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Polyphenol rich green tea waste hydrogel for removal of copper and chromium ions from aqueous solution

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ABSTRACT

In this study, green tea waste (GTW) was used to synthesize the iron oxide (IO) nanoparticles (IO@GTW) to facilitate the adsorption of heavy metals from wastewaters. To satisfy structural integrity needs, the synthesized IO@GTW was incorporated into a polyvinyl alcohol (PVA)/alginate polymer network to obtain PVA/alginate/IO (PAI) hydrogels. Experimental techniques of transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR) were subsequently used to confirm the successful synthesis of IO nanoparticles. Scanning electron microscopy (SEM) established the porous microstructure of PAI hydrogels, while FT-IR analysis revealed the physical incorporation of IO@GTW in PAI hydrogels. The adsorption of Cu^{2+} and Cr^{6+} on PAI hydrogels was subsequently investigated. The present study was able to show that the removal ratio and adsorption capacity of the synthesized PAI hydrogels depended on the pH, initial concentration of metal ions in the solution, and contact time. The equilibrium isotherms of Cu^{2+} and Cr⁶⁺ adsorption were well-described using Langmuir and Freundlich isotherm models. The adsorption kinetics of Cu^{2+} can be modelled using the pseudo-second-order model, and the adsorption kinetics of Cr^{6+} can be modelled using both pseudo-first-order and intraparticle diffusion models. This study, therefore, demonstrates the functionality of integrating green tea waste in a polymeric composite to perform as an effective and green adsorbent for heavy metal removal, thus indicating the viability of its future application in wastewater treatment operations.

1. Introduction

The discharges of toxic metal ions in aquatic ecosystems may cause severe environmental contamination due to the bioaccumulation in the food chain (Gong et al., 2012). According to Bolisetty et al. (2019), water pollution has affected the lives of millions of people around the world, not only by increasing risk factors for illness, diseases, and death but also by the continuous reduction of the available drinkable water. A

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Fig. 1. Schematic illustration of the synthesis of iron oxide nanoparticles (IO@GTW) using green tea waste. The prepared nanoparticles were incorporated into PVA/ alginate hydrogel for Cu^{2+} and Cr^{6+} adsorptions from an aqueous solution, and then the treated water was re-used for tea cultivation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

The designation of polyvinyl alcohol/algi	nate/iron oxide nanoparticles (PAI)
hydrogels.	

Hydrogels	PAI ₁	PAI ₂	PAI_3	PAI ₄
PVA	0.2 g	0.2 g	0.1 g	0.1 g
Alginate	0.2 g	0.1 g	0.2 g	0.3 g
IO@GTW nanocomposite	0.1 g	0.2 g	0.2 g	0.1 g

similar assertion was presented by Zhang et al. (2007) and Ge et al. (2014). Furthermore, According to the work of Nriagu and Pacyna (1988) heavy metals such as copper, nickel, zinc, cadmium, and lead are toxic. Additionally, Liu et al. (2008) also identified chromium and mercury as highly toxic. Among all toxic metals, copper (Cu) exists extensively in the environment since it is widely used in paints and pigments, paper, and pulp and copper polishing (Qiu et al., 2012). Additionally, chromium (Cr) is used in the leather tanning, electroplating, nuclear energy, and textile industries (Sarin and Pant 2006). Notably, Cr exists in two oxidation states, namely, Cr^{3+} and Cr^{6+} (Cr(III) and Cr(VI)), where Cr^{6+} is shown to be 500 times more toxic to humans than Cr^{3+} (Kowalski 1994).

Several techniques have been applied for the removal of Cr^{3+} and Cr^{6+} from wastewater, including chemical precipitation, photocatalytic degradation, distillation, membrane filtration, coagulation-flocculation, reverse osmosis, electrodialysis, ion exchange, and adsorption (Jamnongkan and Singcharoen 2016). Among these techniques, the adsorption method has a broad application due to its economic feasibility, production and design simplicity, and reusability (Maapola et al., 2020). Furthermore, adsorption treatments had previously shown a high removal efficiency even under low metal ion concentration conditions (Wang et al., 2014a). Various materials such as agricultural waste activated carbon, zeolite, clay, natural, waste tires, and synthetic

polymers have been reported as suitable adsorbents for metal ion removal from wastewaters in the literature (Shavandi et al., 2012). Specifically, the utilization of waste streams (i.e. agricultural waste, waste tires etc) is anticipated to lead to an overall improvement in environmental outcomes in accordance with the circular bioeconomy paradigm (Okoro et al., 2017).

Waste green tea is abundant in China due to the Chinese people's large consumption (Liu et al., 2017). Tea waste contains beneficial polyphenols, composed of benzene rings and a variety of hydroxyl groups, which have strong reducibility and complexation abilities. Tea waste can therefore form stable complexes with heavy metals, thus facilitating the removal of heavy metals from wastewater (Crane and Scott 2012). Crucially, although tea waste possesses a chemical composition that is indicative of its functionality in heavy metal removal from wastewater, it lacks the structural integrity to be employed in practical wastewater treatment plants. We, therefore, propose the integration of green tea waste polyphenols into a naturally sourced alginate hydrogel as a heavy metal adsorbent. Alginate is a natural polysaccharide mainly composed of β -D-M (mannuronic acid) and α -L-G (guluronic acid). It comprises a large number of cyclic structures, which contain -OH and -COOH groups. As a polymer flocculant with high adsorption capacity, alginate can therefore interact with many divalent cations through a tilted egg-box (*i.e.*, Ca²⁺, Ba²⁺, and Zn²⁺) (Nie et al., 2019). However, the intramolecular or intermolecular hydrogen bonds in the alginate network hinder the rotation and movement of the molecular chain, resulting in poor toughness and reduced water resistance (Nie et al., 2020). Due to these limitations, synthetic polymers may be integrated into the alginate network to improve the alginate-based hydrogel's mechanical properties. Among many synthetic polymers, polyvinyl alcohol (PVA) is cheap and nontoxic, that may be introduced into the alginate network without inhibiting the removal of heavy metals from wastewater (Majidnia et al., 2015). Lv et al., synthesized



Fig. 2. (a, b) TEM images of IO@GTW nanoparticles at different magnifications; (c) DLS analysis of IO@GTW nanoparticles dispersed in ultrapure water, the photo inserted at the right-bottom of image b was the dried nano-powder stored in a glass bottle; (d) XRD spectrum of IO@GTW nanocomposites.

PVA/sodium alginate beads with embedded Fe^0 – Fe_3O_4 nanocomposites; such beads exhibited a robust performance of reusability in Cr(VI) removal (efficiency of 69.8% after four runs) (Lv et al., 2013). Rahman et al., developed an alginate/PVA composite to remove Mn^{7+} from the industrial wastewater, and subsequently reported that the removal ratio of Mn^{7+} increased by ~63% for alginate/PVA composite compared with that of bare alginate (A Rahman and Devi Wilfred, 2018). Idris et al., also prepared PVA-alginate beads containing maghemite nanoparticles and showed the efficiency of chromium ions removal from an aqueous solution (Idris et al., 2012). Additionally, Isawi fabricated zeolite/PVA/alginate nanocomposite beads to remove heavy metals such as Pb^{2+} and Li²⁺ from wastewater (Isawi 2020). Several studies have also confirmed that PVA/alginate composites have superior mechanical properties compared to bare alginate hydrogel alone (Liu et al., 2018).

The incorporation of nanoparticles in hydrogels leads to improvements in hydrogels' physicochemical properties and endows the hydrogel with new functions, specifically improved selective adsorption (Isawi 2020). Magnetic iron oxide nanoparticles can be synthesized using several methods such as hydrothermal, co-precipitation, ball mill, sol-gel, and microemulsion (Laurent et al., 2008). Dolgormaa et al., designed super-paramagnetic iron oxide nanoparticles (SPION)/gelatin (Gel)/PVA nanoparticles for the removal of Cu^{2+} and Zn^{2+} from an aqueous solution. The results showed that the maximum adsorption capacities of Cu^{2+} and Zn^{2+} for SPIONs/Gel were 47.594 mg/g and 40.559 mg/g, while the maximum capacities of Cu^{2+} and Zn^{2+} for SPIONs/Gel/PVA were 56.051 mg/g and 40.865 mg/g, respectively (Dolgormaa et al., 2018). Dai et al. (2019) also developed magnetic-sensitive hydrogels based on cellulose/PVA and Fe₃O₄ for entrapping molecules. Saif et al., fabricated chitosan/iron oxide and PVA/alginate/iron oxide beads for adsorption of As⁵⁺ from water. The result showed that maximum adsorption capacities of 34.4 mg/g and 40.3 mg/g were achieved by chitosan/iron oxide and PVA/alginate/iron oxide beads (Saif et al., 2019). These iron oxide nanoparticles have been previously synthesized using various green resources, such as medicinal plants (Wang et al., 2014b), fruit peels (Etemadifar et al., 2018), and seed extracts (Venkateswarlu et al., 2014).

In summary, the present study, therefore, seeks to employ waste green tea to synthesize iron oxide (IO@GTW) nanoparticles and investigate the incorporation of the prepared IO@GTW nanoparticles into PVA/alginate polymer network to form a novel composite for the adsorption of Cu^{2+} and Cr^{6+} from aqueous solutions (Fig. 1).

2. Materials and methods

2.1. Materials

Sodium alginate, calcium chloride anhydrous, iron (III) chloride hexahydrate (FeCl₃6H₂O), iron (II) chloride tetrahydrate (FeCl₂4H₂O), copper sulfate (CuSO₄), and potassium dichromate (K₂Cr₂O₇) were purchased from Macklin CO., Ltd. Polyvinyl alcohol (PVA, polymerization degree: ~1799 and hydrolysis degree: ~99%), acetone, ethanol, hydrogen peroxide (30%) and ammonium hydroxide solution (NH₃H₂O, 25–28%) were purchased from Guoyao CO., Ltd. Green tea (*Camellia sinensis*, Tea variety: Xinyang Maojian Tea) was picked from Xinyang (Henan Province, China) and manufactured in Henan Key Laboratory of Tea Plant Biology. Millipore water was used as ultrapure water for all experiments. All the chemicals were used without further purification.



Fig. 3. SEM images of PAI hydrogels at different magnifications. (a, b): PAI₁; (c, d): PAI₂; (e, f): PAI₃; (g, h): PAI₄. For clarity, the zones highlighted, using red dash lines in images c, e, and g, only indicate magnification zones shown in images d, f, and h, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2.2. Preparation of green tea waste

Clean green tea leaves were boiled in ultrapure water at the temperature of 80 $^{\circ}$ C for 1 h, with a green tea/water ratio of 0.02 g/mL imposed. The resulting green tea leaves (after boiling) were washed using ultrapure water, and the redundant water was removed using a suction filter. The obtained waste green tea was dried to constant mass using a vacuum oven at 80 $^{\circ}$ C for 7 h. Finally, the dried tea waste was crushed and sieved before undertaking further experimental investigations.

2.3. Preparation of iron oxide using green-tea-waste (IO@GTW) nanocomposite

1.6 g of FeCl₂·4H₂O and 3.1 g of FeCl₃·6H₂O were dissolved in 80 mL of ultrapure water using a flask and vigorously stirred under the nitrogen atmosphere while maintaining a mixture temperature of 80 °C. 10 mL of ammonium hydroxide solution was added to the mixture, and then 10 g of green tea waste powder was added. The resulting mixture was then agitated while maintaining the temperature at 80 °C by refluxing under the nitrogen atmosphere for 3 h. The resulting suspension was then cooled to room temperature (RT) and subsequently washed thrice using ultrapure water. Finally, the IO@GTW nanocomposite was obtained after drying to a constant mass at a temperature of 80 °C.



Fig. 4. (a) FT-IR spectra of IO@GTW nanocomposites with or without using magnet treatment. (a) FT-IR spectra of PVA, alginate, and prepared hydrogels (PAI₁, PAI₂, PAI₃, PAI₄).



Fig. 5. Swelling kinetics of PAI hydrogels (PAI₁, PAI₂, PAI₃, PAI₄), and the swelling kinetics in the first 50 min as shown in the inserted image.

2.4. Preparation of PVA/alginate/IO@GTW (PAI) hydrogels

0.1 g of IO@GTW nanocomposites was added to 20 mL of ultrapure water and ultrasonicated for 2 h at RT to obtain an IO@GTW suspension. Next, 0.2 g of PVA powder was slowly mixed with the IO@GTW suspension and stirred at 50 °C, for ~5 h, and until PVA was dissolved. 0.2 g of sodium alginate (SA) powder was then added to the solution and further stirred for 3 h at 50 °C. After this, the stirred solution was transferred to a 48-well plate and cooled to RT, then few drops of calcium chloride solution (5%, w/v) were added to each well to function as a cross-linker. After 12 h, the PAI hydrogel was formed and rinsed using ultrapure water thrice. The clean PAI hydrogel was finally stored in a

fridge at a temperature of 4 °C. In this study, four types of PAI hydrogels were fabricated, as shown in Table 1.

2.5. Physicochemical characteristics of IO@GTW nanoparticles

2.5.1. TEM analysis

The prepared IO@GTW nanocomposite powder was dispersed in ultrapure water and sonicated for 30 min. A drop of sonicated IO@GTW suspension was then added to a copper grid and dried using an infrared lamp. The morphology of IO@GTW nanocomposite was observed using transmission electron microscopy (TEM, FEI Tecnai G2 F20) operated at 200 kV.



Fig. 6. Effect of operational parameters on removal ratio of Cu²⁺ and Cr⁶⁺ for PAI hydrogels (PAI₁, PAI₂, PAI₃, PAI₄): (a, b) pH; (c, d) initial concentration; (e, f) contact time.

2.5.2. FT-IR analysis

The functional groups present in the IO@GTW nanocomposite and the PAI hydrogels were studied using attenuated total reflectance/ Fourier transform infrared spectroscopy (ATR/FT-IR, Thermo Fisher, Nicolelis 5), in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. Each spectrum had an average of 64 scans.

2.5.3. XRD analysis

The crystal structure of IO@GTW nanocomposite was assessed using an X-ray diffractometer, operating at ambient temperature, and using Cu K α radiation. A Rigaku Smartlab 9 kW diffractometer, operating at 45 kV and 200 mA with Cu K α radiation ($\lambda=1.5406$ Å) and a spinning sample holder, was used to collect the X-ray diffraction (XRD) patterns. Data were acquired over a 2 θ range of 5°–90°, with a 0.01° step size and a 1 s dwell time.

2.5.4. DLS analysis

The particle size and distribution of IO@GTW nanoparticles were characterized using Dynamic Light Scattering (DLS, Malvern Instruments, Zetasizer NanoZS, 3000E, UK). The prepared IO@GTW sample was dispersed in ultrapure water and ultrasonicated for 30 min before testing.

2.5.6. Swelling ratio

The swelling behavior of the prepared PAI hydrogels after freezedrying was investigated using the conventional gravimetric method. The mass, m_d in kg, of the dried hydrogel was initially determined, and then the dried sample was soaked in ultrapure water at room temperature. After completing a pre-designated time, the sample was retrieved, and the free water on the surface was wiped out using tissue paper, and the mass, m_s in kg, was subsequently determined. The swelling ratio in percentage (*SR*) was calculated using the following equation:

$$SR = \frac{m_s - m_d}{m_d} \times 100 \tag{1}$$

The swelling ratio of each of the prepared hydrogels was recorded until the samples reached a state of 'balanced swelling'.

2.6. Batch adsorption experiments

Batch experiments of PAI hydrogels for the adsorption of Cu^{2+} and Cr^{6+} were undertaken using a thermostatic shaker. The sample PAI hydrogel was introduced into a vial containing the heavy metal ion solution (i.e., copper sulfate, CuSO₄, or potassium dichromate, K₂Cr₂O₇). The adsorption experiments were conducted for various initial concentrations of Cu^{2+} and Cr^{6+} , ranging from 2 mg/L to 100 mg/L. All



Fig. 7. Effect of operational parameters on adsorption capacity of Cu²⁺ and Cr⁶⁺ for PAI hydrogels (PAI₁, PAI₂, PAI₃, PAI₄): (a, b) pH; (c, d) initial concentration. The contact time for all tests is 60 min.

experiments were carried out at the temperature and agitation rate of 30 °C and 180 rpm, respectively. At the end of each experimental run, the PAI hydrogel was retrieved, and the concentration of metal ions in the solution was determined using Atomic Absorption Spectrometry (Atomic Absorption Spectroscopy, AAS, Z-2000 system, Hitachi, Japan). In each batch of testing, the % removal ratio of metal ions using PAI

hydrogel was calculated using the following equation:

$$Removal \ ratio = \frac{C_0 - C_e}{C_0} \times 100$$
⁽²⁾

and, the adsorption capacity was calculated as follows;

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cu²⁺ or Cr⁶⁺ in mg/L, respectively, q_e is the adsorption capacity of PAI hydrogels for the metal ions, in mg/g, m is the weight of PAI hydrogel in g, and V is the volume of solution, in L.

2.6.1. Effect of pH

The influence of pH in the range of 2–6 on the metal adsorption behavior of PAI hydrogel was also investigated. The pH of the initial metal solution was adjusted using 0.1 M HCl. The contact time was maintained at 60 min for a mixture containing 50 mg PAI hydrogel per L of solution. The initial metal solution's pH was set to 2, 3, 4, 5, and 6.

2.6.2. Effect of initial Cu^{2+} and Cr^{6+} concentration

The influence of initial metal concentration (C_0) on adsorption behavior was investigated. For this assessment, the initial concentration of Cu²⁺ or Cr⁶⁺ was specified at 2, 10, 25, 50, and 100 mg/L. The contact time was also specified as 60 min while the pH was maintained at 2, for a mixture containing 50 mg PAI hydrogel per L of solution.

2.6.3. Effect of contact time

The contact time may influence the magnitude of metal adsorption of

the PAI hydrogels; thus, the influence of contact time on metal adsorption efficiency was studied. The effect of contact time was investigated using the metal ion at solution pH condition and an initial metal ion concentration of 4 and 25 mg/L, respectively, for both Cu^{2+} and Cr^{6+} . The effect of contact time was assessed at the different times of 1, 2, 4, 8, 12, 16, 20, 30, 45, and 60 min.

2.7. Adsorption isotherm and kinetics

The Langmuir and Freundlich isotherm models were used to evaluate the equilibrium isotherms of the adsorption of Cu^{2+} and Cr^{6+} and the kinetics of metal ion adsorption using the prepared PAI hydrogels, were subsequently assessed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models with their associated correlation coefficient (R²) values determined (Okoro et al., 2018). The adsorption equilibrium isotherms and adsorption kinetics are summarized below.

The Langmuir model is defined as follows;

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

The Freundlich model is defined as follows;

$$logq_e = \log K_F + \frac{1}{n} logc_e$$
⁽⁵⁾

The pseudo-first-order model is defined as follows;

$$log(q_e - q_t) = logq_e - k_1 t \tag{6}$$

The pseudo-second-order model is defined as follows;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(7)

The intra-particle diffusion model is defined as follows;

$$q_t = k_d t^{\nu_2} + C \tag{8}$$

where $c_e (mg/L)$ is the concentration of metal ions in equilibrium; q_e is



Fig. 8. Langmuir adsorption isotherms of Cu^{2+} (a) or Cr^{6+} (b) on PAI hydrogels, while using pH at 4 and the contact time of 60 min.

the amount of metal ions adsorbed in equilibrium in mg/g; q_m is the maximum adsorption capacity of the adsorbent in mg/g; and q_t denotes the concentration of metal ions, in mg/g and adsorbed at time, t, in min; 1/n denotes an empirical parameter in the Freundlich model; K_L and K_F are the binding constants of the Langmuir equation and the Freundlich equation respectively, k_1 and k_2 represent the pseudo-first-order and pseudo-second-order adsorption rate constants, in min⁻¹ and in g mg⁻¹ min⁻¹; C is a constant and dimensionless; and k_d is the intra-particle diffusion rate constant in mg g⁻¹ min^{-1/2}.

2.8. SEM of PAI hydrogels

The morphologies of the fabricated PAI hydrogels after (and before) metal adsorption were observed using SEM. The PAI hydrogels sample was initially coated with a 10 nm thin platinum layer, using an Emitech K575x sputter coater. After coating, the samples were visualized using a JEOL JSM-6700F field emission scanning electron microscope (JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 5 kV. The images were subsequently generated.



Fig. 9. Freundlich adsorption isotherms of Cu^{2+} (a) or Cr^{6+} (b) on PAI hydrogels, while using pH at 4 and the contact time of 60 min.

2.9. Statistical analysis

Each experiment was performed in triplicate if without a particular explanation, and the results are expressed as mean \pm SDs.

3. Results and discussion

3.1. IO@GTW nanoparticles characterization

In this study, iron oxide (IO@GTW) nanoparticles were synthesized using green tea waste. The morphology and size of IO@GTW nanoparticles were characterized by TEM and DLS, as shown in Fig. 2a–c. The ambiguous nanoparticle outline was observed in TEM images using different magnifications, and the aggregation was observed. The average diameter was challenging to be obtained via Fiji software quantified analysis. The dried IO@GTW nanocomposite powder could be stored in a glass bottle at room temperature (RT), as shown in the photo inserted at the right-bottom of Fig. 2b. The IO@GTW nanocomposite was dispersed in ultrapure water, and the hydrodynamic diameter was quantitatively evaluated by DLS (Fig. 2c). The z-average was 105.34 nm, and the polydispersity index (PDI) value was 0.15, proving that IO@GTW nanoparticles were not aggregated in water.

Furthermore, X-ray diffraction (XRD) was used to analyze the crystal structure of IO@GTW nanocomposite, and the XRD spectrum was shown in Fig. 2d. The crystal faces (2 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), and (4 4 0), were closely matched with the diffraction peaks of magnetite (JCPDS card, No. 77–1545), and the crystal faces (1 1 1), (2 1 0), (2 2 0), (3 1 1), and (4 0 0) were matched with the diffraction peaks of magnetite and maghemite (JCPDS card, No. 25–1402). The peaks from magnetite and maghemite could be distinguished, and some peaks overlapped. Besides, the broad peaks in the range of $10-30^{\circ}$ indicated the incorporation of organic molecules (*i.e.*, chemical groups) from green tea waste in the prepared IO@GTW nanoparticles.



Fig. 10. Kinetic fits for Cu²⁺ adsorption on PAI hydrogels using pseudo-first-order (a), pseudo-second-order (b), and intra-particle diffusion models (c), while using pH at 4, the initial concentration at 50 mg/L.

3.2. PAI hydrogels characterization

The synthesized IO@GTW nanoparticles were incorporated into PVA/alginate hydrogels to obtain PAI hydrogels. The surface morphology and porous topography of dried PAI hydrogels were investigated using SEM, as shown in Fig. 3. The interconnected porous microstructure was displayed for all PAI hydrogel samples; some wrinkles and cavities were observed due to the polymer network's partial collapse during the freeze-dried process. Fig. 3 also shows that the pore wall's morphology for different PAI samples varied, mainly due to the miscibility between PVA and alginate and different concentrations of IO@GTW nanoparticles. The concentration of IO@GTW nanoparticles increased to 40%, the morphology of the hydrogel became more granular with uneven grain sizes (Fig. 3d and f). Furthermore, the images highlighted in Fig. 3d and f showed that different PVA/alginate ratios led to different morphologies even when keeping the concentration of the IO@GTW nanoparticles unchanged.

FT-IR was employed to analyze the chemical groups in IO@GTW nanoparticles and the chemical interaction between PVA, alginate, and IO@GTW nanoparticles, as shown in Fig. 4. In this work, IO@GTW nanoparticles could be obtained using the precipitation (due to their gravity) or magnet treatment, and both FT-IR spectrum were shown in

Fig. 4a. There was no difference in the FT-IR spectrum of IO@GTW nanoparticles using both treatments. The 'sharp' peaks of IO@GTW nanoparticles were observed at wavelengths of 2925 cm⁻¹, 1635 cm⁻¹, 1133 cm⁻¹, and 798 cm⁻¹, representing the typical peaks of iron oxide. The 'broad' peaks observed at the wavelength of 918 $\rm cm^{-1}$ and 798 cm⁻¹ were due to the stretching vibration of the metal oxide group (Fe–O). The broad peak observed at the wavelength of 588 cm^{-1} was due to the maghemite (Periakaruppan et al., 2021). The broad peak observed at the wavelength of 3294 cm⁻¹ corresponded to O-H stretching from phenol or alcohol, while the peak at the wavelength of 2854 cm⁻¹ was due to the contribution of C–H stretching vibration (Vanathi et al., 2014). Finally, C=O stretching of amide groups was responsible for the peak observed at the wavelength of 1599 cm⁻¹ (Vanathi et al., 2014). On the other hand, the FT-IR spectrum of PVA, alginate, and PAI hydrogels was shown in Fig. 4b. For the PVA spectrum, the peak at the wavelength of 3291 cm⁻¹ corresponding to the extension of –OH group, the peak at the wavelength of 2929 cm^{-1} was due to the symmetric stretching of CH₂, and the peak at the wavelength of 1417 cm^{-1} indicated the presence of CH₂ bending. For alginate, the peak at the wavelength of 1590 cm⁻¹ corresponded to the stretching vibration of the conjugated C=O group, and the peaks at the wavelengths of 1095 and 1059 cm⁻¹ was due to the stretching vibration of C–O–C groups and



Fig. 11. Kinetic fits for Cr⁶⁺ adsorption on PAI hydrogels using pseudo-first-order (a), pseudo-second-order (b), and intraparticle diffusion models (c), while using pH at 4, the initial concentration at 50 mg/L.

indicative of the presence of a sugar structure (Wang et al., 2020). The spectra of PAI hydrogels did not display apparent chemical interaction between PVA, alginate, and IO@GTW nanoparticles, proving that IO@GTW nanoparticles were mainly physically incorporated into polymer networks of PVA/alginate.

The swelling behavior of PAI hydrogels in water was analyzed, as shown in Fig. 5. It was observed that all PAI samples had a fast swelling rate in the first 10 min and then attained equilibrium at 60 min. The swelling and equilibrium swelling ratio of PAI hydrogels mainly depended on the organic/inorganic ratio. Samples PAI₁ and PAI₄ with a higher polymer concentration showed a higher swelling ratio than PAI₂ and PAI₃. However, sample PAI₁ displayed a higher swelling ratio (around 1287.7%) than PAI₄ (1201.7%); and PAI₂ performed a higher swelling ratio (1034.5%) than PAI₃ (956.6%), mainly because PAI₁ and PAI₂ had a higher content of PVA (40 wt%) than PAI₄ and PAI₃ (20 wt %), and PVA is a water-soluble polymer.

3.3. Cu (II) and Cr (VI) adsorption evaluation

We investigated the potential removal ability of the prepared PAI hydrogels on Cu^{2+} and Cr^{6+} . The influence of variations in the pH, initial

concentration (C_0), and contact time on the removal ratio of Cu²⁺ and Cr^{6+} is highlighted in Fig. 6. Fig. 6a and b show that at a constant initial concentration of 50 mg/L for Cu^{2+} or Cr^{6+} and a contact time of 60 min, decreasing the pH of the solution from 6 to 2, leads to an increase in Cu²⁺ removal efficiency; however, Cr⁶⁺ removal efficiency was observed to increase initially and then decrease. These observations suggest that differences in the adsorption mechanism exist. This inverse correlation between pH decreases and the increased Cu²⁺ removal efficiency may be due to the formation of copper chloride ion complexes (i.e., $CuCl_4^{2-}$) in such (low pH) acid solutions. This is because the reduction of the pH enhances the concentration of H⁺ ions protonating the adsorbent surface, leading to an increase in the electrostatic attractions of the anions of the copper ion complex and the adsorbent. Similarly, at low pH value, chromium, which may exist in the form of $\mathrm{HCrO}_4^-,$ is readily adsorbed on the adsorbents via electrostatic charges. At higher pH values, however, complexes of CrO_2^{-4} and $Cr_2O_2^{-7}$ forms, which are less well adsorbed to the adsorbents, are generated (Abdelwahab et al., 2007).

At the pH value of 4 and contact time of 60 min, both Cu^{2+} and Cr^{6+} removal efficiencies decreased with increasing initial concentration from 2 mg/L to 100 mg/L. The higher initial concentration of metal ions



Fig. 12. SEM images of PAI hydrogels after Cu^{2+} adsorption using different magnifications, (a_1, a_2) : PAI₁; (b_1, b_2) : PAI₂; (c_1, c_2) : PAI₃; (d_1, d_2) : PAI₄. EDX analysis of Cu^{2+} absorbed PAI hydrogels, (a_3, a_4) : PAI₁; (b_3, b_4) : PAI₂; (c_3, c_4) : PAI₃; (d_3, d_4) : PAI₄, pH = 4; initial concentration: 50 mg/L; contact time: 60 min.

may cause more available binding sites on the surface of the adsorbent. However, the capacity of available active sites may decrease, leading to the decrease of metal ions removal efficiency. The removal ratio of metal ions was also significantly influenced by the contact time. At the pH condition of 4 and the initial concentration of 50 mg/L, both Cu^{2+} and Cr⁶⁺ removal ratios increase as contact time increases. Fig. 6 also shows that for Cu²⁺ and Cr⁶⁺, removal ratios present rapid increases in the first 10 min for Cu^{2+} and 20 min for Cr^{6+} and then reach equilibrium values. Fig. 6c and d show that sample PAI₄ hydrogel present the highest removal ratio for Cu^{2+} (59.78%) and Cr^{6+} (52.12%) while sample PAI₂ hydrogel possessed the lowest removal ratio \sim 40% for Cu²⁺ and \sim 43% for Cr⁶⁺. These observations are consistent with the trends in the alginate content since PAI₂ hydrogel had the lowest alginate content of 20 wt% and PAI₄ hydrogel had the highest alginate content of 60 wt%. The removal ratio of Cu²⁺ for PAI hydrogels in this work is lower than that of magnetic bentonite/carboxymethyl chitosan/sodium (Mag-Ben/CCS/ Alg) hydrogel fabricated by Zhang et al.; however, it takes 90 min for Mag-Ben/CCS/Alg hydrogel to reach equilibrium, and for PAI hydrogels, it takes around 30 min to the maximum value. Besides, the maximum adsorption capacity of Cu²⁺ for PAI hydrogels could reach over 60 mg/g as the initial concentration over 100 mg/L, which is close to the maximum adsorption capacity for Mag-Ben/CCS/Alg hydrogel at 56.79 mg/g (Zhang et al., 2019).

The above observations, therefore, confirm that alginate in PAI hydrogels played a critical role in the removal of metal ions, possibly because the 'egg-box' structure of alginate can capture much more metal ions than PVA. For samples PAI₁ and PAI₃ with the same content of alginate, PAI₁ shows a higher metal ions removal ratio (~52.34% for Cu²⁺, and ~48.44% for Cr⁶⁺) compared to the metal ions removal ratio (~48.46% for Cu²⁺, and ~46.32% for Cr⁶⁺) when PAI₃ hydrogel is used. This observation is due to the higher content of PVA in the PAI₁ hydrogel

of 40 wt% compared to the PVA in the PAI₃ hydrogel of 20 wt%. Due to the increase of PVA content, there is an associated increased in the number of hydroxy groups in PAI hydrogels, which are then available for the adsorption of more metal ions in conjunction with the functional groups in alginate (Cao et al., 2021).

Additionally, the adsorption capacity of Cu²⁺ and Cr⁶⁺ for PAI hydrogels was studied, as shown in Fig. 7. The Cu^{2+} adsorption capacity for all PAI samples increases with decreasing the pH of the metal ions solution. The Cu $^{2+}$ adsorption capacity shows the lowest values (38.2 \pm 1.91 mg/g for PAI_1, 36.1 \pm 1.80 mg/g for PAI_2, 37.2 \pm 1.86 mg/g for PAI_3, and 41 \pm 2.05 mg/g for PAI_4) at a pH of 6. The obtained Cu $^{2+}$ adsorption capacity values for PAI hydrogels in this work are higher than Cu^{2+} adsorption capacity when cellulose hydrogels (28.4 mg/g) (Teow et al., 2018) or carboxymethyl cellulose-based hydrogels (0.2–2.5 mg/g depends on pH from 5 to 9) are employed (Baiya et al., 2019). However, the Cr^{6+} adsorption capacity shows the highest values (59.1 \pm 2.96 mg/g for PAI_1, 55.2 \pm 2.76 mg/g for PAI_2, 58.2 \pm 2.91 mg/g for PAI_3, and 61.2 \pm 3.06 mg/g for PAI_4) at a pH of 4. The adsorption capacity of PAI hydrogels on both Cu²⁺ and Cr⁶⁺ influenced by pH was similar to the results of the metal ions removal ratio. At the constant pH value of 4 and contact time of 60 min, the adsorption capacity for both metal ions increased with increasing the initial concentration of Cu^{2+} or Cr^{6+} solution. This observation is expected since higher metal concentrations lead to increments in the concentrations of metals adsorbed. Furthermore, sample PAI₄ showed the highest adsorption capacity (45.2 \pm 2.26 mg/g for Cu²⁺ and 61.2 \pm 3.06 mg/g for Cr⁶⁺), and PAI₂ exhibited the lowest adsorption capacity (39.2 \pm 1.96 mg/g for Cu^{2+} and 55.2 \pm 2.76 mg/g for Cr^{6+}) at a pH of 6, and the same results were observed at different pH values,. These observations further demonstrated that alginate in PAI hydrogels played an important role on the adsorption of the metal ions.



Fig. 13. SEM images of PAI hydrogels after Cr^{6+} adsorption using different magnifications, (a₁, a₂): PAI₁; (b₁, b₂): PAI₂; (c₁, c₂): PAI₃; (d₁, d₂): PAI₄. EDX analysis of Cr^{6+} absorbed PAI hydrogels, (a₃, a₄): PAI₁; (b₃, b₄): PAI₂; (c₃, c₄): PAI₃; (d₃, d₄): PAI₄. PAI₄. PAI₄ = 4; initial concentration: 50 mg/L; contact time: 60 min.

3.4. Adsorption isotherm

Langmuir isotherm (equation (4)) and Freundlich isotherm (equation (5)) were used to describe the equilibrium behavior between metal ions (Cu^{2+} or Cr^{6+}) adsorbed on PAI hydrogels and metal ions in the solution for initial concentrations ranging from 2 mg/L to 100 mg/L. The Langmuir model indicates that monolayer adsorption onto the homogeneous surface occurred, with equivalent binding sites. The Langmuir adsorption isotherms of metal ions on PAI hydrogels are shown in Fig. 8.

The Freundlich model indicates that surface heterogeneity supports binding sites of various affinities. The Freundlich adsorption isotherms are displayed in Fig. 9. It was found that the adsorption of Cu^{2+} or/and Cr^{6+} on the prepared PAI hydrogels could be described by both Langmuir and Freundlich models since both models had comparable mean R^2 values of 0.974 and 0.978, respectively, based on the adsorption data sets.

3.5. Adsorption kinetics

In this section, the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to quantitatively analyze the adsorption kinetics of metal ions of Cu^{2+} and Cr^{+6} on PAI hydrogels, and the kinetic fitting results are shown in Fig. 10 and Fig. 11, respectively.

Fig. 10 shows that the adsorption kinetics of Cu^{2+} ions on PAI hydrogels can be best described using the pseudo-second-order model with the high correlation coefficients, R^2 , greater than 0.99 in all cases. The intraparticle diffusion model is also applicable to describe the adsorption kinetics of Cu^{2+} ions on PAI hydrogels. The adsorption kinetics of Cu^{2+} ions, however, shows the lowest correlation coefficients, R^2 , which ranged from 0.81 to 0.85, when the pseudo-first-order model

is employed. However, the correlation coefficients are improved to a mean value of \sim 0.93 when model fittings are only assessed for the first 12 min (images inserted in the top-right of Fig. 11a–d). This observation is due to the high adsorption rates observed initially, leading to large removal ratios, as discussed earlier above.

On the other hand, Fig. 11 shows that the adsorption kinetics of Cr^{6+} ions on PAI hydrogels are well described by both pseudo-first-order and intraparticle diffusion models, as demonstrated by the mean R^2 values of 0.973 and 0.978, respectively. The pseudo-second-order model, however, presents the poorest correlation with an R^2 value of 0.885.

3.6. Morphology of PAI hydrogels after metal adsorbed

After metal adsorption experiments, the PAI hydrogels were freezedried, and their morphologies were also investigated by SEM and EDX analysis and the results presented in Fig. 12 and Fig. 13. Fig. 12 displays the SEM images of Cu^{2+} absorbed PAI hydrogels and the EDX analysis results. Fig. 13 displays the SEM images of Cr^{6+} absorbed PAI hydrogels and the EDX analysis results. Figs. 12 and 13 show that the interconnected porous microstructures of PAI hydrogels are retained after metal adsorption, such that in each case, the adsorbed metal ion is represented using yellow lines in the SEM images. The SEM images also show that granular sediment is present on the surface of the pore wall. Furthermore, deposited particles are observed for sample PAI₄ compared to samples PAI₁, PAI₂, and PAI₃. The elemental composition of the deposited area was analyzed using EDX, with the elements of carbon (C), oxygen (O), sodium (Na), chlorine (Cl), sulfur (S), iron (Fe), platinum (Pt) and copper (Cu), also detected.

4. Conclusion

Recognizing the need to explore novel pathways for waste green tea management, the presence of hydroxyl and phenolic groups in waste green tea suggested the functionality of waste green tea in the adsorption of heavy metal ions from wastewaters. The present study focused on the adsorption of the highly polluting metal ions of Cu^{2+} and Cr^{6+} from aqueous solutions. Concerns of the poor structural integrity of the waste green tea led to its incorporation into a fabricated hydrogel composite composed of PVA, alginate, and iron oxide (IO) nanoparticles. Experimental investigations of the adsorption capacity of the fabricated hydrogels containing waste green tea (PAI hydrogels), as the active ingredient, showed that the adsorption of Cu²⁺ and Cr⁶⁺ was significantly dependent on the contact time, solution pH, and initial metal ion concentration. Additional investigations regarding adsorption equilibria and adsorption kinetics were also undertaken. The study was able to demonstrate the sufficiency of Langmuir and Freundlich isotherm models for the adsorption of Cu^{2+} and Cr^{6+} using the waste green teabased adsorbents. Similarly, the adsorption kinetics for Cu^{2+} and Cr^{6+} were shown to be best described using the pseudo-second-order model and the first order model, respectively. The study therefore established that the use of waste green tea as the active agent for heavy metal adsorption, thus providing an opportunity to explore alternative and novel uses of this significant waste stream, while, simultaneously resolving the undisputed waste management challenge. This study clearly serves to promote improved environmental outcomes and reinforces the prevailing global need for paradigm transitions to a circular based economy.

Declaration of competing interest

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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