme S1.

**3.3. Swelling Behavior.** The swelling and retention of the  $nFe_3O_4$ @Fe(FAC)@rGOH beads were found quite fast, and Figure 9a demonstrates the swelling ratio (at 25 °C) and retention (at 60 °C). The high swelling capacity can favorably swell the internal pores of hydrogels to make the high-quality transportation of Cr(VI) and PNP within hydrogels possible. Furthermore, the high swelling capacity can also increase the surface of  $nFe_3O_4$ @Fe(FAC)@rGOH beads, making the adsorptive sites fully exposed to Cr(VI) and PNP. Therefore,



**Figure 9.** (a) Swelling ratio (25 °C) and water retention of nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads (60 °C) and (b) the effect of temperature on the swelling ratio.

high swelling capacity of hydrogels was conducive to the improvement of adsorption capacity toward investigated pollutants. As noticed, the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads can absorb about 65% water within 1 h at room temperature, while the swelling equilibrium reached at 3 h. Water penetration represents the major step, during the swelling process of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, while the large pores of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads confirmed by BET surface area analysis (section 3.1) supported channels for water molecule transfer between the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads and solution quickly. On the other hand, the swollen nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were dried at 60 °C and led to immediately shrinking in the hydrogel bead network. The retention value only decrease to 65% even after 3 h, representing the strong interconnection in the porous structure of  $nFe_3O_4(a)$ Fe(FAC)@rGOH beads.5

The thermosensitivity of the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was monitored by the swelling ratio at temperature (25–55 °C), and the results are shown in Figure 9b. The swelling ratio values decreased from 95.26 to 33.09% on-going from 25 to 60 °C. This behavior is related to the hydrophilic property of –OH and –COOH groups along the backbone of the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads. In addition, the temperature increase causes disturbance in the H-bonding between the nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads networks to enhance the shrinking of the polymeric structure.<sup>59</sup>

**3.4. Single and Simultaneous Adsorption of Cr(VI) and PNP.** Figure 10 illustrates the separate adsorption of Cr(VI) (199.35, 100.37, and 288.0 mg g<sup>-1</sup>) and PNP (110.31, 75.09, and 179.52 mg g<sup>-1</sup>) onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), rGOH, and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, respectively. rGOH had a





**Figure 10.** Regeneration of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.

lower adsorption compared to magnetic MOFs and nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads, which may be related to the possible agglomeration of hydrogels during the adsorption. It was concluded that supporting of rGOH with polymeric frameworks of magnetic MOFs to form nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads could enhance the adsorption capacity of Cr(VI) and PNP compared with  $nFe_3O_4@Fe(FAC)$  and rGOH. On the other hand, the adsorption capacities of Cr(VI) slightly decreased by 2.0, 2.94, and 6.95% for nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC), rGOH, and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads, respectively, Supporting information, Figure S4. Additionally, the adsorption capacities of PNP decreased to 10, 7.14, and 3.55% for adsorption onto  $nFe_3O_4@Fe(FAC)$ , rGOH, and  $nFe_3O_4@Fe(FAC)@rGOH$ beads, respectively. Finally, it can be concluded that the evaluated nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were efficiently removed Cr(VI) and PNP in both cases of single and simultaneous adsorption processes.

**3.5. Regeneration and Reuse of nFe\_3O\_4@Fe(FAC)@rGOH Beads.**The most significant requirements for the regeneration of hydrogel are the reversible adsorption and hydrogel stability. The reuse of the hydrogel was of great significance due to its economic impact. Eluting with mineral acid solution (HCl with a concentration of 5.0 mol L<sup>-1</sup>) was monitored in this study. The removal efficiency values were found to slightly decrease to 88.59 and 87.94% for Cr(VI) and PNP, respectively, after five rounds (Figure 10). Excellent regeneration ability compared with other previously reported hydrogels. The adsorption capacity of magnetic poly-(APTMACI) hydrogel toward arsenic ions decreased from 130 to 60 mg/g after five cycles (45%).<sup>60</sup>

### 4. CONCLUSIONS

Reduced graphene oxide hydrogel-combined-magnetic metal– organic frameworks (nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads) were successfully prepared to combine the advantages of both magnetic MOFs and rGO hydrogels for the decontamination of wastewater from heavy metal ions, Cr(VI) and organic pollutant, and *p*-nitrophenol (PNP). The fabricated nFe<sub>3</sub>O<sub>4</sub>@ Fe(FAC)@rGOH beads were characterized by SEM, TEM, FTIR, and BET analyses. Compared with the adsorption behaviors of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) and rGOH, a considerable increase in the removal capacity of the investigated pollutants onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was evident. The experimental data that referred simultaneous Cr(VI) and PNP removal by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads were 288.42 and 197.38 mg g<sup>-1</sup> under the optimum conditions. PNP adsorption onto nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads was well fitted to the pseudo-first-order kinetics, while the adsorption of Cr(VI) was described by the pseudo-second. The thermodynamic study confirmed physisorption as the predominant mechanism in the PNP removal by  $nFe_3O_4@Fe(FAC)@rGOH$  beads, while chemisorption controlled the adsorption of Cr(VI) ions. The collected results demonstrate that  $nFe_3O_4@Fe(FAC)@rGOH$  beads are an excellent and potential hydrogel-composite adsorbent for the simultaneous removal of Cr(VI) and PNP from wastewater compared with other previously reported adsorbents (Table 5).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.0c00890.

(Scheme S1) Possible binding interaction between Cr(VI)/PNP and  $nFe_3O_4@Fe(FAC)@rGOH$  beads; (Figure S1) EDX of  $nFe_3O_4@Fe(FAC)@rGOH$  beads: before adsorption and after Cr(VI) adsorption; (Figure S2) XRD of  $nFe_3O_4@Fe(FAC)$  compared with  $nFe_3O_4$ , Fe(FAC) and GO compared with graphite; (Figure S3) XRD of  $nFe_3O_4@Fe(FAC)@rGOH$  beads at different pHs; (Figure S4) comparison between single and simultaneous adsorption of target pollutants; (Table S1) instrumentations and their specifications; and effects of (Table S2) pH, (Table S3) time, (Table S4), concentration, (Table S5) ionic strength, and (Table S6) temperature on the removal of Cr(VI) and PNP by  $nFe_3O_4@Fe(FAC)@rGOH$  beads (PDF)

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#### Notes

The author declares no competing financial interest.

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This Article was retracted on May 20, 2021.

# **Supporting information**

Title page

Magnetic Metal-organic frameworks Embedded in Reduced graphene oxide hydrogel network as a promising hybrid nanocomposite for Cr(VI) and p-nitrophenol removal

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**Scheme S1.** Possible binding interaction between Cr(VI)/PNP and nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads.



**Fig. S1.** EDX of nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads a) before adsorption and b) after Cr(VI) adsorption.





**Fig. S2.** XRD of a) nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC) compared with nFe<sub>3</sub>O<sub>4</sub>, Fe(FAC) and b) GO compared with graphite.



Fig. S3. XRD of  $nFe_3O_4@Fe(FAC)@rGOH$  beads at different pHs.





Fig. S4. Comparison between single and simultaneous adsorption of target pollutants.

**Table S1.** Instrumentations and their specifications.

Instrument	Data	Specifications
Fourier transform infrared spectrophotometer FT-IR <b>BRUKER Tensor 37</b>	FT-IR spectrum	KBr pellets, 400 - 4000 cm <sup>-1</sup>
Brunauer–Emmett–Teller (BET) <b>BELSORP-mini II, BEL Japan</b>	specific surface area of a sample and pore size distribution	Liquid nitrogen, Vacuum system (10-4 Torr)
Scanning electron microscope SEM JSM-5300, JEOL	SEM images	Sputtering coating (JEOL-JFC-1100E), 25 KV
Energy-dispersive X-ray spectroscopy (EDX)	EDS spectrum	interaction of some source of X-ray excitation and a sample
High resolution-transmission electron microscopy HR-TEM <b>JEM-2100</b>	HR-TEM images	dispersing the powder in ethanol by ultrasonic vibration and on a Cu grid, 200 KV

**Table S2.** Effect of pH on the removal of Cr(VI) and PNP by  $nFe_3O_4@Fe(FAC)@rGOH$  beads (Contact time = 30 min, adsorbent dose= 20 mg, concentration = 100 mg/L)<sup>a</sup>.

рН	Adsorption capacity (mg/g)				
	Cr(VI)	PNP			
1	288.03	150.55			
2	280.18	157.37			
3	270.09	170.39			
4	200.15	180.92			
5	188.39	188.18			
6	180.30	192.34			
7	177.76	197.59			
8	168.64	180.78			
9	166.10	177.08			
10	165.94	175.71			

<sup>a</sup> Adsorption capacity of Cr(VI) and PNP are based on triplicate runs within the range ±0.3-1.1 mg/g.

**Table S3.** Effect of time on the removal of Cr(VI) and PNP by  $nFe_3O_4@Fe(FAC)@rGOH$  beads (pH for Cr(VI) = 2, pH for PNP = 5, adsorbent dose= 20 mg, concentration = 50 mg/L)<sup>a</sup>.

Time (min)	Adsorption c	apacity (mg/g)
	Cr(VI)	PNP
10	225.28	150.88
20	250.19	166.49
30	260.75	170.76
40	265.30	174.07
50	268.91	178.15
60	273.08	184.37
120	277.45	189.92
150	285.67	193.36
180	288.85	197.39

<sup>a</sup> Adsorption capacity of Cr(VI) and PNP are based on triplicate runs within the range ±0.25-0.79 mg/g.

**Table S4.** Effect of concentration on the removal of Cr(VI) and PNP by  $nFe_3O_4@Fe(FAC)@rGOH$  beads at different temperature (pH for Cr(VI) = 2, pH for PNP = 5, contact time = 20 min, dose = 20 mg)<sup>a</sup>.

Concentration	Adsorption capacity (mg/g)								
(mg/L)		Cr(VI)			PNP				
	25 °C	35 °C	45 °C	55 °C	25 ℃	35 °C	45 °C	55 °C	
5	50.37	90.13	110.39	130.63	72.19	130.08	155.62	173.95	
10	95.64	160.76	180.74	200.52	117.35	130.93	155.18	173.44	
20	145.91	250.82	270.33	290.15	167.61	180.17	205.83	223.52	
30	180.50	290.19	310.59	330.41	202.77	280.68	305.51	310.18	
40	200.73	310.33	330.75	350.36	222.60	290.66	325.49	342.63	
50	222.08	320.15	340.99	360.74	244.43	308.53	335.50	351.57	
60	225.34	330.39	350.18	370.99	247.81	310.66	338.08	363.92	
70	238.86	335.10	355.06	375.18	260.92	322.94	341.37	370.17	
80	240.47	336.75	356.52	376.20	262.07	335.08	344.40	372.66	
90	250.64	337.38	357.17	377.49	272.39	338.16	348.58	375.28	
100	255.03	338.77	358.34	378.14	277.74	339.73	349.91	378.36	

<sup>a</sup> Adsorption capacity of Cr(VI) and PNP are based on triplicate runs within the range ±0.03-1.08 mg/g.

**Table S5.** Effect of ionic strength on the removal of Cr(VI) and PNP by  $nFe_3O_4@Fe(FAC)@rGOH$  beads (pH for Cr(VI) = 2, pH for PNP = 5, contact time = 20 min, dose = 20 mg)<sup>a</sup>.

Concentration NaCl	Adsorption capacity (mg/g)	
	Cr(VI)	PNP
0	288.42	197.39
0.01	274.37	188.33
0.05	272.09	170.76
0.1	266.14	166.34
0.5	260.95	152.50
1	258.31	150.97

<sup>a</sup> Adsorption capacity of Cr(VI) and PNP are based on triplicate runs within the range ±0.82-1.24 mg/g.

**Table S6.** Effect of temperature on the removal of Cr(VI) and PNP by nFe<sub>3</sub>O<sub>4</sub>@Fe(FAC)@rGOH beads (pH for Cr(VI) = 2, pH for PNP = 5, contact time = 20 min, dose = 20 mg)<sup>a</sup>.

Temperature (K)	Adsorption capacity (mg/g)	
	Cr(VI)	PNP
298	288.42	197.39
303	289.15	199.81
308	308.14	202.36
313	309.67	205.94
318	310.88	206.91
323	311.78	207.04
328	312.08	208.79

<sup>a</sup> Adsorption capacity of Cr(VI) and PNP are based on triplicate runs within the range  $\pm 0.51$ -0.75 mg/g.