



공학석사 학위논문

Adsorption of acetaminophen and ibuprofen to sucrose-derived spherical carbon materials: Multi-factor experiments and modeling

수크로스 기반의 탄소구체를 이용한 아세트아미노펜과 이부프로펜 흡착: 다중변수실험과 모델링

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Adsorption of acetaminophen and ibuprofen to sucrose-derived spherical carbon materials: Multi-factor experiments and modeling

A THESIS SUBMITTED TO THE DEPARTMENT OF LANDSCAPE ARCHITECTURE AND RURAL SYSTEMS ENGINEERING AND THE COMMITEE ON GRADUATE STUDIES OF SEOUL NAIONAL UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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아세트아미노펜과 이부프로펜 흡착:

다중변수실험과 모델링

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Abstract

Acetaminophen (AAP) and Ibuprofen (IPF) are among the most prescribed nonsteroidal anti-inflammatory drugs recently, but they are not readily removed in conventional wastewater treatments. Here, we investigate the adsorption characteristics of contaminants (AAP and IPF) onto spherical carbon materials (SCMs), which was synthesized through hydrothermal carbonization of sucrose followed by calcination. Single-factor experiments were performed by varying the pH, contact time, temperature, adsorbent dose, and initial contaminants concentration. The maximum adsorption capacity for AAP is 92.0 mg/g and IPF is 95.6 mg/g. The SCMs were successfully regenerated after methanol washing. The Raman, FTIR, XPS spectra and pH experiments data suggest that π - π interaction, n- π^* interaction, hydrogen-bond formation, and electrostatic repulsion could take place between the SCMs and contaminants. Those mechanisms were explored and visualized with molecular modeling using CHEM3D. A pore-filling mechanism could contribute to the adsorption in view of the molecular size of contaminants and the average pore diameter of the SCMs. Multi-factor adsorption experiments were executed with pH, temperature, SCMs dosage, and initial contaminants concentrations as input variables and contaminants adsorption capacity as an

output variable, and an artificial neural network (ANN) model with 2 hidden layers were developed to sufficiently describe the adsorption data. Further analyses with additional experimental data confirm that the ANN model possessed good predictability for multi-factor adsorption. In the ANN model, initial contaminants concentration was most important factor, according to the relative importance of the input variables.

Keywords: Spherical carbon materials, Adsorption, Acetaminophen, Ibuprofen, Molecular modeling, Artificial neural network

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1. Introduction

1.1. Background

In the past decade, pharmaceuticals and personal products (PPCPs) have been continuously detected in water environment, and emerged as a new concern among researchers (Ren et al., 2020). Nonsteroidal anti-inflammatory drugs (NSAIDs) are prescribed for treatment of human and animal diseases to relieve pain and fever as well as reduce inflammation (Ghemit et al., 2019). As micropollutants, NSAIDs are found widely in aquatic environments, causing adverse impacts on animals and human beings (Wang et al., 2020; Priyan et al., 2021).

Various treatment processes such as chemical precipitation, ion exchange, membrane filtration, oxidation, and adsorption are used to remove contaminants from wastewater (Ghosh et al., 2022). Adsorption is an especially attractive technique for pollutant removal because of its cost effectiveness, energy efficiency, less sludge production and simple operation (Oba et al., 2021). Suitable adsorbents must be utilized to effectively treat wastewater.

1

1.1.1. Contaminants

Acetaminophen (AAP), also known as N-acetyl-para-aminophenol or paracetamol, is an analgesic and non-steroidal anti-inflammatory drug frequently prescribed to treat fever and pain (Moussavi et al., 2016). It is also an emerging pharmaceutical micropollutant because it is not easily removed by conventional wastewater treatment, and it has been detected in water bodies worldwide, posing risks to aquatic environments and human health (Kollarahithlu and Balakrishnan, 2021). Effective treatment techniques are therefore necessary to remove AAP from polluted water, and adsorption is considered a favorable approach because of its cost-effectiveness and ease of use (Cabrita et al., 2010). Various types of adsorbents have been tried to the adsorption of AAP in aqueous solutions, including orange peels (Afolabi et al., 2020), chestnut shells (Parus et al., 2020), waste cotton seeds (Sivarajasekar et al., 2018), coconut shells (Yanyan et al., 2018), seed husks (Quesada et al., 2019), sugarcane bagasse (Vera et al., 2021), vegetable waste (Villaescusa et al., 2011), silica gel (Spaltro et al., 2021), silica nanocomposites (Kollarahithlu and Balakrishnan, 2021), organo-sepiolite (Gómez-Avilés et al., 2021), cellulose (Benosmane et al., 2021), and chitosan (Malesic-Eleftheriadou et al., 2021).

Ibuprofen (IPF) is a 2-(4-isobutylphenyl) propionic acid (chemical

formula C13H18O2) that is primally prescribed for the treatment of fever, pain, and inflammation. IPF is one of the most prescribed nonsteroidal antiinflammatory drugs (NSAIDs) currently and is released continuously into aquatic environments through urinary excretion of humans and animals. IPF has been commonly detected in surface water at a concentration level up to a few µg/L, posing adverse effects to aquatic organisms and human health (Davarnejad et al., 2018). As a pharmaceutical micropollutant, IPF is not readily removed in conventional wastewater treatment. Therefore, efficient removal of IPF from water and wastewater is of crucial concern to environmental researchers worldwide. Various treatment techniques have been explored to remove IPF from aqueous solutions, including photocatalytic methods, Fenton-based oxidation, hybrid ozonation, ultrasonic treatments, and adsorption (Brillas, 2022).

1.1.2. Spherical carbon materials (SCMs)

Spherical carbon materials can be prepared from biomass, saccharides, and carbohydrates using hydrothermal treatment, arc discharge, chemical vapor deposition, thermal plasma, and laser ablation (Deshmukh et al., 2010). Spherical carbon materials have gained the attention of environmental researchers because of their potential as adsorbents for aqueous contaminants (Nieto-Márquez et al., 2011). Recently, a number of researchers prepared spherical carbon materials from monosaccharides (glucose and xylose) and disaccharides (sucrose) through simple hydrothermal synthesis with no activation procedure and applied them to the removal of inorganic and organic contaminants in aqueous solutions (Tran et al., 2020; Tran et al., 2017; Gupta et al., 2019; Yoo et al., 2021; Xu et al., 2021). For example, Tran et al. (2017) synthesized saccharide-derived spherical biochar (spherical carbon materials) from three saccharides (glucose, xylose, and sucrose) through hydrothermal carbonization followed by calcination in a porcelain crucible. When the spherical carbon materials were applied to the adsorption of cationic contaminants such as Cu(II), Pb(II), and methylene green 5, the adsorption capacities toward these contaminants were decreased in the order of glucosebiochar > sucrose-biochar > xylose-biochar. Gupta et al. (2019) prepared monodispersed carbon nanospheres from glucose, xylose, and sucrose using hydrothermal treatment and applied them to the photocatalytic degradation of

methylene blue. Yoo et al. (2021) synthesized spherical carbon materials from sucrose through facile hydrothermal carbonization, reporting that they had a far greater adsorption capacity toward diclofenac compared with hydrothermally prepared glucose-derived spherical carbon materials (Xu et al., 2021). These studies suggest that saccharide-based spherical carbon materials prepared through a hydrothermal method are promising adsorbents for contaminant removal due to the simplicity of their preparation and low production costs compared with activated carbon materials.

Based on a literature review, spherical carbon materials (SCMs) were prepared in this study from pure sucrose through hydrothermal carbonization and post-annealing processes.

1.2. Objective

This study focused on three objectives. The first objective was to examine the characteristics of the SCMs before and after contaminants adsorption using analytical instruments. These included Raman spectroscopy, thermal analysis, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The second objective was to explore the adsorption characteristics of the SCMs toward contaminants through adsorption experiments and model analyses. Adsorption experiments were implemented to examine the influences of pH, contact time, adsorbent dosage, initial contaminants concentration, and temperature on the contaminants removal rate. Molecular modeling with CHEM3D software was performed to better understand and visualize the adsorption mechanisms of contaminants onto the SCMs. The third objective was to develop an artificial neural network (ANN) model based on the adsorption data acquired from multifactor experiments. ANN model was adopted to optimize the AAP and IPF adsorption process.

2. Literature Reviews

2.1. Adsorption of AAP using carbon-based adsorbents

Carbon materials are used as adsorbents to remove AAP from aqueous solutions. These include activated carbons (Nguyen et al., 2020; Streit et al., 2021; Dutta et al., 2015; Rao et al., 2021), biochars (Grisales-Cifuentes et al, 2021; Tran et al., 2020), microporous/mesoporous carbons (Jedynak et al., 2019), graphene oxides (Moussavi et al., 2016), graphene nanoplatelets (Rosli et al., 2021), carbon nanotubes (Yanyan et al., 2018; Ivanković et al., 2021), and fly ash-based carbon (Galhetas et al., 2014). Several researchers have explored the adsorption characteristics of carbon-based adsorbents toward AAP using single-factor experiments (Nguyen et al., 2020; Streit et al., 2021; Dutta et al., 2015; Rao et al., 2021; Grisales-Cifuentes et al, 2021; Tran et al., 2020; Jedynak et al., 2019; Rosli et al., 2021; Ivanković et al., 2021; Galhetas et al., 2014). They examined the effects of solution pH, adsorbent dosage, initial concentration, contact time, and temperature on the adsorption of AAP, reporting that carbon-based adsorbents can effectively remove AAP from aqueous solutions. More recently, multi-factor experimental approaches have been applied to explore the adsorption characteristics of AAP on carbon-based materials (Afolabi et al., 2020; Sivarajasekar et al., 2018). Afolabi et al. (2020) examined the adsorption of AAP on chemically modified orange peel

using multi-factor experiments. They applied an artificial neural network (ANN) to investigate the simultaneous effects of three input variables (initial AAP concentration, contact time, and temperature) on a target variable (adsorption efficiency). They then developed an optimal ANN model with a three-layered architecture (input, hidden, and output layers) to successfully predict AAP adsorption efficiency on chemically modified orange peel (Afolabi et al., 2020). Sivarajasekar et al. (2018) investigated and optimized the adsorption of AAP on waste cotton seed–activated biomass. They used a response surface methodology (RSM) to develop a second-order polynomial equation to express the relationship between five input variables (adsorbent dosage, initial AAP concentration, contact time, pH, and temperature) and response (percentage removal of AAP) (Sivarajasekar et al., 2018).

2.2. Adsorption of IPF using carbon-based adsorbents

For the removal of IPF from water, researchers synthesized functionalized adsorbents based on various materials such as silica particles, iron oxides, metal organic frameworks (MOFs), and clays (Obradović et al., 2022; Sun et al., 2019; Ramírez et al., 2021; Kollarahithlu and Balakrishnan, 2021). These adsorbents included iron nanoparticle-based composites (Ali et al., 2016), zeolite-based hybrid adsorbent (Bandura et al., 2021), surface-modified bentonite (Ghemit et al., 2019), aluminated silica nanoparticles (Kamarudin et al., 2015), dendrimer-modified halloysite (Kurczewska et al., 2020), modified montmorillonite and mica (Martín et al., 2019), and copper-doped MIL-101(Fe) (Xiong et al., 2021). Furthermore, carbon-based materials such as biomass-derived activated carbons, carbon nanotubes, commercial granular activated carbons, and acid-modified kola nut husk have been applied for the adsorption of IPF (Dubey et al., 2010; Álvarez-Torrellas et al., 2016; Nourmoradi et al., 2018; Ali et al., 2019; Bello et al., 2021). As examples, Cho et al. (2011) prepared single-walled carbon nanotubes, multiwalled carbon nanotubes (MWCNTs), and oxidized MWCNTs for the adsorption of IPF in aqueous solutions. Iovino et al. (2015) analyzed the adsorption of IPF onto granular activated carbon. Al-Yousef et al. (2021) synthesized coca shellbased adsorbents with and without plasma and glycine functionalization for IPF adsorption.

2.3. Adsorption of contaminants using SCMs

Regarding application of spherical carbon materials to adsorption of AAP, one study recently reported by Tran et al. (2020) examined AAP adsorption on spherical biochar (micron-sized spherical carbon materials) in aqueous solutions. Spherical biochar from pure glucose was synthesized through a two-stage process of hydrothermal carbonization and pyrolysis. They explored the adsorption characteristics of AAP on glucose-derived spherical biochar by examining the influences of pH, ionic strength, contact time, initial AAP concentration, and temperature in single-factor experiments (Tran et al., 2020). Further studies are needed to extend our knowledge of adsorption characteristics and mechanisms of AAP onto spherical carbon materials hydrothermally synthesized from sucrose.

Recently, spherical carbons have drawn the attention of researchers involved with water and wastewater treatment due to their applicability as adsorbents to remove inorganic and organic contaminants from aqueous solutions (Jia et al., 2016; Tran et al., 2018; Li et al., 2020; Dong et al., 2020; An et al., 2022). Wei and Cai (2020) hydrothermally synthesized N-doped spherical carbon from waste peanut hulls for Cr(VI) removal from aqueous solutions. Tran et al. (2019) applied glucose-derived spherical activated carbon for the adsorption of dyes and phenol. Zhao et al. (2017) prepared spherical activated carbon from sucrose for toluene adsorption. Chowdhury et al. (2016) used spherical activated carbon derived from lignocellulosic biomass for Cu(II) adsorption. These studies recommend spherical carbons as promising adsorbents for aqueous contaminant removal. Limited studies have been reported for the application of spherical carbons for the adsorption of IPF in aqueous solutions so far. Ulfa et al. (2020) prepared carbon microspheres via a co-templating method, with sucrose as a carbon precursor and a mixture of Pluronic F127 and gelatin as a co-template. They synthesized the carbon microspheres from the mixture of Pluronic F127, gelatin, and sucrose through hydrothermal treatment followed by pyrolysis under nitrogen flow and used them for IPF adsorption in aqueous solutions. Xu and An (2016) modified commercial spherical activated carbon by polymerized ionic liquid and applied the adsorbent for the removal of IPF from water. However, in these case of studies using SCMs, only the results of adsorption experiments were analyzed, and no additional information was obtained through modeling.

3. Materials and Methods

3.1. Synthesis of the SCMs

The SCMs was synthesized following the procedures modified from the studies of Zhao et al. (2017) and Joula and Farbod (2015). D(+)-Sucrose (purity 99.5%) purchased from Samchun Chemicals (Pyeongtaek, Republic of Korea) was used as a carbon precursor. A sucrose solution (0.1 M) was prepared in a conical tube and transferred into a Teflon-lined autoclave. The sealed autoclave was put into a heating mantle and heated at 180°C for 8 h. Then, the precipitate was washed in deionized water/ethanol and dried to obtain spherical hydrochar (SH). Thereafter, the hydrochar was placed in an electric furnace and was calcined at 400°C for 0.5 h in air to produce the SCMs.

3.2. Single-factor experiments

3.2.1. Single-factor experiments for AAP adsorption

Single-factor experiments were performed under batch conditions. Adsorption experiments were conducted in duplicate to examine the effects of solution pH, contact time, initial solute concentration, temperature, and adsorbent dose on the adsorption of AAP. These variables were also selected as major factors in prior studies (Mondal et al., 2016; Esfandiari et al., 2017; Gadekar et al., 2019; Mojiri et al., 2019). The chemical characteristics of AAP are summarized in Table 1 (Elbagerma et al., 2010; Igwegbe et al., 2021). Prior to the experiments, AAP (CH₃CONHC₆H₄OH, molecular weight: 151.16 g/mol; purity: \geq 99%; Sigma-Aldrich) was dissolved in deionized water to prepare a stock solution (1,000 mg/L). Unless stated otherwise, the experiments were performed at pH = 6, adsorbent dose = 0.1 g/L, initial AAP concentration = 10 mg/L, contact time = 24 h, and temperature = 30°C . Detailed experimental conditions are described in Table 2. Polypropylene conical tubes containing the SCMs and AAP solution (solution volume = 30mL) were shaken at 150 rpm in an incubator for 24 h, and then the slurry was passed through a 0.2 µm membrane filter. The AAP concentration was determined by high-performance liquid chromatography equipped with an Eclipse Plus C18 column (5 μ m, 4.6 mm \times 150 mm) and a diode array

detector lamp. A mixture of deionized water and acetonitrile (30:70) was used as a mobile phase. The flow was 1.5 mL/min, and the injection volume was 20 μ L. The run time was 15 min, and the detection wavelength was 243 nm. The removal rate was calculated using Eq. 1, whereas the adsorption capacity was using Eq. 2.

Experimental data were explored using kinetic (Plazinski et al., 2009), equilibrium (Liu et al., 2008), and thermodynamic models (Lima et al., 2019) models in Eq. 3, 4, 5.

Regeneration and reuse experiments for the SCMs (adsorbent dosage 0.1 g/L and initial AAP concentration 100 mg/L) were carried out over five cycles with methanol (99.5% pure) as an elution solution. After the AAP adsorption experiment, the SCMs were cleaned with deionized water and immersed in methanol for 24 h. The regenerated SCMs were washed again with deionized water, and dried overnight in an oven at 65 °C before reuse.

Removal rate

$$R_e = \frac{(C_0 - C_e)}{C_0} \times 100$$

 R_e = Removal rate (mg/g)

 C_0 = initial AAP concentration (mg/L)

 C_e = equilibrium AAP concentration (mg/L)



$$q_e = \frac{(C_0 - C_e)V}{m}$$

 q_e = Adsorption capacity (mg/g)

$$V =$$
 volume of solution (L)

$$m = mass of adsorbent (g)$$

■ Kinetic models

$$q_t = q_e[1 - \exp(-k_1 t)]$$
$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

pseudo-first-order model

pseudo-second-order model

(3)

(2)

Equilibrium models

 $q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$

 $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$

 $q_e = \frac{Q_m (K_g C_e)^n}{1 + (K_g C_e)^n}$

 $q_e = K_F C_e^{1/n}$ Freundlich model

Redlich-Peterson model

$$K_e^0 = \frac{(K_g \cdot 1000 \frac{mg}{g} \cdot MW_a) \cdot [Ad]}{\gamma}$$
$$\Delta G^0 = -R_c T ln(K_e^0)$$
$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$
$$ln(K_e^0) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

 $) \cdot [Ad]^0$

(5)

Characteristics	Acetaminophen (AAP)
Chemical formula	C ₈ H ₉ NO ₂
Chemical structure	HN
Molar mass (g/mol)	151.16
Solubility in water at 25°C (mg/L)	14,000
рКа	10.96
Log K _{ow}	0.49

Table 1. Characteristics of acetaminophen (AAP) used in the study.

Experiments	Initial concentration (mg/L)	Contact time (min)	рН	Temperature (°C)	Adsorbent dosage (g/L)
Equilibrium test	0.5, 1, 2, 5, 10, 50, 100, 200, 500	1440	6	30	0.1
Kinetic test	10	15, 30, 60, 120, 240, 360, 1440	6	30	0.1
pH test	10	1440	2, 4, 6, 8, 10, 12	30	0.1
Temperature test	10	1440	6	10, 20, 30, 40	0.1
Dosage test	10	1440	6	30	0.05, 0.1, 0.2, 0.3, 0.4, 0.5

 Table 2. Detailed conditions of single-factor experiments. (AAP)
3.2.2. Single-factor experiments for IPF adsorption

Adsorption of IPF onto the SCMs was explored under batch experimental conditions. The chemical properties of IPF are provided in Table 3 (Nallani et al., 2011; Oba et al., 2021). The adsorption experiments were conducted under the following conditions unless stated otherwise: initial IPF concentration 10 mg/L, SCMs dose 0.1 g/L, pH 4, contact time 24 h, and temperature 30°C. Detailed experimental conditions are described in Table 4. A stock solution (15 mg/L) was arranged by melting IPF (purity \geq 98.5%; Daejung Chemicals & Metals, Siheung, Republic of Korea) in deionized water. Conical tubes holding the SCMs and IPF solution (solution volume = 30 mL) were shaken at 150 rpm for 24 h, and then the slurry was passed through a 0.2 µm membrane filter. A high-performance liquid chromatography furnished with an Eclipse Plus C18 column and a diode array detector lamp was used to analyze the IPF concentration at a wavelength of 220 nm. Regeneration experiments for the SCMs (initial IPF concentration 10 mg/L and SCMs dosage 0.1 g/L) were executed with methanol (99.5% pure) as an eluant. After the adsorption experiment, the SCMs was rinsed with deionized water followed by being immersed in methanol for 24 h and rinsed again with deionized water. Prior to reuse, the SCMs was dried in an oven at 65°C. This cycle was repeated five times.

Characteristics	Ibuprofen (IPF)
Chemical formula	$C_{13}H_{18}O_2$
Chemical structure	HO
Molar mass (g/mol)	206.28
Solubility in water at 25°C (mg/L)	21
pKa	4.91
Log K _{ow}	3.97

Table 3. Characteristics of ibuprofen (IPF) used in the study.

Experiments	Initial concentration (mg/L)	Contact time (min)	рН	Temperature (°C)	Adsorbent dosage (g/L)
Equilibrium test	0.1, 0.5, 1, 2, 5, 10	1440	4	30	0.1
Kinetic test	10	15, 30, 60, 120, 240, 360, 1440	4	30	0.1
pH test	10	1440	2, 4, 6, 8, 10, 12	30	0.1
Temperature test	10	1440	4	10, 20, 30, 40	0.1
Dosage test	10	1440	4	30	0.05, 0.1, 0.2, 0.3, 0.4, 0.5

 Table 4. Detailed conditions of single-factor experiments. (IPF)

3.3. Characterization of the SCMs

The SCMs was characterized by analytical instruments with the specifications detailed in Table 5. A field emission scanning electron microscope was used to visualize the morphology of the SCMs. An electrophoretic light scattering spectrophotometer was employed to measure the zeta potentials and hydrodynamic diameters of the SCMs. A powder X-Ray diffractometry (XRD) was utilized in the 2θ range from 10° to 60° to obtain the XRD spectrum of the SCMs. Surface area and pore size distribution analyzers were used to measure the BET surface area and pore size of the SCMs by N₂ adsorption-desorption. A thermogravimetric analyzer was employed under a nitrogen atmosphere (heating rate = 10 °C/min, heating up to 800 °C) to explore the thermal properties of the SCMs including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). A Raman spectroscopy was used to analyze the chemical structure of the SCMs through scanning from 1000 to 2200 cm⁻¹ at an excitation wavelength of 532 nm. A FTIR spectrophotometer using KBr pellets was utilized to identify functional groups on surface of the SCMs in the spectral range of 500 to 4000 cm⁻¹. An XPS instrument with Al K α radiation (hv = 1486.6 eV) was employed to explore the elemental and binding energy on the SCMs. The stability tests of the SCMs were conducted in the solutions of pH 2 and 7.100 mg of the SCMs was added into 40 mL

solution in a polypropylene conical tube and stirred in a shaking incubator (150 rpm, 24 h, and 30 $^{\circ}$ C). The dry mass of the SCMs was quantified after reaction.

Table 5. Specification of the analytical instruments used in the study.

Instrument	Model	Company
Field Emission Scanning Electron Microscope	JSM-6700F	JEOL Ltd., Tokyo, Japan
Electrophoretic Light Scattering Spectrophotometer	ELS Z-1000	Otsuka Electronics, Tokvo, Japan
Surface Area and Pore Size Distribution Analyzers	BELSORP- MAX	MicrotracBEL, Osaka, Japan Bruker
Powder X-Ray Diffractometry	D8 Advance	Karlsruhe,
Thermogravimetric Analyzer	SDT650	Germany TA instruments, New Castle, DE, USA Thermo Fisher
Raman Spectroscopy	DXR2xi	Scientific, Waltham, MA,
Fourier Transform Infrared Spectrometer	Vertex-80V	Bruker, Karlsruhe, Germany
X-ray Photoelectron Spectroscopy	K-Alpha+	Scientific, Waltham, MA, USA
High-performance liquid chromatography	1260 Infinity II	Agilent, Santa Clara, CA, USA

3.4. Computational studies

A molecular modeling study was executed to explore the adsorption characteristics of AAP and IPF onto the SCMs. CHEM3D software (version 20.0, PerkinElmer, Waltham, MA, USA) was employed to visualize 3D structure models of the SCMs, AAP and IPF. In view of the computation cost and accuracy, twelve aromatic rings were used to represent the chemical structure of the SCMs. The MM2 was used as an energy minimization method for geometry optimization of the SCMs and contaminants. The extended Hückel theory was adopted to compute partial atomic charges of each chemicals within their optimized geometry. The interactions between adsorbent and contaminants were analyzed through molecular modeling.

3.5. Multi-factor experiments and ANN

3.5.1. ANN modeling for AAP adsorption

Multi-factor experimental conditions were designed based on the singlefactor experiments using a central composite design. Solution pH (A), temperature (B), adsorbent dosage (C), and initial AAP concentration (D) were selected as input variables, and adsorption capacity was the output variable. The number of experimental points (4 center points, 8 axial points, and 16 factorial points) was calculated using Eq. 6 Based on the experimental ranges and levels in Table 6, a central composite design matrix was created using Design Expert software (Table 7). Adsorption experiments were performed in duplicate for each experimental point. ■ Central composite design

 $N = 2^k + 2k + C_p$

- k = number of input variable (= 4)
- 2^k = number of factorial point (= 16)
- 2k = number of axial point (= 8)
- C_p = number of center point (= 4)

Input variable	Level				
	-2	-1	0	+1	+2
Solution pH	2	4	6	8	10
Temperature (°C)	10	17.5	25	32.5	40
Adsorbent dosage (g/L)	0.05	0.10	0.15	0.20	0.25
Initial AAP concentration (mg/L)	20	40	60	80	100

Table 6. Experimental ranges and levels used in the central composite design (AAP).

		Input	variable		Adsorptio	n capacity
Exp.		inpu	, and the		(mg	g/g)
(AAP)	А	В	С	D	Observed	Predicted
		(°C)	(g/L)	(mg/L)	00501700	(ANN)
1	4	17.5	0.1	80	87.9	91.6
2	6	25	0.25	60	65.3	56.1
3	4	17.5	0.2	40	35.7	34.5
4	6	25	0.15	60	58.9	58.2
5	4	17.5	0.2	80	45.3	44.8
6	8	17.5	0.2	80	36.2	35.9
7	8	17.5	0.1	80	66.8	61.0
8	8	32.5	0.2	40	53.4	48.5
9	4	32.5	0.2	80	36.6	40.7
10	8	32.5	0.1	40	44.9	48.3
11	6	25	0.05	60	59.2	58.2
12	8	17.5	0.2	40	33.0	31.5
13	6	25	0.15	60	32.5	32.3
14	4	32.5	0.1	40	56.2	58.2
15	6	25	0.15	60	30.7	37.3
16	6	10	0.15	60	56.5	58.0
17	6	25	0.15	60	39.3	38.6
18	4	32.5	0.1	80	64.1	61.2
19	4	32.5	0.2	40	61.2	57.9
20	10	25	0.15	60	42.9	48.3
21	8	17.5	0.15	40	63.0	58.8
21	8	32.5	0.1	80	58.3	58.2
23	4	17.5	0.1	40	76.0	75.6
23	8	32.5	0.1	80	46.7	48.2
25	6	25	0.15	100	50.6	51.8
25	6	40	0.15	60	52.7	50.6
20	6	25	0.15	20	54.9	58.8
28	2	25	0.15	20 60	30.5	27.8
20	1	17.5	0.15	80	94.1	91.6
30	-	25	0.1	60	17 3	56.1
31	1	17.5	0.23	40	31.8	34.5
32	-	25	0.15	4 0 60	57.0	58.2
32	0	175	0.15	80	<i>J</i> 7.0	J0.2 14 9
33	4	17.5	0.2	80	41.2	44.0
25	0	17.5	0.2	80	53.5	55.9
33 26	0	17.5	0.1	80 40	33.1	01.0
20 27	0	32.3 22.5	0.2	40	4/.0	40.3
3/ 28	4	32.3 22.5	0.2	8U 40	40.0	40.7
38 20	8	32.3 25	0.1	40	51.0	48.3
39	6	25	0.05	60	56.8	58.2
40	8	1/.5	0.2	40	55.4	31.5
41	6	25	0.15	60	30.2	32.3
42	4	32.5	0.1	40	59.9	58.2

Table 7. Central composite design matrix along with observed and predicted adsorption capacities from ANN modeling (AAP).

12	(25	0.15	(0	24.9	27.2
43	6	25	0.15	00	34.8	51.3
44	6	10	0.15	60	55.1	58.0
45	6	25	0.15	60	36.1	38.6
46	4	32.5	0.1	80	61.7	61.2
47	4	32.5	0.2	40	58.0	57.9
48	10	25	0.15	60	44.6	48.3
49	8	17.5	0.1	40	56.9	58.8
50	8	32.5	0.2	80	56.5	58.2
51	4	17.5	0.1	40	71.3	75.6
52	8	32.5	0.1	80	51.9	48.2
53	6	25	0.15	100	52.7	51.8
54	6	40	0.15	60	46.5	50.6
55	6	25	0.15	20	60.5	58.8
56	2	25	0.15	60	26.7	27.8
	-	ã	~ ~ 1		1	

 $\frac{56}{\text{A} = \text{pH}, \text{B} = \text{Temperature}, \text{C} = \text{SCMs dosage}, \text{D} = \text{Initial AAP concentration}}$

3.5.2. ANN modeling for IPF adsorption

The ANN modeling approach can be applied to develop a non-parametric predictive model for pollutant adsorption to adsorbents (Esfandiari et al., 2017). Prior to the ANN model development, adsorption experiments for IPF onto the SCMs were performed under multi-factor conditions with four input variables (A = pH; B = temperature; C = SCMs dosage; D = initial IPF concentration) and an output variable (IPF removal rate). A central composite design (Eq. 6) was used to establish the experimental conditions with the experimental ranges and levels presented in Table 8. The central composite design matrix, which was set up using the Design Expert software (version 13, Stat-Ease, Minneapolis, MN, USA), is presented in Table 9. The number of experimental points (N = 28) was composed of 16 factorial points, 8 axial points, and 4 center points. The adsorption experiments were performed in duplicate for each experimental point. The ANN model was developed using the experimental data (Table 9) through a three-phase development process consisted of training, validating, and testing phases. Fifty-six experimental data points were randomly divided into training (34 points), validating (11 points), and testing (11 points) subsets. In the ANN model development, the Levenberg-Marquardt algorithm was used with the mean squared error as an error function.

Input variable			Level		
	-2	-1	0	+1	+2
Solution pH	2	4	6	8	10
Temperature (°C)	10	17.5	25	32.5	40
Adsorbent dosage (g/L)	0.05	0.10	0.15	0.20	0.25
Initial IPF concentration (mg/L)	2	4	6	8	10

Table 8. Experimental ranges and levels used in the central composite design (IPF).

E····		Input	variable		Adsorption cap	acity (mg/g)
Exp.	А	В	С	D	Observed	Predicted
(IFF)		(°C)	(g/L)	(mg/L)	Observed	(ANN)
1	10	25	0.15	6	1.2	1.2
2	8	32.5	0.1	8	18.7	18.4
3	4	17.5	0.2	4	8.3	8.3
4	4	17.5	0.1	4	10.9	11.7
5	6	25	0.15	6	13.3	13.3
6	8	32.5	0.2	8	14.1	14.5
7	6	25	0.15	10	26.1	26.5
8	4	32.5	0.2	4	14.5	14.4
9	6	25	0.15	2	5.3	5.2
10	8	32.5	0.1	4	7.8	6.5
11	8	17.5	0.1	8	13.4	13.7
12	6	25	0.15	6	12.7	13.3
13	2	25	0.15	6	16.5	16.9
14	6	25	0.15	6	13.8	13.3
15	6	10	0.15	6	7.4	7.4
16	4	32.5	0.2	8	20.7	20.7
17	4	17.5	0.1	8	19.9	19.1
18	8	32.5	0.2	4	5.5	5.5
19	8	17.5	0.2	8	9.8	9.7
20	4	32.5	0.1	4	24.2	23.7
21	8	17.5	0.1	4	4.0	4.0
22	4	32.5	0.1	8	30.9	30.4
23	4	17.5	0.2	8	15.2	14.8
24	6	25	0.25	6	8.6	8.8
25	6	25	0.15	6	13.1	13.3
26	8	17.5	0.2	4	3.6	2.7
27	6	40	0.15	6	18.8	19.4
28	6	25	0.05	6	19.8	20.0
29	10	25	0.15	6	1.1	1.2
30	8	32.5	0.1	8	18.3	18.4
31	4	17.5	0.2	4	7.4	8.3
32	4	17.5	0.1	4	12.4	11.7
33	6	25	0.15	6	13.3	13.3
34	8	32.5	0.2	8	14.9	14.5
35	6	25	0.15	10	26.4	26.5
36	4	32.5	0.2	4	14.3	14.4
37	6	25	0.15	2	4 9	5.2
38	8	32.5	0.1	4	6.3	6.5
39	8	17.5	0.1	8	14.0	13.7
40	6	25	0.15	6	13.0	13.3
41	2	25	0.15	6	14.9	16.9
42	6	25	0.15	6	12.9	13.3
43	6	10	0.15	6	6.6	74
44	4	32 5	0.15	8	20.5	20.7
		52.5	0.2		20.0	20.7
				33		

Table 9. Central composite design matrix along with observed and predicted adsorption capacities from ANN modeling (IPF).

45	4	17.5	0.1	8	18.3	19.1
46	8	32.5	0.2	4	5.8	5.5
47	8	17.5	0.2	8	10.7	9.7
48	4	32.5	0.1	4	23.6	23.7
49	8	17.5	0.1	4	3.6	4.0
50	4	32.5	0.1	8	30.0	30.4
51	4	17.5	0.2	8	14.4	14.8
52	6	25	0.25	6	8.9	8.8
53	6	25	0.15	6	13.1	13.3
54	8	17.5	0.2	4	2.9	2.7
55	6	40	0.15	6	19.9	19.4
56	6	25	0.05	6	23.4	20.0

A = pH, B = Temperature, C = SCMs dosage, D = Initial IPF concentration

4. Results and Discussion

4.1. Adsorption characteristics onto the SCMs

4.1.1. Adsorption characteristics for AAP

The influence of contact time on the adsorption was investigated using kinetic experiments. Kinetic adsorption models (Eq. 3) were used to fit the adsorption data with nonlinear regressions. The related parameters are presented in Table 10. The kinetic data for AAP adsorption (Fig. 1b) demonstrate that AAP adsorption occurred rapidly for up to 1 h and retarded thereafter, approaching equilibrium at 360 min. The adsorption of AAP on the SCMs was slow. Several researchers have demonstrated that AAP adsorption on activated carbon reaches an equilibrium within 60 to 1440 min (Spaltro et al., 2021; Nguyen et al., 2020; Streit et al., 2021; Jedynak et al., 2019). A pseudo-second-order model provides the best fit for the kinetic data, suggesting that chemisorption is the rate-limiting step as strong bonds between the SCMs and AAP form. Other studies reported that a pseudosecond-order model best represents the AAP adsorption on activated carbon (Nguyen et al., 2020), mesoporous carbon (Jedynak et al., 2019), and doubleoxidized graphene oxide (Moussavi et al., 2016).

The effect of initial concentrations of AAP on the adsorption was

examined using equilibrium experiments at temperatures between 10 and 40 °C. Equilibrium models (Eq. 4) were used to fit equilibrium data with nonlinear regressions. The related parameters are tabulated in Table 11. Liu model fitting is shown in Fig. 1c. Freundlich, Langmuir, and Redlich-Peterson model fittings are presented in Fig. 2. The Liu model provides the best fit for the adsorption data. Similar results have been reported by Jedynak et al. (2019) who found that, among three isotherm models (Freundlich, Langmuir, and Freundlich-Langmuir), the Freundlich-Langmuir model best described the adsorption data of AAP on ordered mesoporous carbon. In our study, the theoretical maximum AAP adsorption capacities determined from a Liu model (mg/g) were in the decreasing order of 92.0 (10 °C) > 89.5 (20 °C) > 84.5 (30 °C) > 77.3 (40 °C). These were within the literature values (6.32– 267 mg/g) for carbon-based adsorbents (e.g., activated carbon, graphene oxides, biochar, and mesoporous carbon) (Table 12). The favorability of AAP adsorption on the SCMs was evaluated using the dimensionless favorability parameter (R_L) derived from Langmuir model. The calculated values of R_L ranged from 0.01 to 0.95 (Table 11), indicating that AAP adsorption on the spheres was favorable.

Temperature is an important factor affecting the adsorption of contaminants by adsorbents. Drawing on equilibrium adsorption data (Fig.

1c), thermodynamic analysis in a temperature range of 10 to 40°C was performed to explore how adsorption of AAP on the SCMs responds to temperature change (Fig. 1d). Thermodynamic models (Eq. 5) were used to determine thermodynamic parameters (Table 13). The negative values of Gibb's free energy change (ΔG° , -20.6 to -21.1 kJ/mol) imply spontaneous adsorption of AAP on the SCMs. The positive value of the entropy change $(\Delta S^{\circ}, 12.8 \text{ J/K} \cdot \text{mol})$ indicates an increment of entropy in the adsorption process. The negative value of the enthalpy change (ΔH° , -17.1 kJ/mol) implies the exothermic nature of the adsorption. The AAP adsorption capacity decreased as temperatures rose from 10 to 40 °C. Our results agree with those of previous studies showing that AAP adsorption on carbon-based adsorbents, including glucose-derived spherical biochar (Tran et al., 2020), tea wastederived activated carbon (Dutta et al., 2015), and double-oxidized graphene oxide (Moussavi et al., 2016), is exothermic. However, Nourmoradi et al. (2018) reported AAP adsorption on oak acorn-derived activated carbon was endothermic.

As with the initial concentrations of adsorbates, the dose of the adsorbent is a major factor that should be considered in the design and operation of an adsorption system. The influence of the dose of the SCMs on the adsorption of AAP is illustrated in Fig. 1e. As the adsorbent dose increased from 0.05 to 0.5 g/L, the removal rate of AAP was enhanced from 17.9% to 64.3% because the surface sites available on the adsorption increased. However, in the same dose range, the adsorption capacity was declined from 34.9 to 12.5 mg/g, indicating that the amount of adsorbed AAP per unit mass of the SCMs decreased.

The reusability of carbon materials in the adsorption of AAP has been studied by several researchers (Nguyen et al., 2020; Tran et al., 2020; Rosli et al., 2021) who have regenerated activated carbon, graphene nanoplatelets, and biochar using chemical treatments with various desorbing agents. Nguyen et al. (2020) regenerated commercial activated carbon using desorbing agents such as distilled water (pH 2 and pH 12), 0.2 M NaOH, 0.2 M HCl, 0.2 M NaCl, methanol, and ethanol. They reported that methanol and ethanol had far superior AAP desorption efficiencies compared with other desorbing agents. Tran et al. (2020) reported similarly that methanol and ethanol were more efficient than other agents in AAP desorption on biochar. In our study, five adsorption-desorption cycles of regeneration and reuse were performed using methanol as a desorbing agent (Fig. 1f). As regeneration and reuse repeated from the first cycle to the fifth, the AAP adsorption capacity decreased from 60.1 to 34.6 mg/g, indicating that 40.5% of the adsorption capacity was lost over five cycles. Our results show that the SCMs can be successfully

regenerated and reused for AAP adsorption. Rosli et al. (2021) reported that AAP removal efficiency of graphene nanoplatelets decreased from 95.58% to 71.45% over four adsorption-desorption cycles, with 5% ethanol-deionized water used as a desorbing agent.

Kinetic model		Model pa	rameter	
Pseudo-first-order				
$q_e (mg/g)$	k ₁ (1/min)	\mathbb{R}^2	χ^2	SAE
23.2	3.43E-2	0.867	2.07	15.6
Pseudo-second-or	der			
q _e (mg/g)	k_2 (g/(mg·min))	\mathbb{R}^2	χ^2	SAE
25.2	1.69E-3	0.963	0.653	8.82
Elovich				
α (mg/(g·min))	β (g/mg)	\mathbb{R}^2	χ^2	SAE
4.11	0.258	0.951	1.06	10.0

Table 10. Kinetic model parameters obtained from AAP adsorption to the SCMs.



Fig. 1. Single factor adsorption experiments data (AAP): (a) pH, (b) contact time, (c) initial concentration, (d) temperature, (e) adsorbent dosage, and (f) regeneration.





 $% \quad K_e^0 = \frac{(1000K_g \cdot molecular \ weight \ of \ adsorbate) \cdot [Adsorbate]^0}{\gamma}$

 K_g = constant of the best isotherm model fitted (L/mg) [Adsorbate]⁰ = standard concentration of the adsorbate (1 mol/L) γ = activity coefficient (dimensionless)

Madal	Denometono	Temperature (°C)				
Model	Parameters	10	20	30	40	
	$K_F (mg^{1-(1/n)} \cdot L^{1/n}/g)$	15.097	13.168	11.396	9.459	
	1/n	0.278	0.300	0.317	0.340	
Freundlich	\mathbb{R}^2	0.911	0.911	0.905	0.890	
	χ^2	8.975	9.072	9.992	13.127	
	SAE	43.987	42.999	43.672	50.973	
	Q _m (mg/g)	61.188	59.804	59.559	58.304	
	K _L (L/mg)	0.696	0.298	0.173	0.107	
	R _L	0.01 - 0.74	0.01 - 0.87	0.01 - 0.92	0.02 - 0.95	
Langmuir	\mathbf{R}^2	0.751	0.861	0.922	0.973	
	χ^2	72.002	27.986	15.246	8.562	
	SAE	101.820	73.315	51.073	27.632	
	K _R (L/g)	14.659	8.163	1.316	0.394	
	a _R (1/mg)	224.850	127.415	24.907	9.675	
	g	0.717	0.729	0.779	0.837	
Redlich-Peterson	\mathbb{R}^2	0.913	0.927	0.949	0.971	
	χ^2	14.001	7.409	5.433	5.513	
	SAE	42.574	39.274	34.959	26.742	
	Kg (L/mg)	0.042	0.038	0.028	0.021	
	Q _m (mg/g)	92.005	89.487	84.480	77.309	
	n	0.518	0.491	0.575	0.688	
Liu	\mathbb{R}^2	0.964	0.968	0.976	0.976	
	χ^2	10.554	6.417	2.522	6.369	
	SAE	40.266	37.627	23.780	29.186	

Table 11. Equilibrium model parameters obtained from AAP adsorption to the SCMs.



Fig. 2. Equilibrium model fittings to AAP adsorption data: (a) Freundlich, (b) Langmuir, and (c) Redlich–Peterson.

Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Spherical carbon materials (SCMs)	92.0	This study
Hyper-crosslinked cellulose	30.7	Benosmane et al. (2021)
Biochar obtained from oil palm fiber	7.3	Grisales-Cifuentes et al. (2021)
Amine functionalized superparamagnetic silica nanocomposite	58	Kollarahithlu and Balakrishnan (2021)
Chitosan zwitterionic derivative	27	Malesic-Eleftheriadou et al. (2021)
Granular activated carbon	6.32	Rao et al. (2021)
Graphene nanoplatelets	56.21	Rosli et al. (2021)
Sludge-derived activated carbon	145	Streit et al. (2021)
Commercial activated carbon	221	Nguyen et al. (2020)
Spherical biochar	286	Tran et al. (2020)
Ordered mesoporous carbons	400	Jedynak et al. (2019)
Activated carbon derived from oak acorn	45.45	Nourmoradi et al. (2018)
Double-oxidized graphene oxide	704	Moussavi et al. (2016)
Tea waste derived activated carbon	195.95	Dutta et al. (2015)
NH4Cl-induced activated carbon	233	Mashayekh-Salehi and Moussavi (2016)
Vegetable wastes	2.18	Villaescusa et al. (2011)
Activated carbons from urban and industrial residues	267	Cabrita et al. (2010)

Table 12. Maximum adsorption capacity for AAP reported in the literature.

Temp. (°C)	T (K)	Kg (L/mg)	K _e ⁰ (-)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(K·mol))
10	283.15	0.042	6281.5	-20.6	-17.1	12.8
20	293.15	0.038	5691.1	-21.1		
30	303.15	0.028	4213.6	-21.0		
40	313.15	0.021	3187.9	-20.9		

Table 13. Thermodynamic model parameters obtained from AAP adsorption to the SCMs.

4.1.2. Adsorption characteristics for IPF

The adsorption characteristics of the SCMs toward IPF can be explored through adsorption studies in terms of adsorbent dosage, contact time, initial IPF concentration, temperature, and solution pH. The adsorbent dosage is an important factor that should be analyzed for efficient operation of adsorption process. In our study, the SCMs dosage was varied from 0.05 to 0.5 g/L to examine its effect on the adsorption capacity and removal rate of IPF (Fig. 3a). At a SCMs dosage of 0.05 g/L, the adsorption capacity was 24.0 mg/g. When the dosage increased to 0.3 g/L, the adsorption capacity dropped gradually to 12.3 mg/g. As the dosage rose to 0.5 g/L, the adsorption capacity declined slowly to 11.5 mg/g. Unlike the adsorption capacity, the removal rate increased linearly from 12.8 to 61.2% with an increase in the dosage from 0.05 to 0.5 g/L. This inverse trend between adsorption capacity and removal rate in response to the adsorbent dosage change could be ascribed to the fact that the number of available adsorption sites increased as the adsorbent dosage rose, whereas the mass of adsorbed contaminant per unit mass of the adsorbent was reduced.

Equilibration time is a crucial factor in the design of adsorption system. It demonstrates how a fast reaction can reach a state of equilibrium during the adsorption process. Kinetic experiments were executed to determine the equilibration time by varying the contact time between IPF and the SCMs from 10 to 1,440 min (Fig. 3b). The kinetic data show that the adsorption reached the equilibration time at 360 min. IPF adsorption on the SCMs was a slow process. The equilibration time for IPF adsorption was quantified over a wide time range of 20 to 1,440 min depending the types of carbon-based adsorbents (Ali et al., 2019; Hanbali et al., 2020; Ulfa et al., 2020; Costa et al., 2021). Kinetic adsorption models are applied to explore the adsorption characteristics from kinetic adsorption data. In this study, the pseudo-firstorder, pseudo-second-order, and Elovich models (Eq. 3) were used to analyze the kinetic adsorption data with nonlinear regressions (Fig. 3b). The kinetic model parameters are tabulated in Table 14. Based on the errors functions (R^2 , χ^2 , and SAE), the pseudo-second-order model best described the data, suggesting that chemisorption is the rate-limiting step, and strong chemical bonds formed between the SCMs and IPF. Our findings agree well with reports, revealing that the pseudo-second-order model was the best fit model to IPF adsorption kinetics of activated carbon (Streit et al., 2021), mesoporous carbon (Jedynak et al., 2019), and mesoporous carbon microspheres (Ulfa et al., 2020).

The maximum adsorption capacity is an important characteristic of adsorbents, and it can be quantified by varying initial concentrations of adsorbate in equilibrium experiments. Based on the plot of equilibrium adsorbate concentration versus adsorption capacity, the maximum adsorption capacity of the adsorbent toward a specific adsorbate is determined. In this study, equilibrium experiments were performed to assess the maximum adsorption capacity of the SCMs toward IPF in the temperature range of 10 to 40°C (Fig. 3c). Equilibrium isotherm models such as Freundlich, Langmuir, Redlich-Peterson, and Liu models (Eq. 4) were employed to investigate the adsorption characteristics with nonlinear regressions. The model parameters are tabulated in Table 15. Equilibrium model fittings with Freundlich, Langmuir, and Redlich–Peterson are also exhibited in Fig. 4. According to the error functions, the Liu model best described the adsorption data (Fig. 3c), with the theoretical maximum IPF adsorption capacities (mg/g) in the increasing order of 42.3 (10° C) < 64.1 (20° C) < 78.4 (30° C) < 95.6 (40° C). The Liu model is a Freundlich-Langmuir type isotherm that is used to represent adsorption on both homogeneous and heterogeneous surfaces of adsorbents (Liu and Liu, 2008). Jedynak et al. (2019) performed an equilibrium study for IPF adsorption to activated ordered mesoporous carbons, reporting that the Freundlich-Langmuir model best described the adsorption data among Freundlich, Langmuir, and Freundlich-Langmuir isotherms. In the literature, the maximum IPF adsorption capacities of carbon materials (activated carbons, carbon microspheres, microporous/mesoporous

carbons, etc.) varied from 19 to 239.8 mg/g (Table 16).

In the adsorption process, reaction temperature usually affects interactions between adsorbents and adsorbates. To explore the thermodynamic properties of an adsorbent toward a specific contaminant, adsorption experiments were conducted under different temperatures, and thermodynamic parameters such as Gibbs free energy change, enthalpy change, and entropy change were acquired to analyze how adsorption reaction responds to temperature change. In relation to IPF adsorption, some researchers noted the exothermic nature of adsorption process. Ali et al. (2016) examined the adsorption of IPF to iron nanoparticle composites in the temperature range of 20-30°C; they found that adsorption capacity was reduced as temperature increased. Ramírez et al. (2021) also reported that the IPF adsorption to magnetite-FeBTC MOF composite declined with an increase of temperature from 20 to 45°C. However, others reported the opposite trend (endothermic) of IPF adsorption to adsorbents. Pap et al. (2021) observed that the IPF adsorption capacity of P-doped microporous carbon was augmented with an increase in temperature from 22 to 42°C. Nourmoradi et al. (2018) also examined the enhancement in IPF adsorption capacity of activated carbon with an increase in temperature from 15 to 45°C. These studies indicate that the thermodynamic nature of IPF adsorption is closely associated with the type of adsorbents. In our study, the

equilibrium adsorption data in the temperature range of 10 to 40°C were analyzed using thermodynamic equations (Eq. 5) to determine the thermodynamic properties of IPF adsorption to the SCMs (Fig. 3d). In the thermodynamic parameters (Table 17), the negative Gibbs free energy changes (ΔG° , $-21.4 \sim -26.6$ kJ/mol) suggest that the adsorption was a spontaneous reaction. The positive entropy change (ΔS° , 174.9 J/K·mol) implies an increase of entropy during the adsorption. The positive enthalpy change (ΔH° , 27.9 kJ/mol) indicates that the adsorption of IPF to the SCMs was endothermic. Our results agreed well with the studies, displaying the endothermic nature of IPF adsorption to surface-modified activated carbons (Ali et al., 2019), polyamidoamine-grafted halloysite (Kurczewska et al., 2020), chitosan zwitterionic derivative (Malesic-Eleftheriadou et al., 2021), and cationic surfactant-modified minerals (bentonite, kaolin and zeolite) (Obradović et al., 2022).

In the application of adsorbents for pollutant removal from aqueous solutions, the reusability of adsorbents is a crucial issue arising from water and wastewater treatment. In relation to IPF adsorption, several researchers regenerated adsorbents such as activated bamboo waste (Reza et al., 2014), activated date seed biochar (Chakraborty et al., 2020), pine wood biochar (Essandoh et al., 2015), pepper stem biochar (Naima et al., 2022), and functionalized silica nanocomposite (Kollarahithlu and Balakrishnan, 2021) using solvent-washing methods. Reza et al. (2014) regenerated activated bamboo waste using eluents such as water, HCl, NaOH, methanol, ethanol, and acetic acid. They revealed that methanol had far better IPF desorption efficiency than other eluents. Essandoh et al. (2015) also successfully used methanol for the IPF desorption from pine wood biochar. In our study, methanol was employed for the regeneration of the SCMs (Fig. 5), demonstrating that it could be successfully regenerated for the IPF adsorption. During the five cycles of regeneration and reuse experiments, the IPF adsorption capacity was reduced from 27.1 to 10.6 mg/g, indicating a 60.9% reduction in the adsorption capacity over the five cycles. Chakraborty et al. (2020) reported that the IPF removal rate of steam activated date stone seed biochar declined from 92.43 to 69.54% after five cycles of regeneration with methanol, whereas that of chemically activated date stone seed biochar was reduced from 85.26 to 61.89%.



Fig. 3. Single factor adsorption experiments data (IPF): (a) adsorbent dosage, (b) contact time, (c) initial concentration, and (d) temperature.


- - - -

Kinetic mode	1	Model p	arameter		
Pseudo-first-order	model				
q _e (mg/g) 20.7	k ₁ (1/min) 1.52E-2	R ² 0.924	χ^{2} 2.81	SAE 15.4	
Pseudo-second-or	Pseudo-second-order model				
q _e (mg/g) 23.4	k₂ (g/(mg·min)) 7.20E-4	R ² 0.982	χ^2 0.784	SAE 7.36	
Elovich model					
α (mg/(g·min)) 1.07	β (g/mg) 0.241	R ² 0.980	χ^{2} 1.01	SAE 8.17	

Table 14. Kinetic model parameters obtained from the adsorption of IPF onto the SCMs.

Equilibrium model	Doromotor		Temperature (°C)			
Equilibrium model	Parameter	10	20	30	40	
	$K_{F} (mg^{1-(1/n)} \cdot L^{1/n}/g)$	5.370	6.948	9.542	13.119	
	1/n	0.505	0.509	0.569	0.611	
Freundlich model	\mathbb{R}^2	0.978	0.907	0.957	0.974	
	χ^2	0.699	3.386	2.870	2.442	
	SAE	4.073	11.052	10.917	10.995	
	Q _m (mg/g)	14.061	20.252	26.834	32.110	
	K _L (L/mg)	0.755	0.909	1.273	1.784	
Langmuir model	\mathbb{R}^2	0.882	0.762	0.781	0.766	
-	χ^2	10.994	12.641	21.083	16.754	
	SAE	8.105	19.579	28.583	36.982	
	K_{R} (L/g)	0.559	1.187	1.311	1.570	
	$a_R\left((L/mg)^g\right)$	7.642	12.815	18.465	30.961	
	g	0.742	0.572	0.601	0.621	
Redlich-Peterson model	\mathbb{R}^2	0.974	0.917	0.951	0.961	
	χ^2	13.303	11.599	9.470	6.808	
	SAE	4.190	9.452	11.954	13.576	
	Kg (L/mg)	0.044	0.071	0.101	0.137	
	$Q_m (mg/g)$	42.320	64.085	78.364	95.619	
	n	0.770	0.889	0.892	0.930	
Liu model	\mathbb{R}^2	0.982	0.923	0.957	0.969	
	χ^2	9.787	13.137	7.836	7.077	
	SAE	9.417	8.690	7.751	9.019	

Table 15. Equilibrium model parameters obtained from the adsorption of IPF onto the SCMs.



Fig. 4. Equilibrium model fittings to IPF adsorption data: (a) Freundlich, (b) Langmuir, and (c) Redlich–Peterson.

Adsorbents	Maximum adsorption capacity (mg/g)	References
Spherical carbon materials (SCMs)	95.6	This study
Acid-modified kola nut husk	15.87	Bello et al. (2021)
Amine functionalized superparamagnetic silica nanocomposite	59	Kollarahithlu et al. (2021)
Chitosan zwitterionic derivative	19	Malesic- Eleftheriadou et al. (2021)
P functionalized microporous carbon	20.54	Pap et al. (2021)
Sludge-derived activated carbon	105.91	Streit et al. (2021)
Cocoa shell biomass-based adsorbents	38.95	Al-Yousef et al. (2021)
Mesoporous carbon microspheres	56.9	Ulfa et al. (2020)
Surface functionalized activated carbon	53.91	Ali et al. (2019)
Ordered mesoporous carbons	193.03	Jedynak et al. (2019)
Activated carbon derived from oak acorn	96.15	Nourmoradi et al. (2018)
Carbonaceous materials	239.8	Alvarez-Torrellas et al. (2016)
Granular activated carbon	38.37	Iovino et al. (2015)

Table 16. Maximum adsorption capacity for IPF reported in the literature.

Temp.	Т	Kg	Ke ⁰	ΔG°	ΔS°	$\Delta \mathrm{H}^{\circ}$
(°C)	(K)	(L/mg)	(-)	(kJ/mol)	$(J/(K \cdot mol))$	(kJ/mol)
10	283	0.044	8998.2	-21.4	174.7	27.9
20	293	0.071	14601.4	-23.3		
30	303	0.101	20867.3	-25.0		
40	313	0.137	28221.5	-26.6		

Table 17. Thermodynamic parameters determined from IPF adsorption onto the SCMs.



Fig. 5. Regeneration experiments for IPF adsorption onto the SCMs.

4.2. Characterization of the SCMs

The FESEM images in Fig. 6 illustrate the spherical particles synthesized from hydrothermal carbonization followed by calcination. In comparison to the SH with an average hydrodynamic diameter of 633.4 ± 231.0 nm (Fig. 6b), the SCMs had smaller size with a diameter of 345.9 ± 80.9 nm (Fig. 6d). Also, the SCMs showed a narrow particle size distribution relative to the SH, demonstrating that the particle size was diminished due to calcination at high temperature. The N₂ adsorption-desorption curves for the SCMs are presented in Fig. 7a. The specific surface area of the SCMs was determined to be 257.3 m^2/g from the BET analysis. However, the N₂ adsorption-desorption curves could not be acquired for the SH, indicating that pore structure was not well developed in the SH during the hydrothermal treatment of sucrose at 180°C. A similar finding was observed by Zhao et al. (2017) who reported that spherical hydrochar, which was hydrothermally synthesized at 180°C from sucrose, had almost no pore structure. In our study, the pore-size distribution curve (Fig. 7b) illustrates the mesoporous carbon nature of the SCMs with an average pore diameter of 2.27 nm and a total pore volume of $0.17 \text{ cm}^3/\text{g}$ from the BJH analysis.



Fig. 6. FESEM images and hydrodynamic diameter distribution of (a, b) SH, and (c, d) SCMs.







Fig. 7. Analyses of surface area and pore size distribution of the SCMs: (a) N_2 adsorption-desorption curves and (b) pore size distribution curve.

In the XRD spectra (Fig. 8), the SH showed a wide diffraction peak near 22°, which is the (002) reflection of amorphous carbon (Yu et al., 2019; Wang et al., 2018). Zhao et al. (2017) demonstrated that during the hydrothermal synthesis of hydrochar from sucrose, a broad diffraction peak was generated near 22°, indicating the formation of an amorphous carbon structure. In our study, the XRD spectrum of the SCMs indicates that the wide diffraction peak was shifted to around 24° after calcination at high temperature, and the spacing between the amorphous layers decreased. Our results reveal that no crystal structure of graphite was created during the synthesis of the SCMs through hydrothermal carbonization of sucrose followed by calcination. Preliminary adsorption experiments at two different experimental conditions (Table 18) indicate that the SCMs had far higher IPF removal rate compared to the SH. Therefore, further analyses and adsorption experiments were focused on the SCMs.



Fig. 8. XRD spectra of the SH and SCMs.

Table 18. IPF removal rate from preliminary experiments for comparison between spherical hydrochar (SH) and spherical carbon materials (SCMs).

Ех	x. 1	Ех	к. 2
SH	SCMs	SH	SCMs
8.9 %	42.7 %	45.5 %	91.0 %

Experimental conditions for Ex. 1: pH = 4, initial IPF concentration = 10 mg/L, adsorbent dose = 0.25 g/L; Experimental conditions for Ex. 2: pH = 2, initial IPF concentration = 2 mg/L, adsorbent dose = 0.10 g/L

The thermogravimetric analysis of the SCMs is presented in Fig. 9. The TGA curve (Fig. 9a) can be divided into three stages before AAP adsorption, whereas it can be separated into four after AAP adsorption. The temperature range, percentage of weight loss, and related reason for each stage is summarized in Table 19. The TGA curve before AAP adsorption included the first (removal of water molecules), the second (decomposition of carboxyl and lactone), and third (carbon combustion and decomposition of phenol and ether) stages (Lima et al., 2019; Oliveira et al., 2017; Wasilewska et al., 2021). The DSC curves (Fig. 9b) exhibited the peaks at 357 and 395 °C, which were associated with partial surface oxidation. The DTA curves (Fig. 9c) showed the peaks at 569 and 591 °C, which were related to carbon combustion along with decomposition of phenol and ether. The TGA curve after AAP adsorption contained the first (removal of water molecules), the second (thermal degradation of adsorbed AAP), the third (decomposition of carboxyl and lactone), and fourth (carbon combustion and decomposition of phenol and ether) stages (Gilpin et al., 2004; Jendrezjewska et al., 2020). The weight loss (7.7%) in the first stage was less than that before AAP adsorption, which can be ascribed to an increment of the hydrophobicity of the SCMs by AAP adsorption (Wasilewska et al., 2021). The thermal degradation of adsorbed AAP in the second stage is supported by the DTA curve peak at 170 °C after AAP adsorption (Fig. 9c).

The thermogravimetric analysis of the SCMs is illustrated in Fig. 10. Before IPF adsorption, the TGA curve contained three stages, whereas it included four stages after IPF adsorption. Table 20 outlines the weight loss percentage and reason for each stage. In the TGA curve before IPF adsorption (Fig. 10a), weight loss occurred due to the desorption of water molecules (1st stage) and decomposition of the functional groups (2nd and 3rd stages). Weight loss took place in the TGA curve after IPF adsorption because of the desorption water molecules (1st stage), thermal degradation of adsorbed IPF (2nd stage), and decomposition of the functional groups (3rd and 4th stages) (Wasilewska et al., 2021; Oliveira et al., 2017; Belmessaoud et al., 2020). In the first stage, the weight loss (8.4%) after IPF adsorption was lower than that (11.4%) before IPF adsorption because hydrophobicity of the SCMs was augmented due to IPF adsorption (Wasilewska et al., 2021; Oliveira et al., 2017). In the DTA curves (Fig. 10b), the peak at 170°C, which emerged after IPF adsorption, confirmed the thermal degradation of adsorbed IPF (Belmessaoud et al., 2020), whereas the peaks at 568 and 591°C were associated with the carbon combustion and decomposition of ether and phenol (Oliveira et al., 2017; Lima et al., 2019). The peaks at 363 and 395°C in the DSC curves (Fig. 10c) were linked with surface oxidation of the SCMs (Wasilewska et al., 2021).



Fig. 9. Thermogravimetric analysis of the SCMs before and after AAP adsorption: (a) TGA curves, (b) DSC curves, and (c) DTA curves.

	Before	otion		After	AAP adsorp	ption	
Stage	Temperature (°C)	Weight loss (%)	Reason	Stage	Temperature (°C)	Weight loss (%)	Reason
1st	0 - 100	11.4	removal of water molecules	1st	0 - 100	7.7	removal of water molecules
2nd	100 - 450	6.9	decomposition of carboxyl and lactone	2nd	100 - 210	8.0	thermal degradation of adsorbed AAP
3rd	450 - 800	44.8	carbon combustion and decomposition of phenol and ether	3rd	210 - 450	6.2	decomposition of carboxyl and lactone
			•	4th	450 - 800	43.8	carbon combustion and decomposition of phenol and ether

Table 19. TGA analysis before and after AAP adsorption onto the SCMs.



Fig. 10. Thermogravimetric analysis of the SCMs before and after IPF adsorption: (a) TGA curves, (b) DSC curves, and (c) DTA curves.

Before IPF adsorption					After	· IPF adsorpt	ion
Stage	Temperature (°C)	Weight loss (%)	Reason	Stage	Temperature (°C)	Weight loss (%)	Reason
1st	0 - 100	11.4	desorption of water molecules	1st	0 - 100	8.4	desorption of water molecules
2nd	100 - 450	6.9	decomposition of carboxyl and lactone	2nd	100 - 210	7.2	thermal degradation of adsorbed IPF
3rd	450 - 800	44.8	carbon combustion and decomposition of phenol and ether	3rd	210 - 450	7.3	decomposition of carboxyl and lactone
				4th	450 - 800	43.2	carbon combustion and decomposition of phenol and ether

Table 20. TGA analysis before and after IPF adsorption onto the SCMs.

The Raman spectra of the SCMs are presented in Fig. 11a, showing two characteristic bands commonly observed from carbon materials (Ulfa et al., 2020). The band appearing at 1,358 cm⁻¹ is the D band, which corresponds to the vibrations of disordered graphitic structure of the SCMs (Xu and An, 2016; Ulfa et al., 2020). The band at $1,572 \text{ cm}^{-1}$ is the G band, which is assigned to tangential vibrations of ideal graphitic structure of the SCMs (Omorogie et al., 2021; Lei et al., 2021). The intensity ratio between the D band and the G band (I_D/I_G) was 1.45, revealing the formation of abundant defects in the SCMs with a low degree of graphitization (Lei et al., 2021; Tran et al., 2020). In the Raman spectra after IPF adsorption, the D band and the G band were observed at 1,350 cm⁻¹ and 1,562 cm⁻¹, respectively. After IPF adsorption, the intensity of the D band noticeably increased from 3,251 to 3,786, whereas the G band increased from 2,240 to 2,691, indicating a large fraction of an electronic charge was transferred from the IPF molecules to the SCMs during the adsorption.

The FTIR spectra of AAP, SCMs, and SCMs after AAP adsorption are illustrated in Fig. 12. The FTIR spectrum of AAP includes various absorption bands (Table 21), indicating the existence of aromatic, amide, and phenol functional groups (Chanda et al., 2015; Zapata et al., 2021; Trivedi et al., 2015). The FTIR spectra reveal the presence of abundant oxygen-containing functional groups on the SCMs (Gong et al., 2011; Li et al., 2020; Sun et al., 2004; Zhang et al., 2015; Kapri et al., 2016; Rezan et al., 2009). The absorption bands detected in the FTIR analysis are listed in Table 22, including O-H stretching vibrations (3,433 cm⁻¹), C=O stretching vibrations (1,728 cm⁻¹), and C-O stretching vibrations (1,263 cm⁻¹). The absorption bands at 1619 cm-1 can be ascribed to the stretching vibrations of C=C (aromatic ring) (Sun et al., 2004; Zhang et al., 2015; Kapri et al., 2016). After AAP adsorption, new absorption bands appeared in the FITR spectrum of the SCMs, including 1,512 cm⁻¹ (C-H bending), 1,430 cm⁻¹ (C-C stretching), and 1,372 cm⁻¹ (C-H bending) in the chemical structure of AAP (Table 21). In addition, the appearance of new absorption bands at 836 cm⁻¹ (C=C bending) and 1,256 cm⁻¹ (C-N stretching) correspond to the aromatic ring and amide group, respectively (Zapata et al., 2021; Trivedi et al., 2015).

The FTIR spectra of IPF, SCMs, and SCMs after IPF adsorption are presented in Fig. 11b. In the FTIR spectra of the SCMs, the stretching vibrations of C=C bond were detected at 1619 cm⁻¹, confirming the presence of aromatic ring in the SCMs (Sun and Li, 2004; Zhang et al., 2015; Kapri et al., 2016). In addition, various oxygen-bearing groups were noticed at 1,263 cm⁻¹ (C-O stretching vibrations), 1,728 cm⁻¹ (C=O stretching vibrations), and 3,433 cm⁻¹ (O-H stretching vibrations) (Wang et al., 2018; Cui et al., 2020; Sun and Li, 2004; Kapri et al., 2016; Rezan et al., 2009) (Table 23).

Numerous functional groups (carboxyl and carbonyl) and an aromatic ring were found in the FTIR spectrum of IPF (Huei et al., 2015, Swain et al., 2015; Carvalho et al., 2020; Abioye et al., 2015; Ramachandran et al., 2016; Janus et al., 2020) (Table 24), and these are involved in the adsorption onto the SCMs. As IPF was adsorbed to the SCMs, new absorption bands emerged in the FITR spectrum of the SCMs, including 1,384 cm⁻¹ (COO- stretching) and 579 cm⁻¹ (C-C deformation) in the structure of IPF (Janus et al., 2020;

Ramachandran et al., 2016).



Fig. 11. (a) Raman spectra of SCMs before and after IPF adsorption, (b) FTIR spectra of IPF and SCMs before and after IPF adsorption.



Fig. 12. FTIR spectra of AAP and SCMs before and after AAP adsorption.

Absorption	Molecular	Functiona	Defense
band (cm ⁻¹)	vibration	l group	Kelerence
2226	N-H	amide	Chanda et al. (2015), Zapata et al.
5520	stretching		(2021)
3162	O-H	phenol	Chanda et al. (2015), Zapata et al.
5102	stretching		(2021)
3035	C-H	aromatic	Zapata et al. (2021), Trivedi et al.
5055	stretching		(2015)
2881	С-Н	alkane	Chanda et al. (2015), Zapata et al.
2001	stretching		(2021)
2794	O-H	phenol	Zapata et al. (2021)
2771	stretching		
1654	C=O	amide	Chanda et al. (2015), Zapata et al.
	stretching		(2021), Trivedi et al. (2015)
1611	C=C	aromatic	Zapata et al. (2021), Trivedi et al.
1011	stretching		(2015)
1564	N-H	amide	Zapata et al. (2021)
	bending		
1506	C-H		Trivedi et al. (2015)
	bending		
1442	C-C		Trivedi et al. (2015)
	stretching		
1371	С-Н		Zapata et al. (2021), Trivedi et al.
	bending		(2015)
1327	C-H		Zapata et al. (2021), Trivedi et al.
	bending		(2015)
1259	C-N	amide	Zapata et al. (2021), Trivedi et al.
	stretching		(2015)

Table 21. Absorption bands and corresponding functional groups of AAP detected from the FTIR analysis.

1227	C-N	amide	Zapata et al. (2021), Trivedi et al.
1227	stretching		(2015)
1170	C-O		Zapata et al. (2021), Trivedi et al.
1172	stretching		(2015)
1109	C-N	amide	Zapata et al. (2021), Trivedi et al.
1108	stretching		(2015)
1015	С-Н	aromatic	Zapata at al. (2021)
1015	bending		Zapata et al. (2021)
060	C-N	amide	Trivedi et al. (2015)
202	stretching		
857	С-Н	aromatic	7apata et al. (2021)
	bending		
837	C=C	aromatic	Zapata et al. (2021), Trivedi et al.
057	bending		(2015)
808	С-Н	aromatic	7apata et al. (2021)
000	bending		
796	С-Н	aromatic	$Z_{apata et al.}(2021)$
170	bending		Zapata et al. (2021)
714	С-Н	aromatic	$Z_{apata et al.}(2021)$
/ 1 1	bending		Zapadi et dl. (2021)
686	C-H	aromatic	Zapata et al. (2021)
000	bending		Zapadi et dl. (2021)
625	C-H	aromatic	Trivedi et al. (2015)
025	bending		

Absorp			
tion	Molecular	Function	Deference
band	vibration	al group	Kelelence
(cm ⁻¹)			
Before A	AP adsorption	1	
3433	О-Н	hydroxyl	Gong et al. (2011); Wang et al. (2018);
	stretching	group	Cui et al. (2020)
2920	C-H	asymmetr	Wang et al. (2018); Cui et al. (2020);
	stretching	ic	Li et al. (2020)
2851	С-Н	symmetri	Cui et al. (2020)
	stretching	с	
1728	C=O	carboxyl	Sun and Li (2004); Zhang et al. (2015);
	stretching	group	Kapri et al. (2016)
1619	C=C	aromatic	Sun and Li (2004); Zhang et al. (2015);
	stretching		Kapri et al. (2016)
1263	C-OH	C-O in	Rezan et al. (2009); Gong et al. (2011);
	stretching	phenols	Sun and Li (2004)
After AA	P adsorption	I	I
3429	О-Н	hydroxyl	Trivadi et al. (2015)
	stretching	group	Trivedi et al. (2013)
1721	C=O	carboxyl	Trivedi et al. (2015)
	stretching	group	
1614	C=C	aromatic	Zapata et al. (2021); Trivedi et al.
	stretching		(2015)
		I	1

Table 22. Absorption bands and corresponding functional groups of the SCMs detected from the FTIR analysis (AAP).

1512	С-Н	from	
	bending	AAP	Trivedi et al. (2015)
		1506	
1430	C-C	from	
	stretching	AAP	Trivedi et al. (2015)
		1442	
1372	С-Н	from	Zamata at al. (2021): Trivadi at al.
	bending	AAP	(2015)
		1371	(2013)
1256	C-N	from	Zapata at al. (2021): Trivadi at al.
	stretching	AAP	(2015)
		1259	(2013)
836	C=C	from	Zapata et al. (2021); Trivedi et al.
	bending	AAP 837	(2015)

Absorptio n band (cm ⁻¹)	Molecular vibration	Functiona l group	Reference
Before IPF	adsorption		
3433	О-Н	hydroxyl	Wang et al. (2018), Cui et al. (2020)
	stretching	group	
2920	С-Н	asymmetri	Wang et al. (2018), Cui et al. (2020)
	stretching	с	
2851	C-H	symmetric	Cui et al. (2020)
	stretching		
1728	C=O	carboxyl	Sun and Li (2004), Kapri et al.
	stretching	group	(2016)
1619	C=C	aromatic	Sun and Li (2004), Zhang et al.
	stretching		(2015), Kapri et al. (2016)
1263	C-OH	C-O in	Rezan et al. (2009), Sun and Li
	stretching	phenols	(2004)
After IPF a	dsorption	ļ	I
3435	О-Н	hydroxyl	Cui et al. (2020)
	stretching	group	
2921	С-Н	asymmetri	Wang et al. (2018), Cui et al. (2020)
	stretching	с	
2853	С-Н	symmetric	Cui et al. (2020)
	stretching		
1727	C=O	carboxyl	Sun and Li (2004)
	stretching	group	

Table 23. Absorption bands and corresponding functional groups of the SCMs detected from the FTIR analysis (IPF).

1626	C=C	aromatic	Sun and Li (2004)	
	stretching			
1263	C-OH	C-O in	Sun and Li (2004)	
	stretching	phenols		
1384	COO-	from IPF	Larray et al. (2020)	
	stretching	1380	Janus et al. (2020)	
579	C-C	from IPF	Ramachandran et al. (2016)	
	deformation	589		

Absorptio n band (cm ⁻¹)	Molecular vibration	Functional group	Reference
2956	C-H stretching	asymmetri	Huei et al. (2015), Swain et al.
		с	(2015)
1721	C=O stretching	carbonyl	Swain et al. (2015), Carvalho et
			al. (2020)
1508	C=C stretching	aromatic	Abioye et al. (2015),
			Ramachandran et al. (2016)
1420	CH-CO		Ramachandran et al. (2016)
	deformation		
1380	COO- stretching	symmetric	Janus et al. (2020)
1231	C-O stretching	carboxyl	Carvalho et al. (2020)
1184	C-O stretching	carboxyl	Huei et al. (2015),
			Ramachandran et al. (2016)
936	CH ₃ rocking		Ramachandran et al. (2016)
	vibration		
780	CH ₂ rocking		Ramachandran et al. (2016)
669	C-H out of plane		Ramachandran et al. (2016)
	deformation		
589	C-C deformation		Ramachandran et al. (2016)

Table 24. Absorption bands and corresponding functional groups of IPF detected from the FTIR analysis.

The XPS spectra of the SCMs are presented in Fig. 13. The wide scans (Fig. 13a) indicate the characteristic peaks of C 1s (285.08 eV, 77.98%) and O 1s (533.08 eV, 22.02%) (Cui et al., 2020; Shi et al., 2020; Rojas et al., 2015). After AAP adsorption, an additional peak of N 1s appeared at 399.94 eV in the wide scan, providing evidence of AAP adsorption (Fig. 13f). The functional groups on the SCMs before and after AAP adsorption are listed in Table 25. Before AAP adsorption, various functional groups were observed in a deconvoluted scan of C 1s (Fig. 13b). The C-O (286.34 eV) and C=O (288.71 eV) bonds suggest that the SCMs contained diverse oxygen-containing functional groups (hydroxyl, ether, lactone, carboxyl, or ester). The π - π bond (291.18 eV) indicates the existence of aromatic rings on the SCMs (Cui et al., 2020; Rojas et al., 2015; Terzyk, 2001). In a deconvoluted scan of O 1s (Fig. 13c), the C=O (531.60 eV) and C-OH (533.52 eV) suggests the existence of quinone and phenol groups, respectively (Shi et al., 2020; Rojas et al., 2015).

Deconvoluted scans of C 1s and O 1s after AAP adsorption are presented in Fig. 13d and Fig. 13e, respectively. Compared to those before AAP adsorption (Fig. 13b and Fig. 13c), the binding energies of C-O and C=O were altered after AAP adsorption. The FTIR spectra (Fig. 12) also show that the C-O (1,263 cm⁻¹) and C=O (1,728 cm⁻¹) bands were shifted to C-O (1,256 cm⁻¹) and C=O (1,721 cm⁻¹) after AAP adsorption. These results suggest that hydrogen-bond formation and $n-\pi$ interactions can contribute to AAP adsorption (Nguyen et al., 2020). Tran et al. (2020) reported that the C-O and C=O peaks in high-resolution scans of C 1s from spherical biochar were altered after AAP adsorption, suggesting that hydrogen bonds and $n-\pi$ interactions may be involved in the adsorption of AAP on spherical biochar.

In our study, the binding energy of π - π was different after AAP adsorption (Fig. 13). In addition, the absorption band of C=C (1619 cm⁻¹) in the FTIR spectra shifted to 1614 cm⁻¹ after AAP adsorption (Fig. 12). These results indicate that π - π interaction can contribute to AAP adsorption. Tran et al. (2020) found that the π - π peak in the C 1s scans changed after AAP adsorption on spherical biochar. Grisales-Cifuentes et al. (2021) reported in FTIR analysis that the band indicating aromatic ring of biochar (1510 cm⁻¹) was more intense after AAP adsorption, suggesting AAP adsorption on biochar through π - π interactions. The XPS wide scans of the SCMs are illustrated in Fig. 14, indicating that the wide scan before IPF adsorption was similar to that after IPF adsorption. The wide scan before IPF adsorption exhibited the characteristic peaks of C 1s (285.08 eV, 77.98%) and O 1s (533.08 eV, 22.02%). After IPF adsorption, the carbon-to-oxygen ratio was altered with C 1s (285.08 eV, 75.17%) and O 1s (532.08 eV, 24.83%). The functional groups on the SCMs before and after IPF adsorption in the XPS analysis are tabulated in Table 26, showing that the

atomic precent of each C 1s or O 1s was changed after IPF adsorption. In the deconvoluted XPS narrow scans of C 1s (Figs. 15a and 15c), various functional groups were observed, including C-O, C=O, and π - π bonds, whereas C=O and C-OH were detected in the deconvoluted XPS narrow scans of O 1s (Figs. 15b and 15d). These indicate that the SCMs contained numerous oxygen-bearing functional groups (hydroxyl, carboxyl, carbonyl, phenol, etc.) along with an aromatic ring (Cui et al., 2020; Shi et al., 2020).



Fig. 13. XPS spectra of the SCMs: (a) wide scans of the SCMs before and after AAP adsorption, (b) high-resolution scan of C 1s before AAP adsorption, (c) high-resolution scan of O 1s before AAP adsorption, (d) high-resolution scan of C 1s after AAP adsorption, and (e) high-resolution scan of O 1s after AAP adsorption, (f) high-resolution scan of N 1s after AAP adsorption.




Before AAP adsorption				After AAP adsorption			
Name	Peak BE	Atomic %	Functional groups	Name	Peak BE	Atomic %	Functional groups
C1s A	284.8	45.98	C-C	C1s A	284.8	43.89	C-C
C1s B	286.34	19.66	C-O	C1s B	286.34	18.62	C-O
C1s C	288.71	9.69	C=O	C1s C	288.63	9.62	C=O
C1s D	291.18	3.11	π - π * (aromatic ring)	C1s D	291.22	3.64	π - π * (aromatic ring)
O1s A	531.6	7.39	C=O	O1s A	531.58	8.07	C=O
O1s B	533.52	14.16	C-OH	O1s B	533.42	15.46	C-OH
				N1s A	399.94	0.69	C-N-C

Table 25. Functional groups of the SCMs detected from the XPS analysis before and after AAP adsorption.



Fig. 14. XPS wide scans of the SCMs before and after IPF adsorption.

	Before	IPF adsorpti	on	After IPF adsorption			
Name	Peak (eV)	Atomic %	Functional groups	Name	Peak (eV)	Atomic %	Functional groups
C1s A	284.80	45.98	C-C	C1s A	284.80	42.41	C-C
C1s B	286.34	19.66	C-O	C1s B	286.36	20.94	C-0
C1s C	288.71	9.69	C=O	C1s C	288.71	8.95	C=O
C1s D	291.18	3.11	π - π * (aromatic ring)	C1s D	291.14	2.71	π - π * (aromatic ring)
O1s A	531.60	7.39	C=O	O1s A	531.74	9.38	C=O
O1s B	533.52	14.16	C-OH	O1s B	533.37	15.62	C-OH

Table 26. Functional groups of the SCMs detected from the XPS analysis before and after IPF adsorption.



Fig. 15. XPS spectra of the SCMs: (a) high-resolution scan of C 1s before IPF adsorption, (b) high-resolution scan of O 1s before IPF adsorption, (c) high-resolution scan of C 1s after IPF adsorption, and (d) high-resolution scan of O 1s after IPF adsorption.



4.3. Adsorption mechanisms and computational studies

4.3.1. Adsorption mechanisms and molecular modeling (AAP)

Adsorption mechanisms for AAP on the SCMs can be explored by varying the pH. Adsorption capacities in a pH range of 2–12 are illustrated in Fig. 1a. The AAP adsorption capacity remained relatively constant at pH 2–10, indicating that solution pH did not play a crucial role in the adsorption of AAP in this pH range. This can be ascribed to the fact that an undissociated (nonionic) form of AAP was predominant in this pH range, according to the species distribution curve of AAP (inset, Fig. 1a). The pKa value of AAP is reportedly 10.96 (Table 1). Similar results have been reported by Tran et al. (2020), who described AAP adsorption on glucose-derived spherical biochar and found that AAP adsorption capacities did not differ in a pH range of 2–10. Others have also reported that the AAP adsorption rates or capacities of vegetable wastes (Villaescusa et al., 2010), activated carbon (Nguyen et al.,2020), and hyper-crosslinked cellulosic adsorbents (Benosmane et al., 2021) remained constant at pH 2–10.

In our study, adsorption mechanisms such as π - π and n- π interactions and hydrogen-bond formation can be involved in AAP adsorption on SCMs at a pH of 2 to 10. The π - π interaction is known as a primary adsorption mechanism for aromatic contaminants on carbon-based adsorbents (Villaescusa et al., 2010; Tran et al., 2020). As presented in Table 22, the SCMs possessed aromatic rings (C=C stretching) on their surfaces, whereas AAP has aromatic rings in its chemical structure (Table 23). Therefore, π - π interaction between the aromatic rings of the SCMs and AAP can occur. Tran et al. (2020) reported that π - π interaction can contribute to the adsorption of AAP on glucose-derived spherical biochar. Meanwhile, n- π^* interaction between the SCMs and AAP can lead to the adsorption. The oxygen ion in the amide group on the AAP (Table 21) can contribute to $n-\pi^*$ interaction with the aromatic ring of the SCMs. Also, the oxygen ion in the carbonyl group on the SCMs (Table 22) can induce to $n-\pi^*$ interaction with the aromatic ring of AAP (Villaescusa et al., 2010; Benosmane et al., 2021; Tran et al., 2020). Nguyen et al. (2020) suggested that $n-\pi^*$ interaction occur between carbonyl oxygen ion (electron donor) on the surface of activated carbon and the aromatic ring (electron acceptor) of AAP. From the CHEM3D analysis, the chemical structures of AAP and the SCMs optimized by the MM2 method are illustrated in Fig. 17a and 17b. Based on these optimized structures, π - π and n- π^* interactions between AAP and the SCMs are visualized in Fig. 18.

Various oxygen-containing functional groups on the SCMs (Table 23) can contribute to hydrogen-bonding formation with AAP (Villaescusa et al., 2010; Benosmane et al., 2021; Tran et al., 2020). The C=O and C-O groups can also contribute to the formation of hydrogen bonds with the hydrogen atom of the hydroxyl group on the surface of AAP through dipole-dipole interactions (Nguyen et al., 2020). Grisales-Cifuentes et al. (2021) reported that phenol, carbonyl, and carboxyl groups are involved in hydrogen bonds between biochar and AAP. The CHEM3D analysis illustrated that hydrogen-bonding can be formed between oxygen atom in the phenol group of AAP and hydrogen atom in the phenol group of the SCMs (Fig. 17c, case 1). As presented in Table 27, the partial atomic charge of oxygen of the adsorbed AAP becomes less negative (electron donor) compared to that of the isolated AAP in the case 1, whereas the charge of hydrogen of the AAP-adsorbed SCMs becomes less positive (electron acceptor) compared to that of the isolated SCMs in the case 1 (Table 28). In the case 2 of hydrogen-bonding formation between hydrogen in the phenol group of AAP and oxygen in the carboxyl group of the SCMs (Fig. 17d), the charge of hydrogen of the adsorbed AAP becomes less positive (electron acceptor) compared to that of the isolated AAP (Table 27), whereas the charge of oxygen of the AAPadsorbed SCMs becomes less negative (electron donor) compared to that of the isolated SCMs (Table 28). In the case 3 (Fig. 17e), hydrogen-bonding occurs between hydrogen in the amide group of AAP (electron acceptor) and oxygen in the carboxyl group of the SCMs (electron donor), whereas hydrogen-bonding takes place between oxygen in the amide group of AAP

(electron donor) and hydrogen in the carboxyl group of the SCMs (electron acceptor) in the case 4 (Fig. 17f).



Fig. 16. Schematic diagram of the adsorption between SCMs and AAP.



Fig. 17. Optimized chemical structures of (a) AAP, (b) SCMs, and (c, d, e, f) hydrogen bonding between AAP and SCMs from the CHEM3D analysis.











Fig. 18. π - π and n- π^* interactions between AAP and SCMs from the CHEM3D analysis.

	Partial atomic charge (eV)						
Atoms of AAP	Icoloted AAD	Adsorbed AAP					
	Isolated AAP	Case 1	Case 2	Case 3	Case 4		
O(1)	-0.7547	-0.7544	-0.7452	-0.7470	-0.6620		
C(2)	0.4173	0.4172	0.4259	0.4252	0.4335		
N(3)	0.3046	0.3050	0.3207	0.3001	0.3447		
C(4)	0.1160	0.1162	0.1230	0.1248	0.1650		
C(5)	-0.1039	-0.1108	-0.1303	-0.1331	-0.1136		
C(6)	-0.0933	-0.0826	-0.1079	-0.1069	0.1452		
C(7)	-0.0839	-0.0913	-0.0916	-0.1176	-0.0823		
C(8)	-0.0985	-0.1012	-0.1140	-0.1578	-0.0851		
C(9)	0.2022	0.2068	0.2030	0.2034	0.2557		
O(10)	-0.2766	-0.2310	-0.2557	-0.2440	-0.1910		
C(11)	-0.1767	-0.1767	-0.1740	-0.1858	-0.1738		
H(12)	0.1006	0.1007	0.1022	0.0944	0.1056		
H(13)	0.0221	0.0221	0.0277	0.0270	0.0414		
H(14)	0.0242	0.0244	0.0297	0.0300	0.2058		
H(15)	0.0165	0.0165	0.0201	0.0299	0.0262		
H(16)	0.0243	0.0244	0.0298	0.0718	0.0340		
H(17)	0.2061	0.2053	0.1748	0.2074	0.2074		
H(18)	0.0427	0.0427	0.0427	0.0429	0.0429		
H(19)	0.0556	0.0555	0.0564	0.0640	0.0545		
H(20)	0.0554	0.0555	0.0566	0.0582	0.0591		

Table 27. Partial atomic charges of isolated AAP and adsorbed AAP on the SCMs.

A tama of	Partial atomic charge (eV)						
Atoms of	Isolated		AAP-adsorbed SCMs				
SCIVIS	SCMs	Case 1	Case 2	Case 3	Case 4		
C(1)	-0.1514	-0.1497	-0.1863	-0.1868	-0.1810		
C(2)	0.0955	0.0951	0.0804	0.0806	0.0744		
C(3)	0.0077	0.0124	-0.0028	-0.0039	-0.0041		
C(4)	0.0688	0.0671	0.0372	0.0387	0.0187		
C(5)	0.0076	0.0067	-0.0223	-0.0233	-0.0254		
C(6)	0.2975	0.3026	0.2845	0.2870	0.2727		
C(7)	0.0071	0.0053	-0.0042	-0.0075	-0.0154		
C(8)	0.0803	0.0665	0.0414	0.0492	0.0489		
C(9)	0.0449	0.0420	0.0269	0.0240	0.0185		
C(10)	0.0822	0.0758	0.0615	0.0523	-0.0190		
C(11)	0.0663	0.0635	0.0230	0.0168	-0.0184		
C(12)	0.1364	0.1537	0.1903	0.1894	0.0848		
C(13)	0.0623	0.0649	0.0442	0.0428	0.0415		
C(14)	0.0728	0.1082	0.1098	0.1065	-0.0197		
C(15)	-0.0114	-0.0173	0.0024	0.0036	0.0002		
C(16)	0.0726	0.0772	0.0524	0.0514	0.0264		
C(17)	0.0480	0.0659	0.0635	0.0625	0.0421		
C(18)	0.0061	0.0126	-0.0141	-0.0183	-0.0223		
C(19)	0.1628	0.1607	0.1243	0.1240	0.0553		
C(20)	0.1198	0.1238	0.1103	0.1086	0.0357		
C(21)	0.0722	0.0693	0.0529	0.0539	0.0431		
C(22)	0.0765	0.0740	0.0579	0.0566	0.0527		
C(23)	-0.1987	-0.1953	-0.1778	-0.1765	-0.2265		
C(24)	0.0111	0.0092	0.0058	0.0066	-0.0095		
C(25)	0.0461	0.0503	0.0394	0.0389	0.0120		
C(26)	-0.0259	-0.0226	-0.0300	-0.0298	-0.0373		
C(27)	-0.0121	-0.0100	-0.0375	-0.0376	-0.0523		
C(28)	0.0562	0.0593	0.0546	0.0544	0.0427		
C(29)	0.0555	0.0613	0.0323	0.0327	-0.0844		
C(30)	0.0619	0.0677	0.0573	0.0558	0.0509		
C(31)	0.1341	0.1322	0.1527	0.1543	-0.0567		
C(32)	0.0892	0.0899	0.0833	0.0820	0.0678		
C(33)	0.0221	0.0240	0.0581	0.0595	-0.0243		
C(34)	0.0168	0.0146	-0.0019	-0.0004	-0.0014		

Table 28. Partial atomic charges of isolated carbon spheres and AAP-adsorbed SCMs.

C(35)	0.0389	0.0374	0.0240	0.0233	0.0030
C(36)	-0.0523	-0.0567	0.1077	0.1110	-0.1333
C(37)	0.0010	-0.0019	0.0071	0.0068	0.0000
C(38)	0.0275	0.0251	0.0530	0.0541	-0.0393
O(39)	-0.2140	-0.2929	-0.1913	-0.2221	-0.2611
C(40)	0.5758	0.5732	0.5509	0.5517	0.5380
O(41)	-0.6482	-0.6538	-0.6426	-0.6252	0.1750
O(42)	-0.9828	-0.9803	-0.9133	-0.9159	-0.8931
H(43)	0.2066	0.1799	0.2125	0.2422	0.1837
H(44)	0.0238	0.0239	0.0286	0.0379	0.0283
H(45)	0.0290	0.0274	0.0264	0.0298	0.0273
H(46)	0.0174	0.0169	0.0235	0.0231	0.0240
H(47)	0.0233	0.0238	0.0276	0.0273	0.0274
H(48)	0.0265	0.0262	0.0311	0.0311	0.0307
H(49)	0.0237	0.0240	0.0293	0.0292	0.0267
H(50)	0.0575	0.0578	0.0584	0.0576	0.0576
H(51)	0.0195	0.0194	0.0238	0.0236	0.0228
H(52)	0.0162	0.0161	0.0237	0.0237	0.0234
H(53)	0.0160	0.0160	0.0256	0.0257	0.0256
H(54)	0.0189	0.0190	0.0261	0.0261	0.0261
H(55)	0.0209	0.0208	0.0236	0.0236	0.0235
H(56)	0.0519	0.0512	0.0528	0.0522	0.0518
H(57)	0.0217	0.0221	0.0282	0.0281	0.0279

Unlike the case at a pH between 2 and 10, the adsorption capacity was negligible at a pH of 12 (Fig. 1a). This can be attributed to the fact that a dissociated (anionic) form of AAP is predominant at pH 12. Electrostatic interactions can play a major role in AAP adsorption at pH 12. The pH_{pzc} value of the SCMs was 3.1, indicating that they were highly negatively charged at pH 12 due to deprotonation of oxygen functional groups. Furthermore, a dissociated (anionic) form of AAP is predominant at pH 12 (inset, Fig. 1a). Therefore, electrostatic repulsion can occur between negatively charged SCMs and anionic AAP. A similar trend was reported previously by Mashayekh-Salehi et al. (2016), who found that the AAP adsorption rate of NH₄Cl-induced activated carbon decreased considerably at pH 12, compared with those at pH 2–10. They attributed this phenomenon to electrostatic repulsion between anionic species of AAP and negatively charged surfaces of activated carbon ($pH_{pzc} = 7.8$) in highly alkaline conditions. As visualized by CHEM3D (Fig. 19), electrostatic repulsion occurs between oxygen atom in the amide group of AAP and oxygen atom in the phenol group of the SCMs. It also takes place between oxygen atom in the deprotonated phenol group of AAP and oxygen atom in the carboxyl group of the SCMs. The CHEM3D analysis (Table 29) shows that as AAP is dissociated above the pK_a value, the oxygen atoms on anionic AAP possess relatively high negative charges. Also, the oxygen atoms on the SCMs have

high negative charges. These charge data indicate that electrostatic repulsion can occur between these oxygen atoms.

Furthermore, pore-filling mechanism can be involved in the adsorption of AAP onto the SCMs. From the CHEM3D analysis, the molecular size of AAP was determined to be $8.94 \text{ Å} \times 7.95 \text{ Å} 4.93 \text{ Å}$ (Fig. 17a). Considering the average pore diameter of the SCMs (18.9 Å), pore filling can partly contribute to the AAP adsorption as a physical adsorption mechanism (Nguyen et al.,2020; Tran et al., 2020).



Fig. 19. Electrostatic repulsion between anionic AAP and SCMs from the CEHM3D analysis.

Atoms of anionic AAP	Partial atomic charge (eV)	Atoms of the SCMs	Partial atomic charge (eV)
O (1)	-0.4752	C(1)	-0.1897
C(2)	0.4998	C(2)	0.0798
N(3)	0.6922	C(3)	-0.0044
C(4)	0.2594	C(4)	0.0379
C(5)	0.0429	C(5)	-0.0220
C(6)	-0.0185	C(6)	0.2790
C(7)	0.0655	C(7)	-0.0085
C(8)	-0.0397	C(8)	0.0527
C(9)	0.4007	C(9)	0.0220
O(10)	-0.6394	C(10)	0.0657
C(11)	-0.1688	C(11)	0.0139
H(12)	0.1041	C(12)	0.1891
H(13)	0.0271	C(13)	0.0423
H(14)	0.0301	C(14)	0.1097
H(15)	0.0231	C(15)	0.0036
H(16)	0.0299	C(16)	0.0512
H(17)	-	C(17)	0.0617
H(18)	0.0429	C(18)	-0.0202
H(19)	0.0585	C(19)	0.1239
H(20)	0.0639	C(20)	0.1076
		C(21)	0.0541
		C(22)	0.0563
		C(23)	-0.1756
		C(24)	0.0070
		C(25)	0.0391
		C(26)	-0.0300

Table 29. Partial atomic charges of anionic AAP and SCMs from CHEM3D analysis.

C(27)	-0.0371
C(28)	0.0541
C(29)	0.0337
C(30)	0.0553
C(31)	0.1551
C(32)	0.0814
C(33)	0.0598
C(34)	-0.0005
C(35)	0.0238
C(36)	0.1129
C(37)	0.0067
C(38)	0.0548
O(39)	-0.9554
C(40)	0.5508
O(41)	-0.6419
O(42)	-0.9186
H(43)	-
H(44)	0.0239
H(45)	0.0264
H(46)	0.0232
H(46) H(47)	0.0232 0.0272
H(46) H(47) H(48)	0.0232 0.0272 0.0311
H(46) H(47) H(48) H(49)	0.0232 0.0272 0.0311 0.0292
H(46) H(47) H(48) H(49) H(50)	0.0232 0.0272 0.0311 0.0292 0.0575
H(46) H(47) H(48) H(49) H(50) H(51)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236
H(46) H(47) H(48) H(49) H(50) H(51) H(52)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236 0.0237
H(46) H(47) H(48) H(49) H(50) H(51) H(52) H(53)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236 0.0237 0.0256
H(46) H(47) H(48) H(49) H(50) H(51) H(52) H(53) H(54)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236 0.0237 0.0256 0.0261
H(46) H(47) H(48) H(49) H(50) H(51) H(52) H(53) H(54) H(55)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236 0.0237 0.0256 0.0261 0.0236
H(46) H(47) H(48) H(49) H(50) H(51) H(51) H(52) H(53) H(54) H(55) H(56)	0.0232 0.0272 0.0311 0.0292 0.0575 0.0236 0.0237 0.0256 0.0261 0.0236 0.0236 0.0236

4.3.2. Adsorption mechanisms and molecular modeling (IPF)

The species distribution of IPF in reply to pH change is depicted in Fig. 21a. It is known that the pK_a value of IPF is 4.91 (Oba et al. 2021). Depending on solution pH, it exists as an undissociated form (IPF) and/or dissociated (anionic) form (IPF⁻) in solution. At pH 2, the IPF species distribution is composed of IPF (99.9%) and IPF⁻ (0.1%), indicating that IPF is almost all in the undissociated form. At pH 4, it consists of IPF (89.9%) and IPF⁻ (11.0%), indicating the dissociated (anionic) form partly contributes to the species composition. However, IPF⁻ became the predominant form at pH 6, with the species distribution of IPF (7.5%) and IPF⁻ (92.5%). At pH 8 and above, IPF is completely dissociated (IPF⁻ = 99.9%). The species distribution suggests that the adsorption of IPF on the adsorbents can be greatly affected by solution pH.

The influence of solution pH on the adsorption capacity of the SCMs toward IPF is illustrated in Fig. 21b. The point of zero charge (pH_{pzc}) of the SCMs was determined to be 3.21 (Fig. 22). At a solution pH of 2, the IPF adsorption capacity was highest and declined steadily up to pH 8. As the pH rose to 10, the adsorption capacity dropped sharply and became insignificant at pH 12. Our results demonstrate that pH was an important factor affecting the adsorption of IPF to the SCMs. The IPF adsorption to carbon materials in

reply to pH changes has been explored by researchers. Streit et al. (2021) studied the IPF adsorption to acid-treated sludge-derived activated carbons $(pH_{pzc} = 7.8)$ in the pH range of 2-9. They reported that the removal rate was high at pH 2–4 (the highest at pH 4) and then decreased significantly in the range of pH 5–9. Costa et al. (2021) examined the adsorption of IPF to activated carbon synthesized from fruit waste (pH_{pzc} = 5.2) in the range of pH 3–10, showing that the adsorption capacity was highest at pH 3 and then dropped steadily as pH rose to 10. Lei et al. (2021) showed that the IPF adsorption capacity of N-doped porous carbon (pH_{pzc} = 3.4) was highest at pH 2, decreased moderately at pH 3–6, and then dropped sharply up to pH 12. These studies showed similar trends of IPF adsorption to the carbon-based adsorbents with a slight difference depending on the pH_{pzc} of the adsorbents.



Fig. 20. Schematic diagram of the adsorption between SCMs and IPF.



Fig. 21. (a) IPF species distribution and (b) IPF adsorption capacity according to solution pH.



Fig. 22. Zeta potentials of the SCMs in response to pH change.

The IPF adsorption to the SCMs can occur via hydrogen-bond formation, π - π interactions, n- π^* interactions, electrostatic interactions, hydrophobic interaction, and pore-filling (Iovino et al., 2015; Tran et al., 2020; Pap et al., 2021; Lei et al, 2021). Hydrogen-bond formation contributes to the adsorption of IPF to the SCMs through dipole-dipole attraction between oxygencontaining functional groups on the SCMs and hydroxyl group in the structure of IPF. Pap et al. (2021) reported that hydrogen bonds were formed between the P-doped microporous carbon and IPF due to the presence of oxygenbearing functional groups (hydroxyl and carboxyl groups). Lei et al. (2021) suggested that hydrogen-bond formation played an important role in the adsorption of IPF on the N-doped porous carbon. The chemical structures of the SCMs and IPF optimized by the MM2 method in the CHEM3D analysis are illustrated in Fig. 23a and 23b, respectively. Hydrogen-bond formation between the SCMs and IPF were explored based on these optimized structures.

Hydrogen bonds could be formed between oxygen atoms (H-bond acceptor) in the carboxyl groups of the CSH and hydrogen atoms (H-bond donor) in the carboxyl group of IPF (Fig. 23c, Tables 30 and 31, case 1). In case 2 (Fig. 23d), hydrogen-bond formation occurs in two ways—between the hydrogen in the phenol group of the CSH (H-bond donor) and oxygen in the carboxyl group of IPF (H-bond acceptor) and between the oxygen in the phenol group of the CSH (H-bond acceptor) and hydrogen in the carboxyl group of IPF (H-bond donor) (Tables 30 and 31, case 2). When IPF exists as anionic IPF (Fig. 23e, case 3), hydrogen-bonding takes place between hydrogen in the phenol group of the CSH (H-bond donor) and oxygen in the carboxyl group of IPF (H-bond acceptor) (Table 32).



Fig. 23. Optimized chemical structures of (a) SCMs, (b) IPF, and (c, d, e) hydrogen bonding between SCMs and IPF from the CHEM3D analysis.





Atoms of the	Partial atomic charge (eV)					
SCMs	Isolated	IPF-adsorbed SCMs	IPF-adsorbed SCMs			
~	SCMs	(case 1)	(case 2)			
C(1)	-0.1514	-0.1826	-0.1847			
C(2)	0.0955	0.0819	0.0849			
C(3)	0.0077	-0.0061	-0.0088			
C(4)	0.0688	0.0398	0.0439			
C(5)	0.0076	-0.0204	-0.0248			
C(6)	0.2975	0.2845	0.2918			
C(7)	0.0071	0.0033	-0.0007			
C(8)	0.0803	0.0532	0.0557			
C(9)	0.0449	0.0319	0.0289			
C(10)	0.0822	0.0724	0.0744			
C(11)	0.0663	0.0297	0.0224			
C(12)	0.1364	0.1824	0.1807			
C(13)	0.0623	0.0473	0.0433			
C(14)	0.0728	0.0846	0.0967			
C(15)	-0.0114	0.0060	0.0088			
C(16)	0.0726	0.0493	0.0476			
C(17)	0.0480	0.0442	0.0472			
C(18)	0.0061	-0.0189	-0.0198			
C(19)	0.1628	0.1203	0.1176			
C(20)	0.1198	0.1034	0.1051			
C(21)	0.0722	0.0572	0.0563			
C(22)	0.0765	0.0607	0.0581			
C(23)	-0.1987	-0.1738	-0.1776			
C(24)	0.0111	0.0056	0.0087			
C(25)	0.0461	0.0386	0.0377			
C(26)	-0.0259	-0.0323	-0.0305			
C(27)	-0.0121	-0.0363	-0.0374			
C(28)	0.0562	0.0512	0.0527			

Table 30. Partial atomic charges for isolated SCMs and IPF-adsorbed SCMs related to hydrogen-bond formation.

C(29)	0.0555	0.0355	0.0357
C(30)	0.0619	0.0512	0.0514
C(31)	0.1341	0.1555	0.1544
C(32)	0.0892	0.0794	0.0797
C(33)	0.0221	0.0574	0.0589
C(34)	0.0168	-0.0008	0.0027
C(35)	0.0389	0.0277	0.0233
C(36)	-0.0523	0.1074	0.1103
C(37)	0.0010	0.0072	0.0077
C(38)	0.0275	0.0537	0.0537
O(39)	-0.2140	-0.1822	-0.1979
C(40)	0.5758	0.5510	0.5534
O(41)	-0.6482	-0.6428	-0.6442
O(42)	-0.9828	-0.9026	-0.9197
H(43)	0.2066	0.2104	0.2203
H(44)	0.0238	0.0295	0.0295
H(45)	0.0290	0.0266	0.0258
H(46)	0.0174	0.0246	0.0231
H(47)	0.0233	0.0271	0.0270
H(48)	0.0265	0.0311	0.0314
H(49)	0.0237	0.0289	0.0289
H(50)	0.0575	0.0568	0.0579
H(51)	0.0195	0.0238	0.0234
H(52)	0.0162	0.0240	0.0238
H(53)	0.0160	0.0258	0.0258
H(54)	0.0189	0.0261	0.0259
H(55)	0.0209	0.0239	0.0237
H(56)	0.0519	0.0542	0.0545
H(57)	0.0217	0.0282	0.0279

	Partial atomic charge (eV)					
Atoms of IPF	Isolated IDE	Adsorbed IPF	Adsorbed IPF			
	Isolated IFF	(case 1)	(case 2)			
C(1)	0.0438	0.0466	0.0459			
C(2)	-0.1364	-0.1344	-0.1346			
C(3)	-0.1364	-0.1346	-0.1344			
C(4)	-0.0771	-0.0695	-0.0699			
C(5)	0.0506	0.0575	0.0562			
C(6)	-0.0503	-0.0668	-0.0669			
C(7)	-0.0572	-0.0756	-0.0756			
C(8)	0.0830	0.0927	0.0857			
C(9)	-0.0590	-0.0787	-0.0771			
C(10)	-0.0500	-0.0668	-0.0664			
C(11)	-0.0453	-0.0407	-0.0397			
C(12)	-0.1143	-0.1131	-0.1104			
C(13)	0.6040	0.6083	0.6041			
O(14)	-0.6084	-0.6471	-0.6328			
O(15)	-0.2105	-0.1759	-0.1719			
H(16)	0.0387	0.0385	0.0383			
H(17)	0.0380	0.0374	0.0374			
H(18)	0.0396	0.0396	0.0392			
H(19)	0.0236	0.0254	0.0255			
H(20)	0.0380	0.0374	0.0374			
H(21)	0.0388	0.0384	0.0384			
H(22)	0.0396	0.0395	0.0393			
H(23)	0.0310	0.0320	0.0322			
H(24)	0.0310	0.0317	0.0327			
H(25)	0.0192	0.0253	0.0253			
H(26)	0.0197	0.0259	0.0258			
H(27)	0.0191	0.0250	0.0249			
H(28)	0.0193	0.0254	0.0253			
H(29)	0.0440	0.0442	0.0493			
H(30)	0.0378	0.0380	0.0377			
H(31)	0.0381	0.0381	0.0378			
H(32)	0.0360	0.0357	0.0353			
H(33)	0.2119	0.2047	0.2090			

Table 31. Partial atomic charges for isolated IPF and adsorbed IPF on the SCMs related to hydrogen-bond formation.

Atoms of	Cha	rge (eV)	Atoms of the SCMs	Cł	Charge (eV)		
anionic IPF	Isolated anionic IPF	Adsorbed anionic IPF (Case 3)		Isolated SCMs	Anionic IPF- adsorbed SCMs (Case 3)		
C(1)	0.0506	0.0437	C(1)	-0.1514	-0.1470		
C(2)	-0.1362	-0.1364	C(2)	0.0955	0.0947		
C(3)	-0.1363	-0.1364	C(3)	0.0077	0.0073		
C(4)	-0.0724	-0.0771	C(4)	0.0688	0.0663		
C(5)	0.0988	0.0502	C(5)	0.0076	0.0079		
C(6)	-0.0439	-0.0503	C(6)	0.2975	0.2983		
C(7)	-0.0209	-0.0575	C(7)	0.0071	0.0065		
C(8)	0.1243	0.0830	C(8)	0.0803	0.0777		
C(9)	-0.0113	-0.0593	C(9)	0.0449	0.0437		
C(10)	-0.0386	-0.0499	C(10)	0.0822	0.0775		
C(11)	0.2802	-0.0460	C(11)	0.0663	0.0607		
C(12)	-0.0923	-0.1142	C(12)	0.1364	0.1313		
C(13)	0.7065	0.5968	C(13)	0.0623	0.0609		
O(14)	0.1655	-0.5891	C(14)	0.0728	0.0645		
O(15)	-0.4625	-0.9491	C(15)	-0.0114	-0.0122		
H(16)	0.0390	0.0387	C(16)	0.0726	0.0709		
H(17)	0.0380	0.0380	C(17)	0.0480	0.0466		
H(18)	0.0396	0.0396	C(18)	0.0061	0.0015		
H(19)	0.0240	0.0236	C(19)	0.1628	0.1541		
H(20)	0.0381	0.0380	C(20)	0.1198	0.1181		
H(21)	0.0390	0.0388	C(21)	0.0722	0.0708		
H(22)	0.0396	0.0396	C(22)	0.0765	0.0757		
H(23)	0.0322	0.0310	C(23)	-0.1987	-0.1923		
H(24)	0.0316	0.0310	C(24)	0.0111	0.0115		
H(25)	0.0198	0.0192	C(25)	0.0461	0.0489		
H(26)	0.0215	0.0197	C(26)	-0.0259	-0.0260		
H(27)	0.0192	0.0191	C(27)	-0.0121	-0.0092		

Table 32. Partial atomic charge of anionic IPF and the SCMs related to hydrogen-bond formation (case 3) in CHEM3D analysis.

H(28)	0.0222	0.0193	C(28)	0.0562	0.0557
H(29)	0.0501	0.0440	C(29)	0.0555	0.0588
H(30)	0.0393	0.0378	C(30)	0.0619	0.0607
H(31)	0.0409	0.0382	C(31)	0.1341	0.1325
H(32)	0.0544	0.0359	C(32)	0.0892	0.0880
H(33)	-	-	C(33)	0.0221	0.0173
			C(34)	0.0168	0.0162
			C(35)	0.0389	0.0344
			C(36)	-0.0523	-0.0540
			C(37)	0.0010	0.0004
			C(38)	0.0275	0.0270
			O(39)	-0.2140	-0.2490
			C(40)	0.5758	0.5750
			O(41)	-0.6482	-0.6503
			O(42)	-0.9828	-0.9837
			H(43)	0.2066	0.2368
			H(44)	0.0238	0.0237
			H(45)	0.0290	0.0286
			H(46)	0.0174	0.0174
			H(47)	0.0233	0.0233
			H(48)	0.0265	0.0265
			H(49)	0.0237	0.0237
			H(50)	0.0575	0.0575
			H(51)	0.0195	0.0193
			H(52)	0.0162	0.0161
			H(53)	0.0160	0.0160
			H(54)	0.0189	0.0189
			H(55)	0.0209	0.0210
			H(56)	0.0519	0.0518
			H(57)	0.0217	0.0217
During the adsorption of IPF to the SCMs, π - π interactions can occur between the aromatic ring of IPF and aromatic rings on the surfaces of the SCMs, which was supported by the Raman spectra of the SCMs (Fig. 11a). The I_D/I_G ratio in the Raman spectra was reduced from 1.45 to 1.41 after IPF adsorption. In the FTIR spectra (Fig. 11c), the C=C band (1619 cm⁻¹) was shifted to C=C (1,626 cm⁻¹) after IPF adsorption. In deconvoluted XPS high resolution scans of C 1s (Fig. 15b), the binding energy of π - π was altered after IPF adsorption. These results suggest that π - π interactions can contribute to the adsorption of IPF to the SCMs. Iovino et al. (2015) reported that the adsorption of IPF onto a granular activated carbon mainly took place through π - π interactions. Lei et al. (2021) also revealed that π - π interactions were involved in the adsorption of IPF on the N-doped porous carbon. Fig. 24a illustrates the π - π interactions between IPF and the SCMs in the CHEM3D analysis. In addition, the adsorption of IPF to the SCMs can also occur through n- π^* interactions between the carbonyl groups on the surface of the SCMs and the aromatic ring of IPF. Pap et al. (2021) suggested that $n-\pi^*$ interactions may be engaged in the adsorption of IPF to the P-doped microporous carbon, which contained phosphate and pyrophosphate groups. Our deconvoluted XPS narrow scans of O 1s (Fig. 15b and 15d) show that the binding energies of C=O and C-OH after IPF adsorption were altered

compared to those before IPF adsorption, suggesting that hydrogen-bond formation and $n-\pi^*$ interactions could contribute to IPF adsorption. The CHEM3D analysis visualized $n-\pi^*$ interactions between IPF and the SCMs (Fig. 24b).

Considering the pK_a value of IPF (4.91) and pH_{pzc} of the SCMs (3.21), electrostatic interactions should be considered as the adsorption mechanism for IPF onto the SCMs. At pH 2, however, electrostatic interactions might be excluded because IPF is almost all in an undissociated form at this pH (99.9%). Compared to pH 2, the adsorption capacity decreased slightly at pH 4 because of the partial presence of anionic form ($IPF^{-} = 11.0\%$) in the species composition. As mentioned above, the pH_{pzc} of the SCMs was 3.21, and so electrostatic repulsion between anionic IPF and the negatively-charged SCMs affected negatively on the adsorption at pH 4, resulting in reduction of the adsorption capacity. As pH rose further to 6 and 8, the adsorption capacity decreased further. This phenomenon was attributed to the fact that the negative role of electrostatic repulsion was intensified because the ratio of IPF⁻ in the species composition was enhanced, and the surface charge of the SCMs became more negative. The adsorption capacity of the SCMs was very low at pH 10 and even became negligible at pH 12 (Fig. 21b). This result was attributed to the fact that IPF is completely dissociated at these pHs (IPF⁻ =

99.99%), whereas the surface of the SCMs became highly negatively-charged due to enhanced deprotonation of oxygen-functional groups. Electrostatic repulsion played a dominant role in the adsorption of IPF at highly alkaline pH range, causing a sharp decrease in the adsorption capacity (Iovino et al., 2015). A similar finding was reported by Pap et al. (2021), who demonstrated that the IPF adsorption capacity of P-functionalized microporous carbon $(pH_{pzc} = 3.1)$ was highest at pH 2, decreased slightly at pH 3-5, and then dropped steeply up to pH 12. They assigned this phenomenon to the fact that the adsorption of IPF onto P-functionalized microporous carbon became unfavorable as pH rose due to electrostatic repulsion between the negativelycharged adsorbent and anionic IPF. Based on the CHEM3D analysis, electrostatic repulsion between the SCMs and anionic IPF was also visualized in Fig. 25. The oxygen atoms of the anionic IPF held comparably large negative charges. At the same time, the oxygens of the SCMs also possessed relatively large negative values (Table 33). The deprotonated carboxyl group of IPF could interact with both deprotonated phenol groups of the SCMs and deprotonated carboxyl group of the SCMs, resulting in electrostatic repulsion.

Hydrophobic interactions could be engaged in the adsorption of IPF to the SCMs. The aromatic ring (hydrophobic part) of IPF could interact with the aromatic ring on the SCMs. Pap et al. (2021) mentioned that hydrophobic

interactions could partly contribute to the adsorption of IPF to the P-doped microporous carbon. Ali et al. (2019) reported that hydrophobic interactions could occur between IPF and ethylamine-functionalized hydrophobic activated carbon. Furthermore, the pore-filling mechanism could be associated with the adsorption of IPF onto the SCMs. From the CHEM3D analysis with an optimized structure of IPF, the molecular size of IPF was computed to be 9.43 Å \times 7.75 Å \times 6.23 Å (Fig. 23b). Given that the average pore diameter of the SCMs was 2.27 nm, pore filling could contribute to the IPF adsorption as a physical adsorption mechanism (Nourmoradi et al., 2018; Pap et al., 2021).



Fig. 24. Interactions between the SCMs and IPF (white = hydrogen; gray = carbon; red = oxygen): (a) π - π interaction and (b) n- π ^{*} interaction.



Fig. 25. Electrostatic repulsion between the SCMs and IPF (white = hydrogen; gray = carbon; red = oxygen).

Atoms of anionic IPF ⁻	Partial atomic charge (eV)	Atoms of the SCMs	Partial atomic charge (eV)
C(1)	0.0437	C(1)	-0.1514
C(2)	-0.1364	C(2)	0.0955
C(3)	-0.1364	C(3)	0.0077
C(4)	-0.0771	C(4)	0.0688
C(5)	0.0503	C(5)	0.0076
C(6)	-0.0503	C(6)	0.2975
C(7)	-0.0576	C(7)	0.0071
C(8)	0.0830	C(8)	0.0803
C(9)	-0.0594	C(9)	0.0449
C(10)	-0.0500	C(10)	0.0822
C(11)	-0.0484	C(11)	0.0663
C(12)	-0.1142	C(12)	0.1364
C(13)	0.5955	C(13)	0.0623
O(14)	-0.6445	C(14)	0.0728
O(15)	-0.9497	C(15)	-0.0114
H(16)	0.0387	C(16)	0.0726
H(17)	0.0380	C(17)	0.0480
H(18)	0.0396	C(18)	0.0061
H(19)	0.0236	C(19)	0.1628
H(20)	0.0380	C(20)	0.1198
H(21)	0.0388	C(21)	0.0722
H(22)	0.0396	C(22)	0.0765
H(23)	0.0310	C(23)	-0.1987
H(24)	0.0310	C(24)	0.0111
H(25)	0.0192	C(25)	0.0461
H(26)	0.0197	C(26)	-0.0259

Table 33. Partial atomic charge of anionic IPF and the SCMs related to electrostatic repulsion in CHEM3D analysis.

H(27)	0.0191	C(27)	-0.0121
H(28)	0.0193	C(28)	0.0562
H(29)	0.0441	C(29)	0.0555
H(30)	0.0378	C(30)	0.0619
H(31)	0.0381	C(31)	0.1341
H(32)	0.0358	C(32)	0.0892
H(33)	-	C(33)	0.0221
		C(34)	0.0168
		C(35)	0.0389
		C(36)	-0.0523
		C(37)	0.0010
		C(38)	0.0275
		O(39)	-0.2140
		C(40)	0.5758
		O(41)	-0.6482
		O(42)	-0.9828
		H(43)	0.2066
		H(44)	0.0238
		H(45)	0.0290
		H(46)	0.0174
		H(47)	0.0233
		H(48)	0.0265
		H(49)	0.0237
		H(50)	0.0575
		H(51)	0.0195
		H(52)	0.0162
		H(53)	0.0160
		H(54)	0.0189
		H(55)	0.0209
		H(56)	0.0519
		H(57)	0.0217

4.4. Multi-factor experiments and ANN

4.4.1. ANN modeling for AAP adsorption

A central composite design matrix with four input variables (A = pH; B = temperature; C = adsorbent dose; D = initial AAP concentration) and an output variable (AAP adsorption capacity) is presented in Table 7.

An ANN model was also constructed with the experimental data (Table 7). An ANN model usually comprises input, hidden, and output layers. Using the MATLAB nntool, the ANN model was developed from the following formula (Eq. 7):

$$\mathbf{y} = \text{Purelin} \left[\boldsymbol{w}_0 \times \text{Tansig} \left(\boldsymbol{w}_2 \times \text{Tansig} \left(\boldsymbol{w}_1 \times \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} + \boldsymbol{b}_1 \right) + \boldsymbol{b}_2 \right) + \boldsymbol{b}_0 \right]$$
(7)

The input variables were normalized between -2 and 2 (Eq. 8).

Development of the ANN model consisted of training, validating, and testing phases. Among 56 data points (Table 7), 34 data points (60%) were used in the training phase to modify and adjust the values of weight and bias to reduce errors between the observed and predicted outputs. Next, 11 data points (20%) were applied to avert overfitting in the validating phase, and the remaining 11 data points (20%) were employed in the testing phase to appraise the fitness of the model to the data (Gadekar et al., 2019). The mean squared error and the Levenberg-Marquardt algorithm were applied for the modeling.

$$x_{n} = 4 \times \frac{(x - x_{min})}{(x_{max} - x_{min})} - 2$$

$$x_{n} : -2 \sim +2$$
(8)

- x : input value
- x_{max} : maximum value of x
- x_{min} : minimum value of x

The structure of an ANN model can significantly affect its performance (Gadekar et al., 2019). It is therefore important to find the best ANN structure during model development by evaluating the performances of the models with various topologies (Table 34). In our study, a topology of 4:11:9:1 (4 input variables, 11 neurons in the 1st hidden layer, 9 neurons in the 2nd hidden layer, and 1 output variable) was selected as the optimal structure (Fig. 26):

$$\begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,11} \end{bmatrix} = \operatorname{Tansig} \left(\begin{bmatrix} \vec{w}_{1,1} \\ \vdots \\ \vec{w}_{1,11} \end{bmatrix} \times \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} b_{1,1} \\ \vdots \\ b_{1,11} \end{bmatrix} \right)$$

$$\begin{bmatrix} h_{2,1} \\ \vdots \\ h_{2,9} \end{bmatrix} = \operatorname{Tansig} \left(\begin{bmatrix} \vec{w}_{2,1} \\ \vdots \\ \vec{w}_{2,9} \end{bmatrix} \times \begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,11} \end{bmatrix} + \begin{bmatrix} b_{2,1} \\ \vdots \\ b_{2,9} \end{bmatrix} \right)$$

$$[f_1] = \operatorname{Purelin} \left(\begin{bmatrix} \vec{w}_{3,1} \end{bmatrix} \times \begin{bmatrix} h_{2,1} \\ \vdots \\ h_{2,9} \end{bmatrix} + \begin{bmatrix} b_{3,1} \end{bmatrix} \right)$$

$$(9)$$

Table 35 presents the values of weights and biases in Eq. 9. The diagnostic plots in Fig. 27 show that the ANN model sufficiently predicted adsorption capacity, with a correlation coefficient value (R) of > 0.97.

The performance of the ANN model, Eq. 9, was further tested using additional multi-factor experiments. A random number generator (RAND function) in Excel was used to randomly choose four experimental conditions from the input variable ranges in Table 6. Observed and predicted adsorption capacities from the additional experiments are presented in duplicate in Table 36 and Fig. 28, along with the percent errors calculated using Eq. 10. In the ANN model, the impact of the input variables on the output variable was prioritized in terms of the relative importance of each variable, which was quantified using Eq. 11. The relative importance was in the order of initial AAP concentration (100%) > adsorbent dosage (92.3%) > temperature (77.6%) > pH (43.6%) (Fig. 29). Our results suggest that initial AAP concentration was the most important input variable affecting AAP adsorption capacity.

I			R		
Topology	MSE	Training	Validating	Test	All
4:8:1	13.873	0.911	0.963	0.85	0.893
4:9:1	9.111	0.967	0.979	0.928	0.961
4:10:01	8.643	0.98	0.973	0.886	0.974
4:11:01	60.984	0.97	0.73	0.988	0.954
4:12:01	21.368	0.981	0.971	0.941	0.971
4:8:8:1	9.232	0.961	0.953	0.999	0.968
4:8:9:1	10.892	0.969	0.974	0.98	0.969
4:8:10:1	13.75	0.978	0.929	0.981	0.975
4:8:11:1	11.836	0.956	0.983	0.925	0.954
4:8:12:1	14.398	0.927	0.968	0.998	0.945
4:9:8:1	16.305	0.959	0.947	0.998	0.968
4:9:9:1	4.668	0.945	0.984	0.994	0.958
4:9:10:1	12.152	0.95	0.956	0.986	0.954
4:9:11:1	22.955	0.973	0.914	0.993	0.974
4:9:12:1	12.83	0.96	0.95	0.986	0.961
4:10:8:1	9.988	0.961	0.983	0.994	0.971
4:10:9:1	4.437	0.949	0.993	0.984	0.966
4:10:10:1	9.637	0.961	0.962	0.993	0.972
4:10:11:1	7.269	0.967	0.983	0.988	0.971
4:10:12:1	4.827	0.909	0.993	0.936	0.923
4:11:8:1	23.099	0.939	0.934	0.786	0.928
4:11:9:1	1.051	0.972	0.996	0.966	0.972
4:11:10:1	34.209	0.963	0.941	0.948	0.956
4:11:11:1	55.21	0.917	0.901	0.83	0.902
4:11:12:1	25.886	0.977	0.931	0.992	0.97
4:12:8:1	16.413	0.959	0.991	0.965	0.97
4:12:9:1	7.431	0.964	0.952	0.749	0.928
4:12:10:1	5.724	0.97	0.995	0.888	0.972
4:12:11:1	4.543	0.801	0.997	0.653	0.799
4:12:12:1	11.142	0.8	0.946	0.994	0.861

Table 34. Comparison of network topologies with various hidden layers and neurons (AAP).



Fig. 26. Structure of ANN model with 11 and 9 neurons in 2 hidden layers (AAP).

		Hidde	n layer 1	[w(1)]			Hidden layer 2 [w(2)]											Output layer [w(3)]									
n	w1 A,n	w1 B,n	w1 C,n	w1 D,n	b1n		w(2)n ł								b2n					w(3)n					b3n		
1	-0.1	1.7	-1.1	1.7	-2.9	-0.2	1.1	0.3	0.4	0.9	1.5	-0.4	0.8	0.7	0.7	-0.8	-2.0	1.0	0.2	-1.1	-0.2	0.1	-0.1	0.4	0.3	-0.8	-0.7
2	-0.6	-1.5	-1.6	-1.9	1.5	-0.9	-0.2	0.5	-0.7	-0.2	-0.6	0.1	0.8	-0.2	-0.4	-0.6	1.3										
3	-0.3	2.3	-2.3	-0.4	-0.5	0.2	-0.7	-0.6	1.1	-0.1	1.0	-0.5	-0.7	0.9	0.5	0.4	-0.8										
4	-0.1	-1.9	-0.1	-0.6	-2.1	0.6	-0.3	0.8	0.3	1.0	0.2	-0.2	-0.4	0.6	0.7	0.0	-0.6										
5	1.5	-0.2	2.6	-1.2	-0.6	-0.7	0.6	0.8	1.0	-1.0	-0.3	0.9	0.3	-0.1	-0.4	0.9	-0.1										
6	0.1	0.4	-2.2	-2.2	-0.2	0.6	0.3	0.7	-0.4	1.4	-0.9	0.5	-0.5	0.9	0.3	0.3	0.8										
7	-0.5	1.6	0.0	-1.7	-1.4	0.4	-0.4	-0.7	0.2	-0.1	0.3	-0.3	1.0	0.5	0.8	0.2	1.0										
8	-0.1	-0.2	-0.1	2.9	1.2	0.5	-0.1	0.2	0.2	0.1	0.4	0.0	1.1	-0.3	1.2	0.3	1.5										
9	-1.7	0.9	2.0	0.5	-1.2	-0.3	0.8	0.6	0.7	1.4	0.8	-0.8	0.5	0.8	0.6	-0.1	2.1										
1 0	0.4	1.3	-1.2	1.6	2.2																						
1 1	1.6	-1.4	-0.3	-0.1	3.1																						

Table 35. Values of weights and biases for each layer and neuron in Eq. 9 (AAP).



Fig. 27. The diagnostic plots of ANN model (AAP).

		Input	variable		Adsorption (mg	n capacity g/g)
Exp.	А	В	С	D	Observed	Predicted
		(°C)	(g/L)	(mg/L)	Observed	(ANN)
A1	4.7	24.5	0.23	57	37.2	41.0 (10.3)
A2	8.2	17.1	0.10	82	63.0	61.3 (2.7)
A3	3.9	18.9	0.07	70	68.6	75.6 (10.3)
A4	5.8	33.2	0.13	36	42.3	39.0 (7.7)
A5	4.7	24.5	0.23	57	36.1	41.0 (13.7)
A6	8.2	17.1	0.10	82	66.0	61.3 (7.1)
A7	3.9	18.9	0.07	70	65.7	75.6 (15.0)
A8	5.8	33.2	0.13	36	41.5	39.0 (6.1)

Table 36. Observed and predicted adsorption capacities obtained from additional multi-factor experiments in duplicate (AAP).

* The numbers in parentheses are the percent errors between observed and predicted values.

Percent error between observed and predicted values

Percent error (%) =
$$\frac{|\text{Predicted value} - \text{Observed value}|}{\text{Observed value}} \times 100$$
 (10)



Fig. 28. Diagnostic plot for additional multi-factor adsorption experiments in the ANN modeling (AAP).

Relative importance of input variables

 $I_i(\%)$

$$=\frac{\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)i,n}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]}\right]}{\max\left\{\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)A,n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]},\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)B,n}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]},\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)B,n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]},\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)B,n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(2)n}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]},\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)B,n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}\right| \times \left|\vec{w}_{(0)n}\right|\right)\right]},\sum_{n=1}^{11}\left[\frac{\left|\vec{w}_{(1)B,n}\right| \times \left|\vec{w}_{(0)n}\right|}{\left(\left|\vec{w}_{(1)}$$

(11)

 I_i = relative importance of each input variable (%)

$$i = input variable (A : i = 1, B : i = 2, C : i = 3, D : i = 4)$$

n = number of neuron

- $\vec{w}_{(1)i,n}$ = weight of input variable 'i' in first hidden layer nth neuron
- $\vec{w}_{(2)n}$ = weight of second hidden layer nth neuron

 $\vec{w}_{(0)n}$ = weight in output layer nth neuron



Fig. 29. Relative importance of four input variables calculated using Eq. 11 (AAP).

4.4.2. ANN modeling for IPF adsorption

The ANN model was developed based on the formula given in Eq. 7, which consisted of input, hidden, and output layers. The input layer includes input variables, whereas the hidden and output layers contain neurons for each layer. In the model development, the input variables were normalized in the range of -2 to 2 using the normalization formula (Eq. 8). Model development was conducted by selecting the best ANN structure from various topologies, which are controlled by the numbers of hidden layers and neurons. In our study, the numbers of hidden layers and neurons varied from 4:8:1 to 4:12:12:1 (Table 37). Based on the lowest MSE value (0.376), the topology 4:9:11:1 was selected as the best structure:

The ANN model contained four input variables, nine neurons in the first hidden layer, eleven neurons in the second hidden layer, and one output variable (Fig. 30). The diagnostic plots in Fig. 31 show that the IPF removal rate was well precited by Eq. 12 (R > 0.99). The weights and biases in each layer and neuron in Eq. 12 are presented in Table 38.

The predictability of Eq. 12 was further assessed using the additional adsorption experiments (Table 39). Four multi-factor experimental conditions were randomly chosen within the range of the input variables in Table 6 using the RAND function in Excel. The diagnostic plot (Fig. 32) illustrates that Eq.

12 had good predictability ($R^2 = 0.921$) for the additional adsorption data. Within the range of the input variables in Table 8, the IPF removal rate of 94% was predicted from Eq. 12 at the optimum condition of pH 2.0, an adsorbent dose of 0.25 g/L, an initial IPF concentration of 2.0 mg/L, and a temperature of 40°C. At this optimum condition, the actual removal rate of 91% was observed from the adsorption experiment. The relative importance analysis was performed to prioritize the influence of input variables on the IPF removal rate. The relative importance was quantified using Eq. 11 with the following order of initial IPF concentration (100%) > solution pH (92.7%) > adsorbent dosage (90.5%) > temperature (57.4%) (Table 40), suggesting that initial IPF concentration was the primary input variable influencing the IPF removal rate.

Topology	MSF		R		
Topology	MDL	Training	Validating	Test	All
4:8:1	0.851	0.993	0.999	0.994	0.994
4:9:1	0.604	0.994	0.999	0.990	0.994
4:10:01	0.989	0.996	0.998	0.997	0.996
4:11:01	0.895	0.988	0.999	0.997	0.989
4:12:01	0.943	0.993	0.998	0.989	0.993
4:8:8:1	1.065	0.995	0.995	0.998	0.995
4:8:9:1	0.680	0.996	0.998	0.984	0.994
4:8:10:1	0.614	0.996	0.999	0.992	0.996
4:8:11:1	0.743	0.996	0.999	0.993	0.996
4:8:12:1	0.781	0.980	0.999	0.999	0.986
4:9:8:1	0.460	0.994	0.999	0.990	0.994
4:9:9:1	0.861	0.970	0.999	0.962	0.975
4:9:10:1	0.975	0.995	0.999	0.991	0.995
4:9:11:1	0.376	0.994	0.999	0.999	0.996
4:9:12:1	0.641	0.996	0.999	0.990	0.996
4:10:8:1	0.901	0.995	0.998	0.997	0.995
4:10:9:1	0.908	0.995	0.996	0.998	0.996
4:10:10:1	0.629	0.995	0.999	0.994	0.996
4:10:11:1	0.557	0.994	0.999	0.996	0.995
4:10:12:1	0.633	0.995	0.999	0.997	0.995
4:11:8:1	0.834	0.997	0.997	0.992	0.996
4:11:9:1	1.081	0.994	0.998	0.998	0.995
4:11:10:1	1.013	0.996	0.997	0.999	0.996
4:11:11:1	0.995	0.993	0.999	0.999	0.995
4:11:12:1	0.958	0.964	0.988	0.986	0.966
4:12:8:1	0.733	0.996	0.997	0.998	0.996
4:12:9:1	0.657	0.995	0.999	0.989	0.995
4:12:10:1	0.727	0.994	0.999	0.991	0.995
4:12:11:1	0.744	0.996	0.998	0.997	0.996
4:12:12:1	0.721	0.996	0.998	0.994	0.996

Table 37. Comparison of network topologies with various hidden layers and neurons (IPF).



Fig. 30. Structure of ANN model with 9 and 11 neurons in 2 hidden layers (IPF).

$$\begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,9} \end{bmatrix} = \operatorname{Tansig} \left(\begin{bmatrix} \vec{w}_{1,1} \\ \vdots \\ \vec{w}_{1,9} \end{bmatrix} \times \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} b_{1,1} \\ \vdots \\ b_{1,9} \end{bmatrix} \right)$$

$$\begin{bmatrix} h_{2,1} \\ \vdots \\ h_{2,11} \end{bmatrix} = \operatorname{Tansig} \left(\begin{bmatrix} \vec{w}_{2,1} \\ \vdots \\ \vec{w}_{2,11} \end{bmatrix} \times \begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,9} \end{bmatrix} + \begin{bmatrix} b_{2,1} \\ \vdots \\ b_{2,11} \end{bmatrix} \right)$$

$$[f_1] = \operatorname{Purelin} \left(\begin{bmatrix} \vec{w}_{3,1} \end{bmatrix} \times \begin{bmatrix} h_{2,1} \\ \vdots \\ h_{2,11} \end{bmatrix} + \begin{bmatrix} b_{3,1} \end{bmatrix} \right)$$

$$(12)$$



Fig. 31. The diagnostic plots of ANN model (IPF).

		Hidde	n layer 1	[w(1)]		Hidden layer 2 [w(2)]									Output layer [w(O)]												
n	w1 A,n	w1 B,n	w1 C,n	w1 D,n	b1n					w(2)n					b2n						w(O)r	1					bOn
1	1.7	-0.9	-0.9	1.2	-2.4	0.9	-0.9	-0.9	0.2	-0.1	-0.1	-0.6	-0.7	-0.1	-1.8	0.4	-0.6	0.3	0.3	0.8	0.0	-0.9	1.0	-0.1	-0.4	0.4	0.8
2	0.7	0.0	-0.1	-2.5	-1.5	-0.7	-1.2	-0.5	0.7	1.1	-0.4	-0.4	-0.8	-0.4	1.3												
3	-2.2	0.4	-0.8	0.0	0.7	0.4	-0.2	-1.2	-1.0	0.2	-0.2	-0.2	-0.7	0.1	-1.1												
4	0.3	-2.0	1.4	0.8	-0.1	0.0	0.8	0.6	0.4	0.2	0.8	-0.8	-0.8	-0.5	-0.7												
5	-1.1	0.5	2.3	-0.3	0.2	-0.6	0.6	0.5	0.1	0.9	-0.7	-0.1	-0.6	-1.2	0.3												
6	1.9	0.4	-0.5	-1.3	0.1	0.3	0.2	1.0	-0.9	-0.3	-0.3	0.5	-0.9	-0.2	0.0												
7	0.8	0.0	1.4	-1.8	1.6	-0.7	0.5	1.1	0.7	-0.1	0.1	-0.1	-0.7	-0.6	-0.5												
8	0.6	1.2	1.4	1.0	2.2	0.3	-1.0	0.4	0.2	0.9	-0.9	0.8	0.3	-1.0	0.8												
9	0.8	0.8	1.0	-1.6	2.7	0.0	0.5	-0.4	0.1	0.6	-0.4	-0.7	1.0	1.0	1.3												
10						-0.8	-0.5	0.1	1.1	-0.5	-0.9	-0.2	0.7	-0.1	-1.4												
11						-0.8	0.0	0.0	0.8	-0.6	-0.3	-0.9	-0.3	0.9	-1.7												

Table 38. Values of weights and biases for each layer and neuron in Eq. 12 (IPF).

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		Input	variable		IPF rer	noval rate (%)
Exp.	А	В	С	D	Observed	ANN predicted
		(°C)	(g/L)	(mg/L)	Observed	AININ predicted
S 1	5.9	36.8	0.08	3	28.8	34.4
S2	7.7	22.4	0.14	9.7	24.6	25.9
S 3	8.9	10.7	0.21	7.4	14.1	22.8
S4	2.2	18.5	0.20	4.6	42.3	40.2
S5	5.9	36.8	0.08	3	30.4	34.4
S 6	7.7	22.4	0.14	9.7	24.3	25.9
S 7	8.9	10.7	0.21	7.4	13.4	22.8
S 8	2.2	18.5	0.20	4.6	42.6	40.2

Table 39. Observed and predicted removal rates obtained from additional duplicated multi-factor experiments (IPF).

Table 38. Relative importance of four input variables toward the IPF removal rate.

	pН	Temperature	SCMs dose	Initial IPF concentration
Relative importance (%)	92.7	57.4	90.5	100



Fig. 32. Diagnostic plot for additional multi-factor adsorption experiments in the ANN modeling. (IPF)

5. Conclusions

5.1. AAP

In this study, the AAP adsorption characteristics of the SCMs, prepared hydrothermally from pure sucrose, were explored using single- and multifactor experiments. The single-factor tests found that the AAP adsorption capacity remained relatively constant at a pH of 2–10, where π - π and n- π^* interactions and hydrogen-bond formation can contribute to adsorption mechanisms. At a pH of 12, the adsorption capacity was negligible due to electrostatic repulsion. The adsorption mechanisms of AAP onto the SCMs were visualized and better understood by molecular modeling with CHEM3D. The kinetic and isotherm data were best fit with a pseudo-second-order model and Liu model, respectively. The equilibrium time for AAP was 360 min, whereas the maximum adsorption capacity was 92.0 mg/g. The adsorption of AAP on the spheres was exothermic, decreasing as temperature rose from 10 to 40°C. The SCMs were successfully regenerated and reused for subsequent adsorption experiments. From the multi-factor tests, the ANN model (topology 4:11:9:1) was developed in the ANN modeling. Further analysis indicates that the ANN model possessed superior predictability on the additional data. In the ANN model, initial AAP concentration was found to be the most important factor.

5.2. IPF

The adsorption characteristics of IPF onto the SCMs were explored in this study. The adsorption experiments show that the equilibration time for IPF was 360 min, and a pseudo-second-order model best described the kinetic data. The Liu model provided the best fit to the isotherm data with a theoretical maximum adsorption capacity of 95.6 mg/g. The IPF adsorption onto the SCMs was endothermic in nature. The instrumental analyses along with pH experiments suggest that hydrogen-bond formation, π - π and n- π^* interactions, electrostatic repulsion, hydrophobic interaction, and pore-filling could contribute to the adsorption of IPF onto the SCMs. Molecular modeling with CHEM3D provided a better understanding and visualization for interactions between the SCMs and IPF. Based on the multi-factor adsorption data, the ANN model with a topology of 4:9:11:1 was developed to adequately predict the IPF removal rate (R > 0.99). Further analyses with the additional adsorption data confirm that the ANN model possessed good predictability for the IPF removal rate.

5.3. General conclusions and recommendations

This study demonstrates that SCMs synthesized from sucrose through hydrothermal carbonization followed by calcination can be an efficient adsorbent for aqueous AAP and IPF removal. The removal mechanisms of contaminants were elucidated through single-factor adsorption experiments and characterization of adsorbent. They were also re-confirmed through molecular modeling using CHEM3D. Multi-factor adsorption experiments data were used as input and output data to build the ANN model. Pollutants removal was optimized with ANN predictions.

It is significant that micropollutants were removed with an eco-friendly adsorbent and additional information was obtained through modeling. However, future studies are necessary to explore the use of SCMs for the adsorption of AAP and IPF in real wastewater samples. ANN model should be continuously trained based on abundant field data, and it would contribute to optimize the wastewater treatment process.

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국문 초록

아세트아미노펜(AAP)과 이부프로펜(IPF)은 최근 들어 가장 많이 처방되는 비스테로이드성 항염증제(NSAID) 중 하나이지만, 기존의 폐수처리 공정에서는 쉽게 제거되지 않는다. 본 연구에서는 수열합 성법과 열처리 공정을 통해 수크로스 기반의 탄소 구체(SCMs)를 합성하고, 오염물질(AAP와 IPF)에 대한 흡착 특성을 조사하였다.

단일 변수 실험(Single-factor experiments)은 pH, 반응 시간, 온도, 흡착제 주입량, 그리고 초기 오염물질 농도를 바꾸어가며 수 행하였다. SCMs를 이용한 AAP의 최대흡착능은 92.0 mg/g, IPF의 최대흡착능은 95.6 mg/g으로 나타났으며, 실험에 사용된 흡착제는 메탄올을 이용하여 효율적으로 재생되었다.

Raman, FTIR, XPS 스펙트럼과 pH 실험 데이터에 따르면 흡착 제와 오염물질 간에 π-π 상호작용, n-π* 상호작용, 수소결합, 그리 고 정전기적 반발력이 발생하는 것으로 나타났다. 이러한 메커니즘 은 CHEM3D를 이용한 분자 모델링을 통해 재검증하고 시각화하여 나타내었다. 또한, 오염물질 분자의 크기와 흡착제의 평균 기공 직 경을 비교하였을 때 pore-filling 메커니즘도 흡착에 기여할 수 있 는 것으로 나타났다.

다중 변수 실험(Multi-factor experiments)은 pH, 온도, 흡착제 주입량, 초기 오염물질 농도를 입력변수로 하고 오염물질 흡착능을 출력변수로 하여 수행하였고, 2개의 은닉층을 갖는 인공신경망 (ANN) 모델을 개발하였다. 이후, 추가 실험 데이터를 ANN 모델에 적용하여 오염물질 흡착에 대해 우수한 예측 가능성을 가지고 있음
을 확인하였다. 완성된 ANN 모델에서 각 입력 변수의 중요도를 평 가하였고, 초기 오염물질 농도가 가장 중요한 요인으로 나타났다.

본 연구 결과를 통해 수크로스로 합성한 탄소구체가 수중의 AAP와 IPF를 효율적으로 제거할 수 있는 흡착제임을 확인하였다. 또한, 분자 모델링을 통해 오염물질의 제거 메커니즘을 재검증하였 고, ANN 모델링을 통해 오염물질 제거를 최적화하고 예측하는 모델 을 구축하였다.

주요어 : 탄소 구체, 흡착, 아세트아미노펜, 이부프로펜, 분자 모델링, 인공신경망

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