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# Hydrothermal tuning of morphology of aluminophosphate (AlPO-14) framework for the adsorption of Rhodamine 6G dye



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# ABSTRACT

A crystalline zeolite material AlPO-14 was synthesized using Taiwanese coal fly ash (CFA) for the separation of cationic dyestuff Rhodamine 6G (R 6G) from aqueous stream. The zeolite synthesis was performed at different fusion ratios (CFA:NaOH) of 1:1, 1:1.5, and 1:2 followed by hydrothermal treatment resulted AlPO-14 zeolite frameworks (Z1, Z2, and Z3). The physico-chemical, structural, functional, morphological aspects of the raw CFA, and the zeolites were characterized via XRF, XRD, FT-IR, SEM, and BET methods. Further, the zeolites were tested their applicability adsorbing the cationic R 6G dye in batch mode. Moreover, the influence of pH, adsorbent dosage, initial dye concentration, temperature, agitation speed, kinetic models, adsorption isotherms on the removal of R 6G onto zeolites were emphasized. The results indicate that, neutral pH favors the separation of R 6G (q<sub>m</sub> = 208.11 mg/g) following Langmuir isotherm model, and best fitted to pseudo-second order kinetic model. Lastly, the adsorbent was responsive to the alkaline medium (NaOH), and can be readily retrieved for reuse, i.e., Z2 can be reused for 5 successive cycles, followed by Z1-3 times and Z3-2 times respectively. In summary, the major note downs were CFA based AlPO-14 had a commercial potentiality in adsorption applications and regarded to be a new entrant into zeolite database.

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# 1. Introduction

In recent years, industrial operations have been aggravated by massive worldwide population growth, and an increased pace of product consumption. This intensification has a negative impact on the blue planet, as evidenced by waste stream effluents, particularly significant loads of dye pollutants. Inadequate treatment of these dye-contaminated effluent streams will jeopardize both the consistency of the aqueous systems utilized as a receptor for its discharge, resulting in water pollution, and the environmental hazards to the entire eco-exposed system [1]. Cationic dyestuff R 6G in fact has a large number of applications in sectors like wool and cartridges. R 6G is a carcinogenic, teratogenic, and genotoxic contaminant that is highly soluble in water and can be present at very low concentrations of 0.001 g/L [2]. Additionally, R 6G can be absorbed through the skin, leading to respiratory inflammations, renal

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failure, and permanent blindness in the event of prolonged exposure [3]. Additionally, there is a compelling need to develop an effective technology for extracting organic dyes from water streams in order to avoid upcoming public health concerns, safeguard the environment, and comply with regulatory standards governing these dye contaminants. In light of these facts, various known conventional technologies for dye removal from aqueous systems have been developed, including ultrafiltration, oxidation, flocculation, and adsorption [4]. Among them, adsorption is an effective method for lowering the concentration of dye pollutants, particularly when high-performance adsorbents are utilized, due to their ease of handling and separation efficacy [5]. However, the practical application of conventional adsorbents, such as activated carbons, is frequently constrained by their low adsorption capacity and inability to be employed on a large scale due to their expensive cost. As a result, there is a critical need for the development of highly efficient adsorbents for the removal of organic dyes, which was the focus of recent studies [6].

On the flip hand, as global energy demand continues to grow, it pushes the limits of coal-based energy, resulting in massive

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quantities of coal combustion wastes, particularly CFA and coal bottom ash (CBA) [7]. Around 700 million tons of CFA production are expected to be skewed by just 20% of the usage prospects for construction materials, while the remainder is left untreated and stored in open landfills [8]. CFA that is left unattended and unprotected is extremely harmful, causing leaching and contaminating ground water bodies [9]. Although, the merit side of the CFA composition having silicon and aluminum precursors expands the opportunities for preparing microporous materials called synthetic zeolites. Additionally, zeolites derived from CFA are renowned and extensively investigated as superior alternatives for natural and conventional adsorbents [10]. In general, zeolites are microporous aluminosilicates with a three-dimensional tetrahedral lattice [TO<sub>4</sub>] and a negative load, where T is silicon or aluminum [11]. AlPO (aluminophosphate) is a novel class of zeolites with remarkable adsorption and molecular sieve capabilities. These zeolites are unique encompassing micropore network with one-dimensional channels, and their inner surface has only one form of sorption site [12]. Additionally, AIPO zeolite micropores are composed of an eight-member ring with a diameter of 7.3A°, crystal lattice parameters a = 13.8A°, c = 8.6A° and are classed as AFN [13]. Furthermore, the known thumb law of aluminosilicate zeolites defines the presence of cations that neutralize the structures negative charge. These cations originate as impurities in the zeolite micropore system and cause energy heterogeneity of the interior surface [14]. Other interesting features of AIPO micropore network include the absence of cations, which provide outstanding thermal stability due to their electrically neutral structure [15]. Thus, due to the dual nature of the hydrophobic-hydrophilic surface morphology of micropore AIPO zeolites, they are considered to be host materials of particular relevance for the sorption of organic and inorganic gases, such as Ar, Ni [16], alcohols, and hydrocarbons [17,18]. Numerous researches have concentrated on the sorption of water, gas sorption, or petroleum cracking using AIPO as a sorbent material, with little or no attention paid to dye contaminant sorption. Additionally, while the AIPO has been synthesized using chemicals in previous studies, no attempt has been made to synthesize the AIPO framework from CFA.

Thus, the present study is focused on two critical aspects of synthesizing AIPO-14 zeolites from CFA; and its adsorption ability of the R 6G dye from aqueous streams. This (synthesis of AIPO-14 from CFA) would be beneficial in two ways: it would alleviate concerns about CFA storage, while also adding a new zeolite to the CFA database.

# 2. Experimental

# 2.1. Sample preparation

# 2.1.1. Chemical and reagents

The CFA used in this study was provided by the Taiwan Power Company, Taichung, Taiwan. Sigma-Aldrich Taiwan provided all of the chemicals (NaOH, HCl, NaAlO<sub>2</sub>, Ethanol, and  $H_2SO_4$ ) and dye R 6G required for the current study, which requires no further purification.

#### 2.2. Pretreatment of CFA

The raw CFA from the coal-fired thermal power plant was finely powdered and screened through a sieve with a mesh size of 75  $\mu$ m mesh. To prevent the effects of moisture and other volatile substances on the carbon content data, the screened CFA sample was dried in a muffle furnace at 373 K. The moisture-free CFA sample was calcined in a muffle furnace for 2 h at 1073 K to remove unburned carbon impurities. It is well known that calcination followed by acid treatment notably reduces impure trace residuals. Thus, calcinated CFA was treated with an acid (HCl) at 363 K for 5 h before being completely rinsed with deionized water and dried in an oven at 373 K.

#### 2.3. Synthesis of AlPO-14 zeolite

The alkaline fusion is the first step in zeolite preparation after CFA pretreatment. Alkali fusion is a traditional method for promoting the dissolution of Si and Al in CFA to produce crystalline and high purity zeolites [19]. As a result, the primary CFA oxides, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> dissolve in alkaline medium (NaOH), generating aluminosilicate gel as a zeolite precursor (Eq. (1)) [20]. NaOH is a classic alkaline agent in zeolite synthesis, since Na<sup>+</sup> ions are known to stabilize zeolite frameworks sub-building units, and are typically needed under hydrothermal conditions (Eq. (2)). The higher the Na<sup>+</sup> concentration, the more water-soluble sodium silicates are generated, culminating in pure phase zeolites. Also, NaOH acts as an activator during the fusing of soluble silicate and aluminate ions in the reaction mixture, as well as during the hydrothermal synthesis, which includes the nucleation and crystallization steps [21].

$$NaOH + xAl_2O_3.ySiO_2 \xrightarrow{Alkalifusion} Na_2SiO_3 + Na_2AlO_2$$
(1)

$$\begin{split} & \text{NaOH} + \text{Na}_2\text{Al}(\text{OH})_4 + \text{Na}_2\text{SiO}_3 \\ & \rightarrow [\text{Nax}(\text{AlO}_2)(\text{SiO}_2)_2.\text{NaOH}.\text{H}_2\text{O}] \end{split} \tag{2}$$

Thus, in the current investigation, the alkali fusion reaction is carried out by mixing pretreated CFA with finely crushed NaOH pellets in various mass ratios of 1:1, 1:1.5, and 1:2, with a fusion temperature ranging from 673 to 873 K. The varying mass ratios and temperature settings were chosen to determine the ideal conditions for the formation of pure phase zeolite materials. The fused CFA and NaOH mixture was cooled to room temperature, fine powdered and transferred to a 250 mL volumetric flask containing 20% sodium aluminate and 100 mL of water. The addition of sodium aluminate (NaAlO<sub>2</sub>) to the fusion mixture allowed for fine tuning of the Si/Al ratio, which is critical for homogenizing the zeolite phase [22]. The slurry was stirred on a magnetic stirrer at 400 rpm for 24 h at ambient room temperature, resulting in the formation of aluminosilicate gel. To minimize external impacts and to assure the reaction mixtures homogeneity, the gel blend was then transferred to hermetically sealed 100 mL PTFE bottles. After 24 h at a constant temperature of 393 K, the crystallized gel was thoroughly rinsed with de-ionized water and filtered using Whatman filter paper. Finally, gel (zeolite AlPO-14) samples were aged at 423 K for 24 h to achieve the optimal physicochemical, morphological, and mechanical qualities. Nine (AlPO-14) zeolites were generated in this manner under various fusion ratio and temperature settings, from which three ideal zeolites were chosen for this investigation (see Table 2) and are referred to as Z1, Z2, and Z3 in the following sections.

# 2.4. Characterization

To ascertain the adsorbents physicochemical properties, it is critical to conduct material characterization using a variety of analytical techniques. The material characterization process begins with determining the intrinsic composition, which can be accomplished using an X-ray fluorescence spectrometer (XRF). As a result, the raw CFA and the zeolite AlPO-14 were additionally analyzed using portable XRF in the current analysis (Bruker 5i Tracer). The raw CFA, AlPO-14 zeolite crystallographic data were gathered using a Cu-K X-ray diffractometer (Bruker Advanced-D825A) operating at 40 kV and 40 mA with a scan step size of 0.01° over a 20

range of 5°-60°. Additionally, morphological investigations of CFA, AlPO-14 were performed using an Ultra-High-Resolution Thermal Field Emissions Scanning Electron Microscope (SEM) (JEOL, JSM-7610F Plus). To make the samples conductive, they were coated with a tiny layer of gold in a sputter coater for two minutes. The N<sub>2</sub> adsorption isotherm at -196 °C was determined using a Micrometrics ASAP 2060; samples were degassed at 573 K for 3 h prior to analysis using a normal methodology. The surface area of the sample (CFA, Zeolite AlPO-14) was calculated using the Brunauer-Emmet-Teller (BET) method, and the pore size distribution was evaluated using the Barrette-Joyner-Halenda (BJH) method. With the aid of the PerkinElmer Spectrum One spectrometer comprising DTGBr detector and split beamer, Fourier-transform infrared spectroscopic analysis (FTIR) was performed. The spectra was recorded in the range of 4000–400 cm<sup>-1</sup> to gain insight about the nature of the compound, functional groups based on the frequencies, peak shapes, and respective intensities. Finally, R 6G adsorption investigations were conducted using a UV-spectrophotometer (PerkinElmer Lambda 850) equipped with a quartz cell with a path length of 1.0 nm and a wavelength of 530 nm.

#### 2.5. Adsorption experiments

Batch adsorption tests were conducted to determine the removal of adsorbate (R 6G) as a function of solution pH, initial adsorbate concentration, contact time, and temperature utilizing zeolites (Z1, Z2, and Z3) as adsorbents. All adsorption experiments were conducted in 100 mL Erlenmeyer flasks fitted with glass stoppers. 1000 mL of 1000 ppm R 6G solution was made in volumetric flasks and then diluted to several concentrations ranging between (100-1000 ppm). Adsorption analysis was performed at various dye concentrations and a final concentration of 300 ppm was chosen for all experimental studies. Moreover, each adsorption experiment was conducted in a 50 mL glass beaker fitted with a lid and containing 30 mL of the 300 ppm initial concentration solution of R 6G dye. Then, using a temperature-controlled orbital sieve shaker set to 303 K and 200 rpm, the temperature, contact time, and agitation rates were tuned. The optimal pH for equilibrium adsorption was determined by taking 30 mL of the dye solution and changing the pH in the range of 2-10 using the appropriate amounts of 0.1 N HCl and 0.1 N NaOH solutions. Finally, upon achieving equilibrium, all samples of variable parameters were collected and the absorbance values were determined using a UV-vis spectrometer pre-calibrated with R 6G at 530 nm. The amount of adsorption and desorption was determined throughout this experiment using the following mathematical expressions Eq. (3) and (4).

$$q_e = \frac{(C_i - C_e)V}{m} \tag{3}$$

$$Desorption\% = \frac{(C_i - C_e)}{C_i} \times 100 \tag{4}$$

where  $C_i$ ,  $C_e$ , V, and m were the initial, equilibrium concentrations (mg/L), volume of the solution (L), and the mass of the adsorbent (g), respectively.

# 3. Results and discussion

#### 3.1. Material characterization

# 3.1.1. X-ray fluorescence analysis

The composition of raw CFA was analyzed using XRF to determine its suitability for alkaline hydrothermal conversion into zeolites. The typical composition of CFA, zeolites (AlPO-14) formed during hydrothermal treatment of CFA is shown in Table 1. The results revealed that CFA has larger quantities of Si and Al, which are precursors to zeolite production. The molar ratio of the Si and Al of CFA 3.10 encouraged the development of AFN type (AlPO-14) zeolites [23]. The molar ratio was significant because it has an effect on the surface morphology of pure phase crystalline zeolites. This was substantially supported through the SEM micrographs, and the textural properties (specific surface area) as the molar ratio decreases, crystallinity increased. The resulting zeolites after the hydrothermal treatment have been measured for their chemistry after the hydrothermal treatment and their molar ratios were 2.32 (Z1), 2.52 (Z2), and 2.43 (Z3) respectively. As mentioned earlier, the molar ratios of the as-synthesized zeolites dropped, which was ideal for the increased crystallinity. Besides, the trace elements other than Si and Al, including Fe, Ca, K, and Mg, are known to be exchangeable cations, altering the composition, crystallinity, and morphology of the sample. Another set of trace components, such as Ti and S, may cause unfavorable secondary reactions. Thus, frequent rinsing with deionized water significantly reduces the unwanted qualities and changes in the properties of newly formed zeolite materials.

# 3.1.2. X-ray diffraction (XRD) analysis

Fig. 1 shows the XRD diffractogram observed during the hydrothermal synthesis of AlPO-14 zeolites. The XRD patterns of unprocessed CFA showed the presence of crystalline mullite at 44.5° [24], quartz 26.6° [25] in higher proportions, and tiny traces of hematite 39.1° [26] were visible too. While the XRD diffractogram of zeolites generated via hydrothermal treatment with varying fusion ratios revealed significant changes in the peaks resembling AFN crystallographic patterns, according to IUPAC classifications. In the case of fusion ratios (1:1, and 1:1.5), the presence of peaks was comparable, demonstrating the zeolites crystallinity, but the relative intensities were different. The  $2\theta$  XRD patterns on the diffractogram validated the zeolite as AlPO-14 [27] matching 20 values at 11.57°, 23.24°, 26.52°, 30.88°, and 37.78° for Z1; 13.15°, 23.26°, 26.63°, 28.26°, 30.26°, 30.88°, 34.10°, 37.27°, and 42.54° for Z2. Whereas, Z3 has a lower zeolite formation, with the best match being  $2\theta$  at 13.65°, 32.21°, 37.78°, and 42.60° respectively. The considerable decrease in peak intensity with increasing fusion ratio (1:2, Z3) indicated the collapse of zeolite structure. This was because the hydroxide anion formed by NaOH solution attacked the silanol groups, Si-O-Si, or Si-O-Al bonds [28]. Breck [29] further said that the crystal frame would become unstable at greater alkalinities due to the dissolution of Si and Al to sodium silicate and aluminate, or of generating undesired compounds other than AIPO-14 zeolite. The obtained AIPO-14 zeolites had a hexagonal crystal structure with cell parameters and volume of a = 9.70  $A^{\circ}$ , b = 9.736  $A^{\circ}$ , and c = 10.202  $A^{\circ}$  with hkl values of (011) and similar observations were made by Iwasaki et al., [30]. As demonstrated by the XRD pattern, CFA was successfully transmuted to AIPO-14 at a regulated fusion ratio of 1:1 (Z1), or 1:1.5 (Z2), resulting in a greater crystallinity of the MFI or AFN phase. However, as the concentration of NaOH increased, all of the diffractive peaks in the treated AIPO-14 gradually decreased, i.e., 1:2 (Z3), similar to ZSM-22 [31].

# 3.1.3. N<sub>2</sub> adsorption–desorption

Fig. 2 (a-c) illustrates the nitrogen adsorption-desorption isotherms for AIPO-14 (Z1, Z2, and Z3) zeolite materials. The different adsorption stages of all zeolites illustrated by the picture are: quick filling of micropores at low pressures, creation of monolayer area also known as isotherms knee, and filling of the mesoporous empty sites at relative pressures > 0.003 [32]. Further, adsorption behavior is governed by interactions between condensed state molecules and adsorbent-adsorptive interactions. According to the figure, the type IV isotherm was best suited to mesoporous materials Z1, Z2, and type III to zeolite Z3. Type IV isotherm was induced by capil-

#### Table 1

Chemical composition of CFA and zeolite of variable fusion ratio (wt.% dry basis).

		Alkali fusion ratio (CFA	A:NaOH)	
Major oxides	Raw CFA	Z1 (1:1)	Z2 (1:1.5)	Z3 (1:2)
SiO <sub>2</sub>	65.87	58.23	61.42	60.58
Al <sub>2</sub> O <sub>3</sub>	21.29	25.07	24.36	24.87
Fe <sub>2</sub> O <sub>3</sub>	4.65	6.89	5.51	5.04
CaO	3.57	4.65	4.68	4.59
P <sub>2</sub> O <sub>5</sub>	1.84	0.98	1.32	0.47
K <sub>2</sub> O	1.29	0.42	0.55	0.51
TiO <sub>2</sub>	1.47	1.41	1.55	1.48
CuO	0.02	0.04	0.02	0.02
MgO	0.97	2.11	0.96	1.84
MnO	0.06	0.07	0.07	0.06
NiO	0.009	0.01	0.007	0.006
ZnO	0.02	0.03	0.03	0.03
Si/Al	3.10	2.32	2.52	2.43

Table 2

Si/Al and BET results of the CFA and the zeolites of variable fusion ratio.

						Before adsorption		After adsorption			
Sample	Si/Al	Fusion ratio (CFA : NaOH)	Fusion temperature (°C)	Sodium aluminate (%)	Crystallization temperature (°C)	BET surface area (m²/g)	$SA_{ext}$ $(m^2/g)$	V <sub>micro</sub> (cm <sup>3</sup> /g)	BET surface area (m²/g)	$SA_{ext}$ $(m^2/g)$	V <sub>micro</sub> (cm <sup>3</sup> /g)
CFA	3.10	-	-	-	-	7.81	4.76	0.0061	-	-	-
Z1	2.32	1:1	400	20	120	31.18	8.46	0.052	-	-	-
		1:1	500	20	120	102.09	9.42	0.070	66.40	5.69	0.048
		1:1	600	20	120	14.78	10.49	0.062	-	-	-
Z2	2.52	1:1.5	400	20	120	104.53	18.03	0.099	-	-	-
		1:1.5	500	20	120	221.83	20.26	0.143	138.46	18.45	0.129
		1:1.5	600	20	120	201.78	18.36	0.152	-	-	-
Z3	2.43	1:2	400	20	120	24.45	17.69	0.108	-	-	-
		1:2	500	20	120	28.93	23.99	0.115	12.44	7.12	0.039
		1:2	600	20	120	13.20	7.79	0.058	-	-	-



Fig. 1. Mineralogy of CFA, AIPO-14 Zeolites (Z1, Z2, Z3) by XRD analysis.

lary condensation followed by hysteresis depending on the adsorption mechanism, temperature, and the pore width reached a certain essential width. The final saturation plateau, of variable length, was a common characteristic of type IV isotherms. Furthermore, mesoporous zeolite aggregate crystals commonly exhibited H4 hysteresis linked with the micropore filling of strong uptake of low  $P/P_0 > 0.65$ . In contrast, there was no discernible monolayer development of the type III isotherm in connection with the weak interactions between adsorbent and adsorbate, and the adsorbed

molecules cluster around favorable spots on the surface of the microporous materials.

#### 3.1.4. Porous texture analysis

Table 2 summarizes the textural parameters of raw CFA and AlPO-14 zeolites formed by N2 adsorption at 77 K. The raw CFA had a specific surface area (SSA) of 7.58  $m^2/g$ , but the improved SSA of the zeolite AlPO-14 (Z1, Z2, and Z3) was reported to be 102.09, 221.83, and 30.09  $m^2/g$ , respectively. The increased surface area was due to the efficient conversion of quartz and mullite phases to dissolving ionic species. Additionally, the fusion agent (NaOH) significantly increased the surface roughness by producing fractures and swelling the zeolite matrix, which aids in exerting pressure on the walls and created vacuum in the matrix pores. Further the pores volume of the raw CFA is 0.0061 cm<sup>3</sup>/g that had been increased to 0.0709 cm<sup>3</sup>/g (Z1), 0.1431 cm<sup>3</sup>/g (Z2), and 0.1018  $\text{cm}^3/\text{g}$  (Z3), respectively. The increase in the pore volume with respect to Z1 and Z2 upon hydrothermal treatment was attributed to the unrestricted entrainment of the N2 molecules and similar to zeolite 4A reported by Jha and Singh [33], whereas, in the case of Z3 the molecular trapdoor effect was visible, and thus the pore volume had remained relatively constant, a common tendency in LTA type zeolites reported by Shang et al., [34]. In addition, Fig. 2 (d-f) depicts the relationship between the volume of a pore and its diameter for zeolites with a cylindrical cage geometry [35].

# 3.1.5. SEM observations

The scanning electron microscope is a well-known and commonly used tool for characterizing morphological characteristics. The morphological features and the surface characteristics of the raw CFA, and the zeolite AlPO-14 are shown in Fig. 3 (a-h). SEM



Fig. 2. Spectra of (a-c) N<sub>2</sub> adsorption-desorption isotherms of the zeolites (Z1, Z2, and Z3) (d-f) BJH pore size distribution of the zeolites (Z1, Z2, and Z3).



Fig. 3. SEM micrographs of raw CFA (a, b), (c, d) Zeolite Z1 (CFA: NaOH -1:1), (e, f) Zeolite Z2 (CFA: NaOH -1:1.5), (g, h) Zeolite Z3 (CFA: NaOH -1:2.0).

micrographs Fig. 3 (a, b) reveal that CFA particles are predominantly spherical due to the presence of feerospinel aggregates (hematite,  $Fe_2O_3$ ) and Si-Al glass [36], with a relatively smooth surface texture and a wide diversity of particle diameters. Additionally, the presence of spherical smooth surface particles explains the larger Si-Al matrix fractions, which serve as a proxy for zeolite production [37]. To begin, at a fusion ratio of 1:1, the SEM micrographs Fig. 3 (c, d) show the initiation of pure phase zeolite crystal formation via aggregated needle-structures. However, the disproportions are readily apparent, i.e., a heterogeneous mixture of needle-shaped and unconverted spherical forms. The reason for this behavior was that the chosen fusion ratio and other parameters were insufficient to entirely displace the Si and Al species and reorganize them into a homogeneous zeolite phase. When the fusion ratio was increased to 1:1.5, the needle-like structures in the zeolite

took on a distinct shape as seen in the SEM image Fig. 3 (e, f). The needle-like structure had been identified as zeolite AIPO-14 and was similar to TON zeolite [31]. The perfect shape of the crystals was ascribed to the adequate dissolution of Si and Al promoted by the fusion treatment followed by the hydrothermal reaction. Further, the needle-like habit of zeolite crystals reflected the structural property of cross-linked chains of silicate tetrahedrons  $T_5O_{10}$  [38]. Fig. 3 (g–h) presents the morphology of the CFA transmuted zeolite of alkali fusion ratio 1:2. The illustration demonstrated an uneven morphology and a complicated combination as the product phase, resulting in the production of agglomerates. As is well known, the appearance of agglomerates and crystallization is indicative of nucleation and conversion to the final zeolite phase. Moreover, the presence of K and Si in CFA results in the formation of a bridge between the oxygen carrier and the ash part, resulting

in increased agglomeration, or the fusion parameters were insufficient to separate Si and Al into distinct phases [39]. In addition, increased alkali and silicate concentrations can result in the development of melt at low temperatures and agglomeration via the creation of alkali silicates.

# 3.1.6. FT-IR analysis

FT-IR spectra reveal minute details about the mineralogical structure of a mineral, and each mineral in the mid-IR range has a distinct absorption pattern. Infrared spectroscopy is a frequently utilized technique for studying aluminosilicates in fly ash and their derivatives (zeolites) in this study, particularly in the presence of amorphous phases. A complete understanding of the functional groups present in raw CFA and finished zeolites enables an assessment of the sorbate adsorption mechanism on sorbents [40]. Fig. 4 (a-d) shows the FTIR spectra of raw CFA and hydrothermally treated zeolites (Z1, Z2, and Z3) in the 4000–400  $\text{cm}^{-1}$  scanning range. In general, the bands below 500 cm<sup>-1</sup> correspond to the bending of Si-O-Si and O-Si-O bonds, and the bands between 500 and 800 cm<sup>-1</sup> correspond to the symmetric stretching of Si-O-Si and Al-O-Si links [41]. The bands between 800 and 1000 cm<sup>-1</sup> represent the loss of CaCO<sub>3</sub> gel, and bands at 1000–1600  $\text{cm}^{-1}$  indicates the gaining of Si-O-Si bond. Finally, the band ranges between 1600 and 3500 cm<sup>-1</sup>, and 3500–4000 cm<sup>-1</sup> are the resultant of stretch-



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ing of –(OH) bond, bending of (H-O-H) vibration, and later is considered as the loss of  $Ca(OH)_2$  [42]. Further, a detailed information of each band related to raw CFA, Z1, Z2, and Z3 in range of 400–4000 cm<sup>-1</sup> are presented and underlined in Table 3.

# 3.2. Adsorption results

### 3.2.1. Effect of pH and the point of zero charge

Solution pH is one of the primary variables determining dye speciation, the magnitude of electrostatic charges [43], the degree

Table 3	
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FT-IR spectra of raw CFA, Zeolites of variable fusion ratio.

Material	Peak (cm <sup>-1</sup> )	Significance
Raw CFA	413	Perpendicular Si-O vibrations
	431	Si-O deformation vibration
	435	Bending mode of Si-O-Al vibration is assigned as T-O
		stretching mode
	450	Si-O bending vibrations
	461	Al-O-Al stretching vibrations
	471	Si-O-Si or O-S-O bending vibrations
	476	T-O bending vibrations
	501	Presence of mullite crystals
	517	Hematite, Si-O-Al
	555	Symmetric stretching of Al-O-Si in mullite
	776	Al-O bond
	795	Si-O symmetric, quartz
	1057	Si-O-Si stretching vibration
	2851	Symmetric aliphatic CH <sub>2</sub> groups
Zeolite -	414	Si-O bending vibrations
Z1	425	Erionite
	435	T-O-T indicating the presence of zeolite precursor
	445	5 membered double rings associated to T-O-T
		(siloxane bonds)
	449	TO <sub>4</sub> tetrahedral bending
	457, 462	Buckling vibration of SI-O-Si or O-SI-O
	467	6-R and D4-R secondary building units of zeolite
	4/5	Bending vibrations of U-SI-U
	483	Internal tetrahedral vibrations of ALO
	490	T O T handing mode of 4 P s
	495	Tetrahedron stretching vibration peak
	881	Al-Fe-OH deformation peak
	961	Asymmetric stretching vibration of T-O-T bond
	1431	Symmetric bending vibrations of CH <sub>3</sub> groups
Zeolite –	413	Perpendicular Si-O vibrations
Z2	425	Erionite
	439	Si-O bending
	444	Tetrahedral Si-O bending
	449	TO <sub>4</sub> tetrahedral bending
	464	Bending vibration of T-O bonds
	475	Bending vibrations of O-Si-O
	480	
	483	Bending vibration of SI-U-SI
	497	Metal oxygen stretching models M–O (M = Si, Ai, Ca, Na)
	508	Bending mode of Characteristic 4-membered rings
	513	Al-O-Si deformation
	557	Beginning of the 4 to 6 membered ring zeolite
		crystallization
	668	Internal linkage vibrations of TO <sub>4</sub>
	960	Antisymmetric stretch of Si-O-H and Si-O-Ti bonds
	1644	Clusters of adsorbed water molecules
Zeolite –	413	Perpendicular Si-O vibrations
Z3	425	Erionite
	444	Tetrahedral Si-O bending
	450	Internal vibrations of tetrahedral Si, and AlO <sub>4</sub>
	475	Bending vibrations of O-Si-O
	633	Bending vibrations of PO <sub>4</sub> groups
	661	Symmetrical stretching vibration of Si-O-Si
	909 1411	Stretching Vibrations of SI-U
	1411	Co3 molecule trap in cavity
	1650	Water deformation mode
		mater accommution mode

Fig. 4. FT-IR spectrum of raw CFA, AlPO-14 zeolites (Z1, Z2, Z3).

of ionization [44], and the surface properties of CFA-dependent adsorbents. Solution pH has an effect on the systems adsorption efficiency, i.e., it either increases or decreases the adsorbent potential by modifying the adsorbent and adsorbent ionizing state. Hence, pH of the solution is regarded as the master variable and is an unavoidable component of the adsorption process. In the present study, the influence of pH was investigated in the range (pH = 2-10) using an ideal adsorbent dosage of 0.05 g, a contact period of 120 min, and a room temperature T = 303 K. The pH of the solution is altered in a controlled manner by adding acidic (0.1 N HCl) and alkaline medium (0.1 N NaOH). Once the pH of the solution had been adjusted to equilibrium, the adsorbent is introduced and allowed to contact the solution for 120 min in an orbital sieve shaker maintained at 303 K. The dye uptake capacity of the zeolite was shown as a function of pH in Fig. 5a and the maximum adsorption capacities of 55.45 mg/g (Z1), 86.29 mg/g (Z2), and 30.35 mg/g(Z3) were noted at pH = 7 and dropped afterwards. The increased adsorption tendency in acidic circumstances was due to increased protonation and neutralization of the adsorbent AlPO-14, which promotes diffusion [45]. In contrast, the adsorption tendency reduces rapidly in a basic/alkaline media due to deprotonation, which forestall the dye molecules from spreading across the sorbent surface [46]. Thus, the neutral state was optimal for the absorption of R 6G onto the adsorbent. Additionally, the isoelectric point of the adsorbate surface clearly characterized the pH effect on the adsorption phenomena. The mechanism was already established by [47], by adjusting 30 mL of the aqueous solution with an initial pH (pH<sub>i</sub>) of (2-10) using 0.1 N HCl, and

0.1 N NaOH. Then, each sample was added 0.05 g of adsorbent and agitated at a constant speed of 200 rpm for 12 h at 303 K, after which the final pH (pH<sub>f</sub>) of the solution was determined. The difference between the final and initial pH was termed as  $\Delta$ pH and it was plotted against the initial pH (pH<sub>i</sub>) to establish the point of zero charge (pH<sub>pzc</sub>). From Fig. 5b, the pH<sub>pzc</sub> of the adsorbent (Z1, Z2, and Z3) were found to be 8.6, 8.4, and 8.8 respectively. At a pH less than or equal to pH<sub>pzc</sub>, the sorbents surface is positively charged and capable of attracting anions from the solution; at a pH greater than or equal to pH<sub>pzc</sub>, the sorbents surface is negatively charged and attracts cations. The pH<sub>pzc</sub> value in the present study was greater the pH, increasing the amount of positively charged anionic adsorbent sites, which favored the adsorption of negatively charged dye ions via electrostatic attraction [48].

## 3.2.2. Effect of adsorbent dosage

In assessing the adsorption capability of R 6G dye on zeolite AlPO-14, adsorption dosage is a crucial parameter. The adsorption propensity diminishes with adsorbent dose, as seen in Fig. 6a. Higher sorption at lower dosage was due to a greater availability of exchangeable sites or surface areas at lower adsorbent concentrations. In addition, all the active sites were completely revealed at lower dosage, although a small fraction of empty sites remained available at higher dosage levels. As a result, higher doses might cause aggregation, which reduced the total surface area of the adsorbent and hence abated adsorption. Besides, the adsorption of the R 6G dye uptake on to AIPO-14 zeolite (Z2) provided a higher sorption tendency of 77.23 mg/g when compared to 57.86 mg/g for



Fig. 5. (a) Effect of pH on the adsorption of the R 6G onto AIPO-14 zeolites (Z1, Z2, Z3), (b) Influence of point of zero charge.



Fig. 6. Influence of various parameters on the uptake of R 6G onto AIPO-14, (a) Effect of dosage, (b) Effect of the agitation speed, and (c) Effect of time.

Z1 and 31.34 mg/g for Z3. The above-mentioned effect was attributed to larger surface area, which allowed for more adsorption sites to stay unsaturated when compared to other zeolites [49]. Furthermore, adsorption decreased due to the lowering of concentration gradient between adsorbent and solution at a constant adsorbent concentration.

# 3.2.3. Effect of agitation speed

The optimal agitation speed is another key variable to optimize the interaction between the dye solution and the solutions adsorption sites. Agitation is one of the major occurrences which affects the distribution of the solution inside the bulk solution and the development of external film boundaries [50]. Moreover, a better mix of solvent and solution is vital as agitation speed determines boundary layer development and promotes mass transmission coefficients [51]. Therefore, the effect on the sorption of the R 6G dye on AlPO-14 zeolite at the pH = 7 was assessed in the current work (100-500 rpm) and the parameters of the ambient temperature were critically assessed. The dye uptake onto AlPO-14 zeolite at variable agitation speed values are plotted and presented in Fig. 6b. The figure indicates, that the agitation speed of 200 rpm was ideal for all the zeolites with a reported adsorption capacity values of (65.04 mg/g for Z1, 90.14 mg/g for Z2, 32.76 mg/g for Z3), respectively. During the low agitation speeds the film transfer coefficients are highly promoted, due to the formation of external boundary layer and thorough mixing of adsorbent and adsorbate [52]. Further, increasing the agitation speed beyond 200 rpm, the adsorption tendency was declined, as the solute and solvency mixture with a superior centrifugal power dominated dye molecules binding ability on the zeolite surface, and were therefore removed from the adsorbent surface [53]. All the three zeolites reported similar phenomenon, and hence lower agitation speed favored adsorption and higher agitation facilitated desorption. In summary, the low agitation speed of 200 rpm found to be optimal and implemented throughout the study.

#### 3.2.4. Effect of contact time

The contact time or the maximum operating time of adsorption are crucial in designing optimal adsorption systems. Fig. 6c shows the variations in the R6G adsorption capacity towards AlPO-14 in the contact time ranges of 0-300 min. The zeolite possesses three distinct stages of adsorption, as indicated by the figure: fast sorption (0-60 min), sluggish adsorption (60-180 min), and lastly a steady plateau (180-300 min). At 300 K, the rate of adsorption is rapid, i.e., 65.04 mg/g for Z1, 85.12 mg/g for Z2, and 32.76 mg/g for Z3. The quick adsorption during the early phase was attributed to the presence of unoccupied binding sites, which resulted in the bulk of the R 6G particles adhering to the AlPO-14 surface, a frequent phenomenon in physical adsorption. As the intact time increased, the bulk of empty sites were filled with dye molecules and the sorbent surface approached saturation [54]. This led to the creation of multilayered lumps of dye molecules rather than adhering to the unoccupied spots, and so the adsorption rate decreases dramatically [55]. Finally, when the sorbent (AlPO-14) reached saturation, i.e., no vacant sites for the attachment or binding of fresh batch R 6G dye molecules were available, the new particles were carried away freely without adhering to the surface, resulting in a flat line or no change in adsorption during 160-300 min. Thus, the optimal contact time for R 6G adsorption onto the AIPO-14 zeolite was defined at 60 min, and the same conditions were used throughout the investigation.

#### 3.2.5. Isotherm studies

Adsorption isotherms provide valuable information on site diffusion across the adsorbent surface, the sorbents overall potential, the adsorbent-adsorbate interaction, and system parameters. There were other isotherm models available, among which the most popular ones were two-parameter Langmuir and Freundlich isotherms. Thus, the experimental equilibrium data for R 6G dye adsorption onto the AlPO-14 zeolite at various concentration ranges (100–1000 ppm) were fitted into both Langmuir and Freundlich isotherm models while retaining the other ideal parameters. The respective equations Eqs. (5), and (6) of Langmuir and Freundlich isotherm models are presented here in

Langmuir isotherm model : 
$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$
 (5)

Freundlich isotherm model : 
$$q_e = K_f C_e^{1/n}$$
 (6)

where  $q_e$  (mg/g),  $q_m$  (mg/g), and  $C_e$  (mg/L) are the equilibrium and maximum adsorption capacities and equilibrium concentration; and  $K_L$  (L/mg),  $K_f$ , and n are the adsorption energy dependent constant, Freundlich adsorption capacity, and intensity measurement constant, respectively.

# 3.2.6. Langmuir isotherm model:

The Langmuir adsorption isotherm implies that the surface phase is a monolayer. The Langmuir isotherm is utilized to characterize the adsorption process in particular, because the unoccupied sites are occupied within an energy-homogeneous adsorption zone [56]. The value of K<sub>I</sub> (fitness factor) a dimensionless constant, is critical in monolayer adsorption since it specifies the feasibility of the proper adsorption process. If the K<sub>L</sub> value is between 0 and 1, it is termed monolayer adsorption; otherwise, it is a multilayer phenomenon. According to the results of the present adsorption study, the value of the K<sub>L</sub> of zeolites (Z1, Z2, and Z3) was between 0 and 1, and the computed  $q_{max}$  for Z1 was 90.14 mg/g, 208.11 mg/g for Z2, and 69.87 mg/g for Z3 respectively. Also, the experimental values for the R 6G dye equilibrium were compared to the theoretical value (see Fig. 7). According to Figure, the computed and experimental data were quite similar, as proven by the regression coefficient  $r^2 = 0.998$  confirms the model fit. Moreover, the value of n > 1 strongly promotes the adsorption phenomenon of R 6G dye onto zeolites.

#### 3.2.7. Freundlich isotherm model:

As already stated, Freundlich isotherm is best suited for multilayer adsorption. The critical parameter in this isotherm model is K<sub>f</sub> (Freundlich adsorption capacity) which represents the feasibility of adsorption [57]. Similarly, the adsorption intensity given by "n" specifies the adsorption model, i.e., n > 1 indicates a highly advantageous adsorption model, n < 1 indicates least favorable adsorption model, and n = 1 indicates a linear adsorption model. In the present experimental study, the value of  $K_f = 22.87 \text{ mg/g}$  for Z1, 15.33 mg/g for Z2, 1.64 mg/g for Z3 and the values of n > 1 for all zeolites respectively; however, the value of the  $r^2$  between the experimental and the calculated values are less (0.9525) compared to Langmuir (0.998) confirms the monolayer adsorption is highly favorable and was believed to be a better fit. Additionally, Table 4 has a full explanation of the variables involved in the Langmuir and Freundlich isotherm models. Further, Table 5 summarizes the literature on R 6G adsorption utilizing various adsorbents.

#### 3.2.8. Dye adsorption kinetic studies

To evaluate kinetic models, the control mechanisms of the adsorption process such as chemical reaction, diffusion control, or mass transfer coefficient, were used [58]. For the full-scale batch process, the kinetics of dye adsorption on adsorbent materials are vital choosing the best operating conditions. Further, kinetic studies demonstrate the rate of solute absorption that regulates the adsorbates residence period at the solution interface [59]. In addi-



Fig. 7. Non-linear adsorption isotherms analysis of R 6 g uptake onto AlPO-14 zeolites under variable concentrations (a) zeolite Z1, (b) Zeolite Z2, (c) Zeolite Z3.

 Table 4

 Equilibrium modeling of data for the removal of R 6G using AlPO-14 (Z1, Z2, and Z3).

Isotherm	Parameters	Z1	Z2	Z3
Langmuir	q <sub>m</sub> (mg/g)	90.14	208.11	69.87
	K <sub>L</sub> (L/mg)	0.0162	0.0175	0.0029
	r <sup>2</sup>	0.994	0.998	0.991
Freundlich	$K_f (mg/g)$	22.87	15.33	1.64
	n	2.82	3.77	1.95
	$r^2$	0.955	0.901	0.951

#### Table 5

Summary of the literature on the separation of R 6G by various adsorbents.

Adsorbent	pН	Adsorption capacity (mg/g)	Reference
Fe <sub>3</sub> O <sub>4</sub> -composited biochar	7	9.42	[3]
Graphite SERS substrate	2	212.72	[67]
Ceria nanoparticles (CeO <sub>2</sub> -NPs)	9.1	87%	[68]
Polyaniline/ZnS nanocomposite	8	80.62	[69]
Ti, and Al mixed nanoparticles	9	142.9	[70]
Fe <sub>3</sub> O <sub>4</sub> Magnetic Nanoparticles	7	150	[71]
Bentonite clay	6	31.14	[72]
Date fibers	6	10.75	[73]
Nanoscale metal-organic framework	6.1	88.62	[74]
NMIL-100(Fe)			
Zeolite ZSM-22/TON	6	195.3	[31]
Zeolite AlPO-14 (Z1)	7	90.14	This
Zeolite AlPO-14 (Z2)	7	208.11	Work
Zeolite AlPO-14 (Z3)	7	69.87	

tion, kinetic studies define the type of adsorption phenomenon, i.e., either physiosorption or chemisorption. Thus, with first order, pseudo-first order, second-order, pseudo-second order kinetic models [60], the temperature dependent adsorption of R 6G dye on to AIPO-14 was further tested. The non-linear forms of the aforementioned kinetic model equations (Eqs. (7), and 8) are as follows:

# Table 6 Kinetic modeling of data for the separation of R 6G using AlPO-14 (Z1, Z2, and Z3).

$$Pseudo \ first \ order: q_t = q_{e1}(1 - exp(-k_1t)) \eqno(7)$$

Pseudo second order kinetics : 
$$q_t = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t}$$
 (8)

where  $q_e (mg/g)$  and  $q_t (mg/g)$  were the adsorbed quantities of R 6G dye onto AlPO-14 zeolites at equilibrium time, rate constants of pseudo-first order and pseudo-second order kinetic models are denoted by k<sub>1</sub>, and k<sub>2</sub> respectively. A full description of the values of the rate constants, concentrations, and values of the correlation coefficients were displayed in Table 6. Further, Table 6 shows that the experimental and the calculated values of the adsorption capacities tend to rise with increase in temperature. Moreover, for all the adsorbents (AIPO-14), the kinetics are best defined in the pseudo-second order kinetic model in comparison with the pseudo-first-order values (see Table 6). Fig. 8 displays the kinetic sorption of AlPO-14 zeolites (Z1, Z2, and Z3) for the adsorption of R 6G under various temperatures ranging between (303-323 K). From the figure, it is evident that the pseudosecond-order kinetic model fits well confirms the rate limiting step is chemisorption [61] which is due to the dominant valence forces that help to exchange or share electrons between the dye and the adsorbent molecules.

# 3.2.9. Influence of temperature

Another critical physico-chemical process parameter is the temperature influence, as temperature can modify the adsorption potential of the adsorbent. Further, a series of experimental studies were conducted to assess the impact of temperature on the adsorption phenomenon of R 6G dye on the AlPO-14 zeolite with an initial dye concentration of 300 ppm, retaining pH = 7, and varying the temperature in the range of 303–323 K and the findings are displayed in Fig. 9a. From the figure, the improved adsorption capability with temperature results in increased mobility of the dye molecules and an increase in the amount of active temperature adsorption sites [62]. In addition, with the temperature, the

Adsorbent				Pseudo-first-order model			Pseudo-second-order model		
	Temp (K)	$q_{e, exp}$ (mg/g)	q <sub>e1, cal</sub> (mg/g)	k1 (1/min)	r <sup>2</sup>	q <sub>e2, cal</sub> (mg/g)	k <sub>2</sub> (g/mg min)	r <sup>2</sup>	
	303	64.01	73.71	0.0014	0.921	64.88	0.0372	0.997	
Z1	313	71.13	73.25	0.0017	0.951	71.34	0.0021	0.994	
	323	79.32	74.55	0.0019	0.927	80.24	0.0025	0.991	
Z2	303	85.40	93.65	0.001	0.894	85.69	0.0650	0.997	
	313	94.15	85.37	0.043	0.918	95.19	0.0045	0.992	
	323	98.26	94.70	0.053	0.947	99.11	0.0044	0.993	
Z3	303	30.22	37.52	0.0009	0.928	31.15	0.0275	0.991	
	313	35.14	42.83	0.0005	0.901	36.08	0.0231	0.990	
	323	42.36	48.53	0.0006	0.914	42.16	0.0245	0.996	



Fig. 8. Non-linear kinetic studies on the sorption of R 6G onto AlPO-14 (a-c) zeolite Z1, (d-f) zeolite Z2, (g-i) zeolite Z3.



Fig. 9. (a) Effect of temperature on the adsorption of R 6G dye onto AlPO-14 zeolites (Z1, Z2, Z3), (b) van't Hoff plot for the adsorption of R 6G dye onto the AlPO-14 zeolites (Z1, Z2, Z3).

enhanced uptake of dye molecules on the zeolite indicated the reaction was endothermic. From these temperature studies, thermodynamic analysis was performed to determine the Gibbs free energy  $\Delta G^{\circ}$ , entropy  $\Delta S^{\circ}$ , and enthalpy changes  $\Delta H^{\circ}$ . The thermo-

dynamic parameters help to explain the adsorption phenomenon, internal energy shifts and swiftness of the reaction. An established set of equations (Eqs. (9)-(12)) are available to evaluate these parameters and are presented as follows:

 Table 7

 Thermodynamic assessment on adsorption of R 6G onto AIPO-14 (Z1, Z2, and Z3).

Sample	T (K)	∆G <sup>o</sup> (kJ/mol)	ΔH <sup>o</sup> (kJ/mol)	ΔS <sup>o</sup> (kJ/mol K)
Z1	303 313 323	-1.4434 -1.3915 -1.6476	6.5	0.0252
Z2	303 313 323	-0.3717 -0.5408 -0.6817	4.3	0.0154
Z3	303 313 323	-1.5154 -1.9467 -2.2355	9.4	0.036

$$\Delta G^{o} = -RTlnK_{c} \tag{9}$$

$$K_{c} = \frac{C_{Ae}}{C_{e}}$$
(10)

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \tag{11}$$

$$\ln K_{c} = -\frac{\Delta G^{o}}{RT} = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R}$$
(12)

where R is the gas constant (J/mol K), T is the absolute temperature (K), K<sub>c</sub> is the distribution constant, the values of the change in enthalpy  $\Delta H^{\circ}$ , and entropy  $\Delta S^{\circ}$  were obtained from the slope and intercept of the plot between ln K<sub>c</sub> Vs 1/T (Fig. 9b) according to Van't Hoff equation. A detailed thermodynamic assessment on the adsorption of the R 6G onto AlPO-14 zeolite is presented in Table 7. From Table, the positive value of the  $\Delta H^{\circ}$  represents the endothermic nature of the reaction which is confirmed through the influence of the temperature studies. Further negative values of Gibbs free energy  $\Delta G^{\circ}$ , positive value of entropy  $\Delta S^{\circ}$  indicate the impetuous adsorption phenomenon. It is well known that the positive values of change in enthalpy and the entropy highly favors the adsorption processes at higher temperatures.

# 3.2.10. Desorption and regeneration studies

In practice, the performance of adsorbent reusability is an important index for the adsorbent, and completely dependent on its adsorption-desorption characteristics. It is always recommended and required to have an adsorbent of better reusability from economic point of view that strengthens the practical utility for commercial scale applications [63]. Thus, a clear understanding on the possibility of regenerating the vacant sites for the next batch of adsorption is highly necessary. Primarily the adsorption test was conducted by taking 0.05 g adsorbent and mixing with 30 mL of the 300 ppm R 6G dye solution, maintaining pH = 7,



Fig. 10. Desorption of R 6G under various eluents.

and temperature of 303 K for 120 min. Then the resultant mixture was dried at room temperature to obtain the solid residue. Further desorption studies were conducted on the residual part using various eluents 0.1 M NaOH, 0.1 N HCl (Kumar et al., 2016), 0.1 N H<sub>2</sub>SO<sub>4</sub>, 100% ethanol as desorbing agents of R 6G loaded zeolite. The selection of eluents is to examine the desorption spectra of different media, such as acidic, basic, and organic solvents, so that the best potential mechanism is chosen. Fig. 10 reveals that a strong degree of desorption towards NaOH accompanied by HCl, H<sub>2</sub>SO<sub>4</sub>, and ethanol respectively. Thus, NaOH has a better regeneration tendency over the other eluents and the reason ascribed for the higher desorption to alkaline medium is that adsorbent surface gains electrons or negative charge that creates a repulsive nature towards the cationic dye, thereby detaching the dye molecules [64]. Furthermore, a successive number of repeated adsorptiondesorption studies were performed on zeolites (Z1, Z2, and Z3) with NaOH as desorbing agent for five successive cycles shown in Fig. 11 (a-c). The results indicate that as the number of cycles increased the adsorption capacity of the recycled adsorbent tends to decline from 63.5 to 5.12 mg/g (Z1), 85.6-55.6 mg/g (Z2), and 30.15–5.56 mg/g (Z3), respectively. Besides, the eluted sorbent was repeatedly washed with deionized water to remove any residual desorbing solution and placed into dye solution for the next cycle. Thus, from the aforementioned study, it is concluded that adsorbent Z1, can be reused for a maximum of 3 cycles, whereas Z2, and Z3 can be utilized for 5 and 2 cycles to adsorb R 6G dye onto zeolite AlPO-14. Thus, it is conclusive that zeolite Z2 has a better potential of reusing compared to the Zeolites Z1, and Z3.



Fig. 11. Reusability studies of the adsorbent (AIPO-14 zeolites Z1, Z2, and Z3) for different cycles.



Fig. 12. Schematic of reaction mechanism of adsorption of R 6G onto AlPO-14 zeolite.

# 3.3. Adsorption reaction mechanism analysis

In an adsorption study the main challenge is to clarify the adsorption mechanism. Due to the fact that the adsorptive dye removal process is of great importance for the advancement of sorbent-based water technology and is especially sensitive to the initial concentration of organic dyes. Fig. 12 presents the schematic of possible reaction mechanism of R 6G dve sorption onto the zeolites (Z1, Z2, and Z3). Adsorption process perhaps includes multiple manners. First, higher removal rates might be associated with larger pore sizes of zeolite Z2 (AlPO-14) formed through hydrothermal treatment of CFA. Further, large pore sizes could provide pore filling effect to adsorb and accommodate large dye molecules rapidly. Thus, significant drop in the pore volume of zeolites (Z1, Z2, and Z3) were observed after the adsorption of R 6G (see Table 2, Fig. S1). This reduction in the both pore size, and volume suggests the interaction between the adsorbate and sorbent surface through van der Waals forces and the hydrogen bonding interactions, respectively.

Nonetheless, defining the adsorption phenomenon, the composition of the adsorbate and the adsorbent surface properties are highly important. In this context, it should be noted that the selected dyestuff R 6G is a cationic dye containing amine group. On the other hand, the zeolite from CFA has Si and Al as it main components. Thus, in the present research, a cationic organic molecule, R 6G was adsorbed onto the surface of zeolites (Z1, Z2, and Z3) mainly through electrostatic interaction. The electrostatic interactions are the resultant of the silanol groups (Si-OH) on the silica rich zeolites. Further, from the pH studies the increase in the adsorption capacity with increasing pH of R 6G solution, suggesting the existence of deprotonated silanol groups in the form of Si-O<sup>-</sup>, possess greater electrostatic interactions with the cationic dye molecule.

Hydrogen bonding is of fundamental significance for the structure and chemistry, and considered as an intermediate of covalent, ionic and van der Waals bonding. This hydrogen bonding makes the structure stronger and stable but readily disintegrated under ambient conditions [65]. Similarly, physiosorption involves the formation of weak physical interactions, where no-exchange of electrons were observed. Moreover, only relatively weak long-range van der Waals forces are formed between the adsorbate and adsorbent. Because of the weaker adsorbate-adsorbent, this type of adsorption can be easily reversed with low activation/ interaction energy, lower than 30 kJ/mol [66]. In the present study, the calculated activated energies (18.4 kJ/mol - Z1, 23.4 kJ/mol - Z2, 11.3 kI/mol – Z3) fell within the range of aforementioned value (30 kJ/mol), and hence the existence of the hydrogen bonding is confirmed. In addition, the silanol groups on the surface of the zeolites (Z1, Z2, and Z3) tends to interact with the amine groups of the R 6G molecules resulting in hydrogen bonding. Hence, the present interaction of CFA based zeolites and the R 6G molecules were mainly on the electrostatic interactions and the hydrogen bonding, with pH as the crucial parameter that defined the adsorption mechanism.

# 4. Conclusions

The present research deals with the synthesis of low cost, ecofriendly, and novel zeolites (AIPO-14) from CFA of different alkaline fusion ratios (Z1-1:1, Z2-1:1.5, and Z3-1:2) followed by hydrothermal treatment. The initial part of the research highlights the importance of choosing the fusion ratio which had a direct influence on the surface features of the zeolite. In this context the optimal fusion ratio chosen ws 1:1.5 (CFA:NaOH), resulted the Z2 with specific surface area of 221.83  $m^2/g$  with 30 times, greater than raw CFA 7.58 m<sup>2</sup>/g, while Z1, and Z2 had the specific surface areas of 102.09  $m^2/g$ , and 30.09  $m^2/g$ , respectively. In the second part, the as-synthesized zeolites were tested their applicability in adsorption of R 6G dye through batch process. The adsorption experimental findings indicate that the neutral conditions (pH = 7) supported higher intake of dye for all the zeolites, satisfying the Langmuir isotherm model with an uptake of 208.11 mg/g, indicating the adsorption phenomenon is monolayer. Further,

pseudo-second order kinetic models fit well, and the thermodynamic studies revealed the adsorption reaction was spontaneous, chemisorption, and endothermic in nature. Finally, the alkaline eluent NaOH best suits for the recycling the adsorbent after the adsorption studies, and the recycle studies revealed that Z2 had the high performance up to 5 cycles, followed by Z1 three cycles and Z3 with two cycles respectively.

#### **Declaration of Competing Interest**

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

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# Appendix A. Supplementary material

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# References

- Ê.L. MacHado, V. DeSales Dambros, L.T. Kist, E.A. Alcayaga Lobo, S.B. Tedesco, C. C. Moro, Use of ozonization for the treatment of dye wastewaters containing rhodamine B in the agate industry, Water. Air. Soil Pollut. 223 (2012) 1753– 1764, https://doi.org/10.1007/s11270-011-0980-9.
- [2] R.K. Anjani Gollakota, Venkata Subbaiah Munagapati, Krushna Prasad Shadangi, Guda Mallikarjuna Reddy, Jet-Chau Wen, Chi-Min Shu, Encapsulating toxic Rhodamine 6G dye, and Cr (VI) metal ions from liquid phaseusing AIPO<sub>4</sub>-5 molecular sieves. Preparation, characterization, and adsorption parameters, J. Mol. Liquids 336 (2021), https://doi.org/10.1016/ j.molliq.2021.116549. 10.1016/j.desal.2009.10.021 116549.
- [3] T. Suwunwong, P. Patho, P. Choto, K. Phoungthong, Enhancement the rhodamine 6G adsorption property on Fe3O4-composited biochar derived from rice husk, Mater. Res. Express. 7 (2020), https://doi.org/10.1088/2053-1591/ab6b58.
- [4] S. Banerjee, M.C. Chattopadhyaya, Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural byproduct, Arab. J. Chem. 10 (2017) S1629–S1638, https://doi.org/10.1016/j. arabjc.2013.06.005.
- [5] L. Sellaoui, E. Paul Hessou, M. Badawi, M. Schadeck Netto, G. Luiz Dotto, L. Felipe Silva Oliveira, F. Tielens, J. Ifthikar, A. Bonilla-Petriciolet, Z. Chen, Trapping of Ag+, Cu2+, and Co2+ by faujasite zeolite Y: New interpretations of the adsorption mechanism via DFT and statistical modeling investigation, Chem. Eng. J. (2020) 127712, https://doi.org/10.1016/j.cej.2020.127712.
- [6] G. Sreelatha, P. Padmaja, Study of Removal of C ationic D yes u sing Palm Shell Powder as A dsorbent, J. Environ. Prot. Sci. 2 (2008) 63–71.
- [7] A.R.K. Gollakota, V. Subbaiah, V. Volli, S. Gautam, J. Wen, C. Shu, Coal bottom ash derived zeolite (SSZ-13) for the sorption of synthetic anion Alizarin Red S (ARS) dye, J. Hazard. Mater. 416 (2021), https://doi.org/10.1016/j. jhazmat.2021.125925 125925.
- [8] A.R.K. Gollakota, C.-M. Shu, S. Gautam, Turning Coal Fly Ash into Zeolite for Effective, Waste Management (2019) 269–290, https://doi.org/10.1007/978-981-13-3281-4\_13.
- [9] C.L. Carlson, D.C. Adriano, Environmental impacts of coal combustion residues, J. Environ. Qual. 22 (1993) 227, https://doi.org/ 10.2134/jeq1993.0047242500220002002x.
- [10] D. Mainganye, Synthesis of zeolites from South African coal fly ash: Investigation of scale-up conditions (2012) 1–114.
- [11] T. Armbruster, M.E. Gunter, Crystal Structures of Natural Zeolites, Rev. Mineral. Geochemistry. 45 (2001) 1–67, https://doi.org/10.2138/rmg.2001.45.1.
- [12] M. Meier, D. Olson, C. Baerlocher, Atlas of zeolite structure types, fourth ed., Elsevier, London, United Kingdom, 1996.
- [13] C. Martin, J. Patarin, J.P. Coulomb, Sorption Properties of AlPO 4–5 and SAPO-5, Zeolite-like Materials 7463 (1998) 1774–1778.
- [14] L.B. McCusker, D.H. Olson, C. Baerlocher, Atlas of Zeolite Framework Types (2007), https://doi.org/10.1016/B978-0-444-53064-6.X5186-X.
- [15] D. Barthomeuf, Acidic Catalysis with Zeolites, Zeolites, Sci. Technol. (1984) 317–346, https://doi.org/10.1007/978-94-009-6128-9\_12.
- [16] S. Moulai, R. Ghezini, A. Hasnaoui, A. Bengueddach, P.G. Weidler, Adsorption behavior of water and xylene isomers on AIPO-5 zeolite modified by different

transition metals, Res. Chem. Intermed. 45 (2019) 1653–1668, https://doi.org/ 10.1007/s11164-018-3692-6.

- [17] M. Gehre, Z. Guo, G. Rothenberg, S. Tanase, Sustainable Separations of C4-Hydrocarbons by Using Microporous Materials, ChemSusChem. 10 (2017) 3947–3963, https://doi.org/10.1002/cssc.201700657.
- [18] V.R. Choudhary, D.B. Akolekar, A.P. Singh, S.D. Sansare, Sorption properties of crystalline molecular sieve AlPO4-5, J. Catal. 111 (1988) 23–40, https://doi.org/ 10.1016/0021-9517(88)90062-0.
- [19] L. Bieseki, F.G. Penha, S.B.C. Pergher, Zeolite a synthesis employing a brazilian coal ash as the silicon and aluminum source and its applications in adsorption and pigment formulation, Mater. Res. 16 (2013) 38–43, https://doi.org/ 10.1590/S1516-14392012005000144.
- [20] M. Inada, Y. Eguchi, N. Enomoto, J. Hojo, Synthesis of zeolite from coal fly ashes with different silica-alumina composition, Fuel. 84 (2005) 299–304, https:// doi.org/10.1016/j.fuel.2004.08.012.
- [21] K. Ojha, N.C. Pradhan, A.N. Samanta, Zeolite from fly ash: Synthesis and characterization, Bull. Mater. Sci. 27 (2004) 555–564, https://doi.org/10.1007/ BF02707285.
- [22] W. Wulandari, T. Paramitha, J. Rizkiana, D. Sasongko, Characterization of Zeolite A from Coal Fly Ash Via Fusion-Hydrothermal Synthesis Method, IOP Conf. Ser. Mater. Sci. Eng. 543 (2019), https://doi.org/10.1088/1757-899X/543/ 1/012034.
- [23] L. Domokos, L. Lefferts, K. Seshan, J.A. Lercher, Applied molecular simulations over FER-, TON-, and AEL-type zeolites, J. Catal. 203 (2001) 351–361, https:// doi.org/10.1006/jcat.2001.3338.
- [24] N.Z. Neville, Synthesis of zeolite (ZSM-5 and Faujasite), and geopolymer from South African coal fly ash By, 2016.
- [25] T. Jones, A. Wlodarczyk, L. Koshy, P. Brown, S. Longyi, K. Bérubé, The geochemistry and bioreactivity of fly-ash from coal-burning power stations, Biomarkers. 14 (2009) 45–48, https://doi.org/10.1080/13547500902965195.
- [26] D. Mainganye, T.V. Ojumu, L. Petrik, Synthesis of zeolites Na-P1 from South African coal fly ash: Effect of impeller design and agitation, Materials (Basel). 6 (2013) 2704–12089, https://doi.org/10.3390/ma6052074.
- [27] M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites Fifth (5th), Revised Edition, Collect. Simulated XRD Powder Patterns Zeolites Fifth Revis. Ed. (2007), https://doi.org/10.1016/B978-0-444-53067-7. X5470-7.
- [28] S. Octaviani, Y.K. Krisnandi, I. Abdullah, R. Sihombing, The Effect of Alkaline Treatment to the Structure of ZSM5 Zeolites, MAKARA Sci. Ser. 16 (2013) 155– 162, https://doi.org/10.7454/mss.v16i3.1476.
- [29] D. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, 1st ed., John Wiley & Sons Ltd, New York, USA, 1974.
- [30] A. Iwasaki, T. Sano, T. Kodaira, Y. Kiyozumi, Growth behaviors of AFI type crystals, Microporous Mesoporous Mater. 64 (2003) 145–153, https://doi.org/ 10.1016/S1387-1811(03)00462-1.
- [31] A.R.K. Gollakota, V. Volli, V.S. Munagapati, J.-C. Wen, C.-M. Shu, Synthesis of novel ZSM-22 zeolite from Taiwanese coal fly ash for the selective separation of Rhodamine 6G, J. Mater. Res. Technol. 9 (2020) 15381–15393, https://doi. org/10.1016/j.jmrt.2020.10.070.
- [32] S. Boycheva, D. Zgureva, K. Lazarova, T. Babeva, C. Popov, H. Lazarova, M. Popova, Progress in the utilization of coal fly ash by conversion to zeolites with green energy applications, Materials (Basel). 13 (2020), https://doi.org/10.3390/MA13092014.
- [33] B. Jha, D.N. Singh, Formation of meso- And micro-pores in fly-ash zeolites using a three-step activation, Acta Geotech. Slov. 11 (2014) 63–69.
- [34] J. Shang, G. Li, R. Singh, P. Xiao, J.Z. Liu, P.A. Webley, Determination of composition range for "molecular trapdoor" effect in chabazite zeolite, J. Phys. Chem. C. 117 (2013) 12841–12847, https://doi.org/10.1021/jp4015146.
   [35] F. Rouquerol, J. Rouquerol, K. Singh, Adsorption by Powders and Porous Solids,
- [35] F. Rouquerol, J. Rouquerol, K. Singh, Adsorption by Powders and Porous Solids, Academic Press, London, United Kingdom, 1999.
- [36] B.G. Kutchko, A.G. Kim, Fly ash characterization by SEM-EDS, Fuel. 85 (2006) 2537-2544, https://doi.org/10.1016/j.fuel.2006.05.016.
   [37] X.L. Zhang, G.J. Wu, T.D. Yao, C.L. Zhang, Y.H. Yue, Characterization of
- [37] X.L. Zhang, G.J. Wu, T.D. Yao, C.L. Zhang, Y.H. Yue, Characterization of individual fly ash particles in surface snow at Urumqi Glacier No. 1, Eastern Tianshan, Chinese Sci. Bull 56 (2011) 3464–3473, https://doi.org/10.1007/ s11434-011-4684-8.
- [38] G.D. Gatta, Y. Lee, Zeolites at high pressure: A review, Mineral. Mag. 78 (2014) 267–291, https://doi.org/10.1180/minmag.2014.078.2.04.
- [39] D. Yilmaz, H. Leion, Interaction of Iron Oxygen Carriers and Alkaline Salts Present in Biomass-Derived Ash, Energy and Fuels. 34 (2020) 11143–11153, https://doi.org/10.1021/acs.energyfuels.0c02109.
- [40] O.B. Belskaya, I.G. Danilova, M.O. Kazakov, R.M. Mironenko, A.V. Lavrenov, V.A. Likholobov, FTIR Spectroscopy of Adsorbed Probe Molecules for Analyzing the Surface Properties of Supported Pt (Pd) Catalysts, Infrared Spectrosc. - Mater. Sci, Eng. Technol. (2012), https://doi.org/10.5772/36275.
- [41] L. Fernández-Carrasco, D. Torrens-Martín, L.M. Morales, S. Martínez-Ramírez, Infrared Spectroscopy in the Analysis of Building and Construction Materials, Infrared Spectrosc. - Mater. Sci, Eng. Technol. (2012), https://doi.org/10.5772/ 36186.
- [42] A. Fauzi, M.F. Nuruddin, A.B. Malkawi, M.M.A.B. Abdullah, Study of Fly Ash Characterization as a Cementitious Material, Procedia Eng. 148 (2016) 487– 493, https://doi.org/10.1016/j.proeng.2016.06.535.
- [43] Y.P. Chang, C.L. Ren, Q. Yang, Z.Y. Zhang, LJ. Dong, X.G. Chen, D.S. Xue, Preparation and characterization of hexadecyl functionalized magnetic silica nanoparticles and its application in Rhodamine 6G removal, Appl. Surf. Sci. 257 (2011) 8610–8616, https://doi.org/10.1016/j.apsusc.2011.05.031.

- [44] F. Haghseresht, S. Nouri, G.Q. Lu, Effects of the solute ionization on the adsorption of aromatic compounds from dilute aqueous solutions by activated carbon, Langmuir. 18 (2002) 1574–1579, https://doi.org/10.1021/la0109031.
- [45] N.D. Tissera, R.N. Wijesena, H. Yasasri, K.M.N. deSilva, R.M. deSilva, Fibrous keratin protein bio micro structure for efficient removal of hazardous dye waste from water: Surface charge mediated interfaces for multiple adsorption desorption cycles, Mater. Chem. Phys. 246 (2020), https://doi.org/10.1016/ j.matchemphys.2020.122790 122790.
- [46] C. Tonin, A. Aluigi, C. Claudia Vineis, Keratin-based Nanofibres, in: A. Kumar (Ed.), Nanofibers, 1st ed., Intech open, Kanpur, India, 2010, p. 13. https://www. intechopen.com/books/advanced-biometric-technologies/liveness-detectionin-biometrics.
- [47] A. Benhouria, M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala, B.H. Hameed, Calcium alginate-bentonite-activated carbon composite beads as highly effective adsorbent for methylene blue, Chem. Eng. J. 270 (2015) 621–630, https://doi.org/10.1016/j.cej.2015.02.030.
- [48] Y. Zhou, Y. Min, H. Qiao, Q. Huang, E. Wang, T. Ma, Improved removal of malachite green from aqueous solution using chemically modified cellulose by anhydride, Int. J. Biol. Macromol. 74 (2015) 271–277, https://doi.org/10.1016/j. ijbiomac.2014.12.020.
- [49] A. Pourjavadi, M. Nazari, S.H. Hosseini, Synthesis of magnetic graphene oxidecontaining nanocomposite hydrogels for adsorption of crystal violet from aqueous solution, RSC Adv. 5 (2015) 32263–32271, https://doi.org/10.1039/ c4ra17103a.
- [50] L.T. Gibson, Mesosilica materials and organic pollutant adsorption: Part B removal from aqueous solution, Chem. Soc. Rev. 43 (2014) 5173–5182, https:// doi.org/10.1039/c3cs60095e.
- [51] I.V. Joseph, L. Tosheva, A.M. Doyle, Simultaneous removal of Cd(II), Co(II), Cu (II), Pb(II), and Zn(II) ions from aqueous solutions via adsorption on FAU-type zeolites prepared from coal fly ash, J. Environ. Chem. Eng. 8 (2020), https://doi. org/10.1016/j.jece.2020.103895 103895.
- [52] H. Bensalah, M.F. Bekheet, S.A. Younssi, M. Ouammou, A. Gurlo, Removal of cationic and anionic textile dyes with Moroccan natural phosphate, J. Environ. Chem. Eng. 5 (2017) 2189–2199, https://doi.org/10.1016/j.jece.2017.04.021.
- [53] S. Chowdhury, R. Mishra, P. Saha, P. Kushwaha, Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk, Desalination. 265 (2011) 159–168, https://doi.org/ 10.1016/j.desal.2010.07.047.
- [54] J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, J. Zhang, R. Han, Q. Xu, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): Kinetics, isotherm, thermodynamics and mechanism analysis, Chem. Eng. J. 259 (2015) 53–61, https://doi.org/10.1016/j.cej.2014.07.101.
- [55] C. Feng, P. Ren, Z. Li, W. Tan, H. Zhang, Y. Jin, F. Ren, Graphene/wastenewspaper cellulose composite aerogels with selective adsorption of organic dyes: Preparation, characterization, and adsorption mechanism, New J. Chem. 44 (2020) 2256–2267, https://doi.org/10.1039/c9nj05346h.
- [56] I. Langmuir, The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, Eucken, Verh. Deut. Phys. Ges. 16 (1918) 1361–1403, https://doi.org/ 10.1021/ja01269a066.
- [57] V.H. Freundlich, Kolloidfillung und Adsorption., Juretzka Gattierung von Zinkblende Und Galmei, [. 20 (1907) 750–754, https://doi.org/10.1002/ ange.19070201806.
- [58] T. Santhi, S. Manonmani, T. Smitha, Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinus communis by adsorption, J. Hazard. Mater. 179 (2010) 178–186, https://doi.org/10.1016/ j.jhazmat.2010.02.076.
- [59] M. Manjuladevi, R. Anitha, S. Manonmani, Kinetic study on adsorption of Cr (VI), Ni(II), Cd(II) and Pb(II) ions from aqueous solutions using activated carbon

prepared from Cucumis melo peel, Appl. Water Sci. 8 (2018) 1-8, https://doi. org/10.1007/s13201-018-0674-1.

- [60] M. Wawrzkiewicz, Z. Hubicki, Removal of tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins, J. Hazard. Mater. 164 (2009) 502–509, https://doi.org/10.1016/j.jhazmat.2008.08.021.
- [61] F. Gomri, G. Finqueneisel, T. Zimny, S.A. Korili, A. Gil, M. Boutahala, Adsorption of Rhodamine 6G and humic acids on composite bentonite-alginate in single and binary systems, Appl. Water Sci. 8 (2018), https://doi.org/10.1007/s13201-018-0823-6.
- [62] L. Yang, J. Hu, L. He, J. Tang, Y. Zhou, J. Li, K. Ding, One-pot synthesis of multifunctional magnetic N-doped graphene composite for SERS detection, adsorption separation and photocatalytic degradation of Rhodamine 6G, Chem. Eng. J. 327 (2017) 694–704, https://doi.org/10.1016/j.cej.2017.06.162.
- [63] S.M. Hossini Asl, M. Masomi, M. Tajbakhsh, Hybrid adaptive neuro-fuzzy inference systems for forecasting benzene, toluene & m-xylene removal from aqueous solutions by HZSM-5 nano-zeolite synthesized from coal fly ash, J. Clean. Prod. 258 (2020), https://doi.org/10.1016/j.jclepro.2020.120688
- [64] S. Sadaf, H.N. Bhatti, M. Arif, M. Amin, F. Nazar, Adsorptive removal of direct dyes by PEI-treated peanut husk biomass: Box-Behnken experimental design, Chem. Ecol. 31 (2015) 252–264, https://doi.org/10.1080/ 02757540.2014.950568.
- [65] K. Andersson, Structure, Bonding and Chemistry of Water and Hydroxyl on, Transition Metal Surfaces (2006).
- [66] T.R. Sahoo, B. Prelot, Adsorption processes for the removal of contaminants from wastewater, Elsevier Inc., 2020. doi: 10.1016/b978-0-12-818489-9.00007-4.
- [67] N. Sykam, N.D. Jayram, G. Mohan Rao, Exfoliation of graphite as flexible SERS substrate with high dye adsorption capacity for Rhodamine 6G, Appl. Surf. Sci. 471 (2019) 375–386, https://doi.org/10.1016/j.apsusc.2018.11.082.
- [68] J. Calvache-Muñoz, J.E. Rodríguez-Páez, Removal of Rhodamine 6G in the absence of UV radiation using ceria nanoparticles (CeO2-NPs), J. Environ. Chem. Eng. 8 (2020), https://doi.org/10.1016/j.jece.2019.103518.
- [69] S. Allahveran, A. Mehrizad, Polyaniline/ZnS nanocomposite as a novel photocatalyst for removal of Rhodamine 6G from aqueous media: Optimization of influential parameters by response surface methodology and kinetic modeling, J. Mol. Liq. 225 (2017) 339–346, https://doi.org/10.1016/ j.molliq.2016.11.051.
- [70] U. Pal, A. Sandoval, S. Isaac, U. Madrid, G. Corro, V. Sharma, P. Mohanty, Chemosphere Mixed titanium, silicon, and aluminum oxide nanostructures as novel adsorbent for removal of rhodamine 6G and methylene blue as cationic dyes from aqueous solution, Chemosphere. 163 (2016) 142–152, https://doi. org/10.1016/j.chemosphere.2016.08.020.
- [71] S.Phoemphoonthanyakit, P.Seeharaj, P.Damrongsak, K.Locharoenrat, Effect of Adsorption Characteristics of Rhodamine 6G Dye Solution in Fe 3 O 4 Magnetic Nanoparticles on Fluorescence Quantum Yield, 2019 (2019).
- [72] A.M. Farhan, A.S. Sameen, Kinetic study of adsorption rhodamine 6G dye from aqueous solutions using bentonite clay, Am. J. Environ. Eng. 4 (2014) 11–17, https://doi.org/10.5923/j.ajee.20140401.03.
- [73] Alizadeh A., Parizanganeh A., Yaftian M.R., Zamani A., Application of Cellulosic Biomass for Removal of Cationic Dye Rhodamine 6G from Aqueous Solutions, Int. J. Waste Resour. 06 (2016).
- [74] S. Duan, J. Li, X. Liu, Y. Wang, S. Zeng, D. Shao, T. Hayat, HF-Free Synthesis of Nanoscale Metal-Organic Framework NMIL-100(Fe) as an Efficient Dye Adsorbent, ACS Sustain. Chem. Eng. 4 (2016) 3368–3378, https://doi.org/ 10.1021/acssuschemeng.6b00434.