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# Encapsulating toxic Rhodamine 6G dye, and Cr (VI) metal ions from liquid phase using AlPO<sub>4</sub>-5 molecular sieves. Preparation, characterization, and adsorption parameters



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# ABSTRACT

Water contamination through textile dyes, metal depositions, and industrial wastes such as coal combustion residues especially coal fly ash (CFA) putting an enormous strain on dwindling planets water resources. Several characterization techniques, such as XRF, XRD, BET, SEM, and FT-IR, were performed to test the inherent properties of raw CFA and the product zeolite (AIPO<sub>4</sub>-5). The fusion ratio (CFA: NaOH) substantially enhanced the specific surface area of the zeolite (219.3 m<sup>2</sup>/g) compared to raw CFA (6.27  $m^2/g$ ). The hydrothermal treatment greatly altered the molar ratio of Si/Al from 3.18 (CFA) to 2.11 (AIPO<sub>4</sub>-5) suggesting higher crystallinity of the product. Further, AIPO<sub>4</sub>-5 molecular sieve was tested its ability in separation of cationic Rhodamine 6G dye (R 6G), and Cr (VI) from liquid phase via batch mode adsorption process. The results indicated that the optimal adsorption conditions were (pH = 7 for R 6G; pH = 2 for Cr (VI); temperature 303 K for both adsorbates; dosage (0.05 g/30 mL-R 6G; 0.1 g/30 mL-Cr(VI); and residence time; 120 min-R 6G, 180 min-Cr (VI) respectively. Further, the Langmuir isotherm model suits well reporting maximum adsorption capacities (qm) as 208.61 (mg/g)-R 6G; 97.32 (mg/g)–Cr (VI)), and best fits to the pseudo-second-order kinetic models. The thermodynamic aspects exhibit the spontaneous and endothermic nature of R 6G dye, and Cr (VI) metal sorption onto AlPO<sub>4</sub>-5 zeolite. From the desorption studies, alkaline eluent 0.1 M NaOH showed better performance in recovering 89.4%, 91% of adsorbent from R 6G dye, and Cr (VI) solutions respectively. Lastly, the reusability studies confirmed that the adsorbent (AIPO<sub>4</sub>-5) had the potential up to three cycles (R 6G), and it is confined to two cycles in case of Cr (VI) metal solution.

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# 1. Introduction

Rapid industrialization, technological advancement, and human actions are regarded as a trio of ecological distress. The polluted hydro-medium in particular is the main threat that the world faces today. Direct release of effluents containing toxic dyes, and heavy metals were regarded as the major contaminants posing deadly risk to the human and aquatic environments.

It is well known that there exists over  $10^5$  commercial dyes, with an annual global production of more than  $7 \times 10^5$  tones [1].

Out of which nearly 0.2 billion tons [2] of global effluent release from tanning industries contaminating the water streams. They are classified into acidic, basic, disperse, azo, diazo, and anthroquinone based complex dyes. Among these, Rhodamine 6G (R 6G) is a monocationic xanthene synthetic cationic dye, widely used in acrylic, nylon, silk and wool dyeing, and requires special attention to handle [3]. The serious problem with R 6G dye is its high solubility in water even at lower concentrations 1.0 mg/L could impart color and unfit for consumption. The water streams containing dye pollutants have severe effects such as restricted light penetration, retarding photosynthetic activity, inhabiting biota growth, and chelating metal ions causing metal toxicity to marine life [4]. Moreover, direct contact, ingestion, and inhalation by humans leads to mutagenic, neurotoxic, teratogenic and carcinogenic effects.

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On the other side, metals like chromium (Cr) [5], lead (Pb) [6], cadmium (Cd) [7], and arsenic (As) [8], are considered as predominant pollutants and known for their toxic nature, persistence in every form, non-biodegradability and the bioaccumulation [9]. From the aforementioned heavy metals, Cr has a specific importance, obtained from the discharge of smelting, mining, metallurgical, electroplating, and other chemical processing industries. Cr owns different oxidation states such as -2, -1, 0, +1, +2, +3, +4, +5, +6 with varied properties and threat levels to the ecological security [10]. Among the various oxidation states Cr (III) and Cr (VI) are highly stable states, and the toxicity is purely dependent on the oxidation states. Normally, Cr occurs as trivalent chromium Cr (III) acts a potential micronutrient and harmless, whereas Cr (VI) is an oxidized form of Cr oxyanions which is highly toxic, readily soluble in water, penetration through food chain via bio-magnification [11], causing distress to the aquatic environment and the biological cells [12]. Further, Cr (VI) exists in water mainly as  $CrO_4^2$ ,  $HCrO_4$ ,  $Cr_2O_7^2$  and so on, depending on the ion concentration and the pH of the water. These forms of Cr are typically more toxic and mobile than the Cr (III) species  $Cr^{3+}$ ,  $Cr (OH)^{2+}$ , and  $Cr(OH)^{+}_{2-}$ . Thus, the migration and transformation of Cr (VI) is of great concern to human health and a big threat to the ecological security.

To mitigate the growing concerns of water contamination many techniques were evolved; such as photocatalysis, adsorption, ozonation, membrane filtration, ion exchange, and biological degradation. Despite of several strategies existing, adsorption technique is proven to be a simple, economical, and promising approach due to the ease of operation and effectiveness. Although adsorption is an amicable approach, the choice of adsorbent is highly debatable due to the lack of universal adsorbent material. Further, rapid progression of energy demands lead to massive quantities of coal combustion residues, otherwise known as coal fly ash (CFA) have a great potential as adsorbent materials [13]. The reason is that the inherent physico-chemical features of CFA containing abundant Si and Al phases tends to form CFA zeolites (CFAZ's) owning to versatile structures, with possible pore designs [14]. Another structural advantage CFAZ's resembling natural zeolites but their irregularities on morphology related to mixed micro-mesoporosity and inclusion of metal oxides obtained from raw CFA proven to be salient advantage in using them as potential adsorbents of dyes and toxic metals from the aqueous streams [15]. By virtue of this effective hydrothermal conversion of CFA to CFAZ's provide relief to the concerns of catastrophes such as CFA leaching to ground waterbodies, reduced landfills, soil and water remediation etc. [16]. Extensive research on CFAZ's has been a harmonizing strategy over the centuries leading to hundreds of commercial zeolites but a little is known about the aluminophosphates framework AlPO<sub>4</sub>-5. The interesting feature of AIPO<sub>4</sub>-5 falls under the AFI type with one dimensional needle-or rod like structure [17,18]. In addition, the preparation of AIPO<sub>4</sub>-5 framework was mainly carried out in the presence of the structure directing agents, and no attempt was reported till date deriving from the CFA.

Thus, the prime focus of the present research is to effectively convert CFA to AlPO<sub>4</sub>-5 via hydrothermal treatment, and test the applicability as an adsorbent in separating R 6G dyestuff, and Cr (VI) metal ions from the aqueous streams. Another aspect of the present study is to elucidate the potentiality of CFA as an adsorbing medium, thereby adding CFA based AlPO<sub>4</sub>-5 into the commercial zeolite database.

# 2. Materials and methods

#### 2.1. Chemical and reagents

CFA in the present study was supplied by the thermal power company, Taiwan. Sigma-Aldrich, Taiwan supplied all the chemicals; NaOH  $\geq$  97%, HCl  $\geq$  37%, NaAlO<sub>2</sub>, Ethanol  $\geq$  99.5%, H<sub>2</sub>SO<sub>4</sub>  $\geq$  99%, NH<sub>4</sub>OH  $\geq$  99%, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, NaNO<sub>2</sub>  $\geq$  97%, HNO<sub>3</sub>  $\geq$  99%, H<sub>3</sub>PO<sub>4</sub>  $\geq$  99%, Na<sub>2</sub>SO<sub>3</sub>  $\geq$  98%, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $\geq$  99%, R 6G dye content 99%, 1,5-Diphenylcarbazide  $\geq$  98%, and acetone that were necessary for the present study. The chemicals and reagents used were of analytical grade with no further purification necessary. Deionized (DI) water has been used throughout the experiment, and the adsorption analysis of R 6G, Cr (VI) onto AlPO<sub>4</sub>-5 were carried out in Perkin Elmer UV–vis spectrophotometer.

# 2.2. Synthesis of CFAZ's (AlPO<sub>4</sub>-5)

Prior to synthesizing CFAZ's, the raw CFA has been pretreated to prepare more effective mesoporous frameworks. The detailed synthesis of the CFAZ's were reported from our previous work [19]. The synthesis process begins with sieving raw CFA to 75  $\mu$ m mesh size, calcined at 1073 K for 4 h to eliminate the unburnt carbon traces. This step was followed by a repetitive DI water washing further remove the impure traces, and left to oven drying at 303 K for 24 h. The calcined CFA is transmuted to zeolite initiating with alkali fusion step. The process of alkali fusion involves the mixing alkali to the raw CFA at fixed mass ratios (1:1.5), followed by fusing at 873 K for 60 min, also known as solution dissolution [20]. During the fusion reaction, the oxides of CFA namely SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> tends to form aluminosilicate gel upon NaOH dissolution [21]. Further, the homogeneous mixtures temperature is gradually reduced to ambient conditions, finely powdered via mortar pestle. The finely ground powder is then transferred to a 250 mL conical flask containing 100 mL of DI water, 20% of NaAlO<sub>2</sub>, and the slurry mixture was agitated on a magnetic stirrer for 24 h at a constant speed of 400 rpm. The percentage of NaAlO<sub>2</sub> highly influence the Si/Al ratio, thereby the final zeolite product, and in the present case 20% has been chosen as optimal value [22]. After 24 h, the gel mixture was transferred to 100 mL polytetrafluoroethylene (PTFE) bottles, hermetically sealed and crystallization reaction was performed at a fixed temperature of 393 K for 24 h. The final crystallized solution was thoroughly rinsed with DI water for several times to obtain neutral pH and filtered with Whatman filter paper. The solid residue on the filter paper was carefully scrapped to a glass petri dish, aged and cured at 423 K for 24 h imparting the strength and optimal surface characteristics to the zeolite material (AlPO<sub>4</sub>-5).

# 2.3. Characterization of CFA, and CFAZ's (AlPO<sub>4</sub>-5)

The physico-chemical properties of the raw CFA and the assynthesized zeolite AlPO<sub>4</sub>-5 was tested using various characterization techniques. To start with, the inherent composition of the raw CFA, product zeolite AlPO<sub>4</sub>-5 were determined using X-ray fluorescence spectrophotometer (Bruker 5i tracer), and confirmed the classification of the selected CFA as Class F. Further, the phase analysis of the samples (CFA, AlPO<sub>4</sub>-5) were verified with X-ray diffraction (XRD, Bruker Advanced-D825A) with Cu-K $\alpha$  radiation over the scanning range of  $2\theta = 5^{\circ}-60^{\circ}$ , at the rate of 0.02° operated at 40 kV and 40 mA. The textural surface properties such as; pore size, and specific surface area were studied with N<sub>2</sub> sorption analysis. Gas adsorption isotherms were performed at 77 K in a surface pore size analyzer (Micrometrics, ASAP 2060), after degassing for 12 h at 423 K. The specific surface area, and the pore size distributions was measured using Brunauer-Emmet-Teller (BET) method, and Barrett-Joyner-Halenda (BJH) methods respectively. The morphological characteristics of the raw CFA, and AlPO<sub>4</sub>-5 were studied via ultra-high-resolution thermal Field Emission Scanning Electron Microscope (JEOL, JSM-7610F Plus) (FE-SEM) analysis. Prior to the SEM scanning, the samples were thoroughly coated with a layer of gold film, followed by sputtering for 180 sec to make the materials conductive. Furthermore, Fourier-transform infrared spectrometer (FT-IR, PerkinElmer Spectrum One) containing DTGBr detector and KBr split beamer was used to evaluate the functional groups of CFA, AlPO<sub>4</sub>-5 at a scanning range of 400-4000 cm<sup>-1</sup>. Finally, the adsorption analysis of both R 6G and Cr (VI) onto AlPO<sub>4</sub>-5 were performed via UV-vis spectrophotometer (PerkinElmer Lambda 850) containing quartz cell of 1.0 nm path length at  $\lambda$  = 530 nm (R 6G) [19], 350 nm for Cr (VI) [23] respectively.

# 2.4. Adsorption experiments

The adsorption equilibrium tests for separating R 6G dye stuff, and Cr (VI) metal contaminants from the aqueous streams using hydrothermally synthesized CFAZ's (AIPO<sub>4</sub>-5) were performed on a batch mode. All the adsorption experiments were carried out in a 100 mL glass-stoppered, Erlenmeyer's flasks. Initially, 1000 mL of 300 ppm R 6G, and Cr (VI) solutions was prepared in volumetric flasks. Each adsorption experiment was performed in a 50 mL glass beaker with tightly sealed lid, and considering 30 mL of the known initial concentration R 6G dye and Cr (VI) solutions. Prior to performing the adsorption studies of the Cr (VI) via UV–vis spectrometer, the following color development method was performed.

# 2.4.1. Preparation of 1,5-diphenylcarbazide solution

The 1,5-diphenylcarbazide solution was prepared by dissolving 250 mg of 1,5-diphenylcarbazide powder in 50 mL of acetone. This functions as an indicator for lower concentration (ppm) solutions and imparts a pink color to the solution when encounters added sulfuric acid in the solution [24].

# 2.4.2. Color development

- The samples were filtered.
- For color development, 2 mL of 1,5-diphenylcarbazide solution and 5 mL of sulfuric acid were added to 20 mL of result samples.
- The solution was shaken for 60–120 sec for development of color. A pink color was imparted in the solution.
- After color development, the samples were analyzed in a UVspectrophotometer to calculate the amount of chromium present in them.

Further, the adsorption experiments were performed by considering 30 mL of R 6G, Cr (VI) solutions, with different concentrations (100–1000 mg/L) were placed. The adsorbent dosages were altered in the range of (0.05–0.4 g/30 mL), and the pH values were gradually tested between 2 and 12 with (0.1 N) HCl, (0.1 N) NaOH solutions. Similarly, the agitation speed effect was tested in the range of (100–500 rpm), equilibrium residence time of adsorption (0–300 min), temperature effects between (303–323 K) respectively. After the attainment of the adsorption equilibrium, the samples were collected in 50 mL centrifuge tubes, and analyzed the initial (C<sub>i</sub>), residual equilibrium concentrations (C<sub>e</sub>) of R 6G and Cr (VI) using UV–vis absorbance according to the calibration method. Eqs. (1)–(2) allow to calculate the removal efficiency/desorption percentage of the R 6G, Cr (VI) and the equilibrium adsorption capacity  $q_e$  (mg/g) as mentioned below [25]:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

Desorption 
$$\% = \frac{(C_i - C_e)}{C_i} \times 100$$
 (2)

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. Each equilibrium adsorption study was performed three times and the average values were considered in the calculation.

# 3. Results and discussion

# 3.1. X-ray fluorescence (XRF) analysis

Fluorescence techniques (XRF) were usually performed to determine the elemental composition of the CFA, as well to ensure the appropriateness of synthesizing CFAZ's. The trace elemental compositions of the raw CFA and the hydrothermally synthesized zeolite AlPO<sub>4</sub>-5 are presented in Table 1. Table 1 indicates the higher oxide proportions of Si (67.87%) and Al (21.29%), which were the precursors of zeolite. Further, the molar ratio of Si/ Al = 3.18 indicated the possibility of forming AFI type zeolites [26]. The molar ratio is used an index as it alters the morphological characteristics of pure phase zeolites. Moreover, the crystallinity had an inverse relation with the molar ratio, thus the newly formed AlPO<sub>4</sub>-5 zeolite reported less molar ratio of 2.11 when compared to the raw CFA. This scenario was thoroughly supported by the FE-SEM analysis and the BET observations presented in the following sections. Apart from the Si, Al favoring the CFAZ's, the other trace compositions of Fe, Ca, K, Mg considered as exchangeable cations, readily alters the structural properties. Whereas Ti, and S induce many unwanted secondary reactions, and hence a repeated deionized (DI) water wash was highly suggested as a pretreatment operational procedure for CFA prior to hydrothermal conversion to zeolite.

# 3.2. X-ray diffractogram (XRD) analysis

Fig. 1 presents the powder X-ray diffraction patterns of raw CFA and hydrothermally synthesized zeolite AlPO<sub>4</sub>-5 respectively. The measured XRD patterns of raw CFA contained quartz as the major constituent, mullite, and hematite in the trace proportions. The presence of these quartz was confirmed with an intense peak at  $2\theta = 20.85^\circ$ , 26.6°, and 42.47° [27], traces of mullite were observed at  $2\theta = 33.13^\circ$ , 35.21° [28], and hematite at 40.86° [27], respectively. On the other hand, the synthesized zeolite AlPO<sub>4</sub>-5 reported amorphous nature with abundant peaks reported in the XRD diffractogram. The characteristic peaks of the synthesized zeolite

Table 1			
Chemical composition of CFA and zeolite (	AlPO₄-5)	(wt.% dry	basis).

Major oxides	Raw CFA	AlPO <sub>4</sub> -5
SiO <sub>2</sub>	67.87	64.42
Al <sub>2</sub> O <sub>3</sub>	21.29	28.62
Fe <sub>2</sub> O <sub>3</sub>	3.65	7.51
CaO	2.57	2.68
K <sub>2</sub> O	1.07	0.35
$P_2O_5$	0.93	0.13
TiO <sub>2</sub>	0.87	0.55
CuO	0.01	0.02
MgO	0.77	0.76
MnO	0.04	0.05
NiO	0.006	0.006
ZnO	0.01	0.025
Si/Al	3.18	2.11



Fig. 1. Mineralogy of CFA, AlPO<sub>4</sub>-5 Zeolite.

from the XRD diffractogram were matched to AlPO<sub>4</sub>-5 at  $2\theta = 12$ . 89°, 19.74°, 24.69°, 30.04°, 33.59°, 37.80°, 40.75°, 42.68°, respectively [29,30]. The matching patterns endorse the single-pure phase formation of the zeolite AlPO<sub>4</sub>-5, resembling AFI type zeolites. Further, the structure of the AFI type zeolites were hexagonal with framework composition of Al<sub>12</sub>P<sub>12</sub>O<sub>48</sub>, and cell parameter values of a = 13.74 Ű, b = 13.74 Ű, c = 8.47 Ű,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ , and  $\gamma =$ 120°, respectively. The similar formation of pure phase amorphous AFI type zeolites were previously reported [31].

#### 3.3. Textural analysis Brunauer-Emmett-Teller (BET)

The textural aspects of the raw CFA and the hydrothermally prepared Zeolite AlPO<sub>4</sub>-5, a resultant of N<sub>2</sub> adsorption isotherms at 77 K are presented in Table 2. Prior to the hydrothermal treatment the surface area of the raw CFA was reported as 6.27  $m^2/g$ , and it is 219.31  $m^2/g$  for the zeolite AlPO<sub>4</sub>-5 after the treatment. This vastly increased surface denoted the conversion of the quartz, mullite, and hematite phase of raw CFA to the dissoluted ionic species. It is known that the surface area of mesoporous silica is greatly enhanced by the development of the micro pores within the walls of the meso pores. Further, the use of alkali fusing agent (NaOH) substantially increased the roughness, fractured the surface, and exerted pressure on to cell walls thereby generating vacant sites. Moreover, the pore volume also reported to be greatly increased from 0.0041 cm<sup>3</sup>/g (raw CFA) to 0.1528 cm<sup>3</sup>/g (AlPO<sub>4</sub>-5). The reason ascribed for the increased pore volume was the unrestricted entrainment of the N2 molecules due to the effective hydrothermal treatment, and similar instances were reported in the literature [32]. Furthermore, the N<sub>2</sub> adsorption/desorption phenomenon of the zeolite AlPO<sub>4</sub>-5, along with the BJH pore size distribution is showcased in Fig. 2. From Fig. 2a. the adsorption isotherm was identified as Type IV, commonly designated to the mesoporous structures according to the International union of Pure and Applied Chemistry (IUPAC). Besides, Type IV isotherm is

characterized by the flat plateau of variable length at saturation point, with a precarious adsorption step at relative pressure of P/ P<sub>0</sub> = 0.4 [33]. In addition, hysteresis loops were correlated to the texture of the adsorbent, and in the present scenario it is defined as H4 loop. As known that H4 loops were observed in the case of complex materials containing both mesoporous and micro pores with a characteristic step down at relative pressure of ca. 0.4. Fig. 2b reveals the relation of pore size distribution and pore volume of AlPO<sub>4</sub>-5 zeolite as 0.1528 cm<sup>3</sup>/g, resembling needle-or rod like crystals and similar instances were reported by [34].

#### 3.4. Field emission scanning electron microscope (FE-SEM) analysis

Scanning electron microscope (SEM) analysis helps to disclose the surface textural, and morphological properties and the materials. The textural and morphological information of the raw CFA prior to hydrothermal treatment and the subsequent product AlPO<sub>4</sub>-5 zeolite are delineated in Fig. 3. According to the SEM micrographs Fig. 3 (a-d), the raw CFA particles are perfectly spherical in shape due to the higher proportions of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> rich in bituminous coals, possessing higher pozzolanic activity [35]. Further, the presence of the hematite  $(Fe_2O_3)$  makes the surface of the raw CFA glassy smooth [36], justifying the suitability of CFA to synthesize zeolites [37]. Similarly, Fig. 3 (e-h) reports the typical formation of AlPO<sub>4</sub>-5 zeolites from the hydrothermal treatment of raw CFA. The FE-SEM micrograph of the zeolite AlPO<sub>4</sub>-5 displayed a cluster of needle-or-rod like one dimensional cylindrical aggregates and similar instances were reported [38]. Further the fusion ratio of CFA and NaOH played a crucial role in forming the perfect shape of the crystal which was due to the proper dissolution of silica and alumina species undergoing hydrothermal treatment. In addition, the needle shape of the crystal is due to the structural arrangement of five tetrahedral sites and ten oxygen atoms as cross-linked chains [39]. In summary, from the FE-SEM analysis it was concluded that the formed zeolite is AlPO<sub>4</sub>-5 falls under the category of AFI type topology possessing excellent structural stability and can be used as an adsorbent. material.

# 3.5. Fourier-transform infrared spectroscopy (FT-IR) analysis

FT-IR spectra provide the preliminary quantitative analysis of the major functional groups presented in native raw CFA and the hydrothermally synthesized AlPO<sub>4</sub>-5 zeolite framework. Moreover the IR technique is vivid in case of the analyzing amorphous phase, especially zeolites to trace the composition of the Al and Si existing in raw CFA prior to hydrothermal treatment and after the product (zeolite) formation. This helps to analyze the feasibility of the adsorbent, and assess the possible adsorption mechanism [40]. In lieu of this, the FT-IR spectra of raw CFA and the as synthesized AlPO<sub>4</sub>-5 zeolite in the range of 400–4000 cm<sup>-1</sup> were shown in Fig. 4 (a-c). The absorption bands of pretreated raw CFA at 450 [41], 470 [42], 500 [43], 1066 cm<sup>-1</sup> [44] (Fig. 4a) corresponded to Si/Al-O bending, bending mode of Si-O-Si, Al-O stretching, and asymmetric stretch of Si-O, Al-O respectively. The peaks ranging between 1600 and 4000 cm<sup>-1</sup> were slightly shifted and identified as water molecules, O-H bonds. Fig. 4b represents the spectrum range of 1600-2800 cm<sup>-1</sup> with bands observed at

Table 2				
Si/Al and BET results	of the raw	CFA, and	the zeolite	(AlPO <sub>4</sub> -5).

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)
CFA	3.18	-	-	- 20	-	7.81	4.76	0.006
AlPO4-5	2.11	1:1.5	500		120	221.98	20.26	0.143



Fig. 2. Spectra of a) N<sub>2</sub> adsorption-desorption isotherm (b) BJH pore size distribution of the zeolite AlPO<sub>4</sub>-5.



Fig. 3. SEM micrographs of raw CFA (a-d), (e-f) Zeolite AlPO<sub>4</sub>-5.



Fig. 4. FT-IR spectrum of raw CFA, AlPO<sub>4</sub>-5 zeolite.

1643, 2358 cm<sup>-1</sup> [45] were reported to be bending vibrational frequency of adsorbed H<sub>2</sub>O molecules, and stretching vibration of the OH group. Fig. 4c shows the spectrum ranging between 2800 and 4000 cm<sup>-1</sup> that were the resultant of the –(OH) stretching bonds, bending H-O-H vibrations and loss of Ca(OH)<sub>2</sub>, respectively [46]. Similarly, the FTIR spectrum of the AlPO<sub>4</sub>-5 zeolite framework have reported significant bending and stretching vibrations at 431 [42], 440 [47], 465 [48], 555 [49], 965 [50], 1644 [51], 2851, 2921 [52], 3704 [43], 3750, and 3800 cm<sup>-1</sup> [51] respectively. These peaks represents the Si–O deformation, Si–O bending, bending vibration of T–O (T = Si, Al), the initiation of ring zeolite crystallization, and asymmetric stretching of Si–O–H, and Si–O–Ti bonds.

# 3.6. Effect of pH

The extent of the speciation, electrostatic interactions [53], and the degree of ionization [54] among the adsorbent and adsorbate is mainly governed by the pH of the solution. Further, pH can either

enhance or diminish the adsorption potential by changing the ionization state of the adsorbent molecule, and hence pH is regarded as master variable in the adsorption phenomenon. Therefore, the effect of the solution pH was studied for the adsorption of R 6G, and Cr (VI) in the range of (2-10) under optimal conditions. The pH of the solution is well maintained adding acidic (0.1 N HCl), and basic (0.1 N NaOH) medium in an appropriate proportions. Once the solution pH was stabilized, two screw cap centrifuge tubes containing 30 mL of pH solution was added with 0.05 g of adsorbent (AlPO<sub>4</sub>-5) in case of R 6G, 0.1 g for Cr (VI), respectively. The centrifuge tubes were placed in a temperature controlled orbital sieve shaker maintained at 303 K for a period of 120 min (R 6G), and 180 min (Cr (VI)). Fig. 5a demonstrates the effect of solution pH on the uptake of R 6G dye and Cr (VI). It is seen from the figure that the maximum removal efficiency (82.29 mg/g) of the R 6G dye was reported at neutral pH condition (pH = 7). However, maximum Cr (VI) uptake (55.36 mg/g) was reported in the acidic zone, i.e., pH = 2. Another important observation is, during R 6G adsorption the uptake phenomenon is gradually increased in the acidic zone, i.e., (pH < 7), which was ascribed to the augmented protonation and neutralization of adsorbent, promoting diffusion, opposing surface charges [55]. A similar trend was reported for Cr (VI) adsorption at acidic zone (pH < 2), ad decreased beyond pH = 2. Thus, optimal pH = 7 is highly suitable in separating R 6G dye stuff, and pH = 2 suits the Cr (VI) adsorption.

# 3.7. Point of zero charge $(pH_{pzc})$

Point of zero charge or isoelectric point analysis clearly interpreted the influence of pH during the adsorption of R 6G and the Cr (VI). The process of point of zero charge was well established and begins by considering 30 mL of the 0.1 N NaCl solution of initial (pH<sub>i</sub>), and adjusting the pH ranging between (2–10) using 0.1 N HCl, and 0.1 N NaOH. 0.05 g of the adsorbent was added to the stabilized 0.1 N NaCl solution, agitated at a constant speed of 200 rpm for 12 h at room temperature 303 K. Then the final pH (pH<sub>f</sub>) of the solution was measured and the difference of (pH<sub>i</sub>-pH<sub>f</sub>) was plotted against pH<sub>i</sub> resulting point of zero charge (pH<sub>pzc</sub>). From Fig. 5b,  $pH_{pzc}$  value is reported to be 7.6, which was greater than pH = 7for R 6G and pH = 2 for Cr (VI) obtained from the pH studies. For  $pH > pH_{nzc}$ , the adsorbent surface possesses negative charges and attracted the cations, whereas in the present study  $pH < pH_{pres}$ means the adsorbent surface is positively charged and had a great affinity towards the anions. In summary, the present study of Cr (VI) adsorption followed the condition pH < pH<sub>pzc</sub>, favoring the adsorption of negatively charged ions promoting electrostatic interactions [56].

#### 3.8. Adsorption reaction mechanism

The adsorption mechanism is a main challenge encountered in any adsorption studies, upon which the surface adjustments and the enhanced of the adsorbent materials were made. To understand the adsorption mechanism, one should have clear understanding on two basic aspects namely; surface of the adsorbent and their respective properties. The selected cationic dyestuff R 6G, and the metal trace Cr (VI) possess amine groups, and the adsorbent AlPO<sub>4</sub>-5 contains Si and Al as its major composition. Thus, the possible adsorption mechanism of the R 6G dye onto the adsorbent surface is mainly due to the electrostatic interactions, and the hydrogen bonding respectively shown in Fig. 6. Nevertheless, the adsorption tendency was only by means of electrostatic interactions with respect to Cr (VI) Fig. 6. It is known that the electrostatic interactions are mainly due to the prevalence of strong covalent bonding, chemisorptive tendency of reaction, existence of Si-OH groups in the adsorbent, and the confirmed existence of the deprotonated silanol (Si-O<sup>-</sup>) probing electrostatic interactions with cationic molecules [56]. Further, augmented uptake of cationic R 6G dyestuff in neutral pH and the Cr (VI) ions under acidic condition onto the anionic adsorbent AlPO<sub>4</sub>-5 surface confirmed the electrostatic interactions [57]. Moreover, the hydrogen bonding of R 6G is the resultant of dominant interactions among the silanol and the amine groups of the adsorbent and adsorbate molecules [58]. In summary, the adsorption mechanism was driven by two key aspects namely pH and the silanol groups existence.

# 3.9. Effect of adsorbent dosage

Fig. 7a represents the effect of AlPO<sub>4</sub>-5 dosage on the adsorption capacity of R 6G, and Cr (VI). The values of the adsorption capacity have been plotted against AlPO<sub>4</sub>-5 dosage at the typical chosen experimental conditions of  $C_0 = 300 \text{ mg/L}$ , temperature = 303 K, contact time = 120 min (R 6G), 180 min (Cr (VI)), and pH = 7 (R 6G), 2 (Cr (VI)). It can be noticeably realized that the removal efficiency decreased significantly from 77.23 to 19.02 mg/g for R 6G. On the other hand, the removal efficiency of Cr (VI) reported increasing trend from 51.27 mg/g (0.05 g) to 52.15 mg/g (0.1 g) and declined thereafter. The increasing phenomenon with respect to the Cr (VI) separation is due to the abundance of the vacant exchangeable sites on the adsorbent surface, and the decreasing pattern is due to the saturated sites on adsorbent surface [59]. Moreover, the decreasing efficiency is also resultant of lowering concentration gradient of adsorbent and solution at a fixed concentration. Thus, the AlPO<sub>4</sub>-5 adsorbent dosage was fixed to be



Fig. 5. (a) Effect of pH on the adsorption of the R 6G onto zeolite AlPO<sub>4</sub>-5, (b) Influence of point of zero charge (pH<sub>pzc</sub>).



Fig. 6. Adsorption mechanism of adsorption of R 6G, Cr (VI) onto zeolite AlPO<sub>4</sub>-5.



Fig. 7. Influence of various parameters on the uptake of R 6G, and Cr (VI) onto zeolite AIPO<sub>4</sub>-5, (a) Effect of dosage, (b) Effect of the agitation speed, (c) Effect of time.

0.05 g/30 mL for the adsorption of R 6G, and 0.1 g/30 mL for the Cr (VI) respectively throughout the experimentation.

# 3.10. Effect of agitation speed

The interactions of adsorbate and adsorbent is demarcated by the agitation pace of the adsorption reaction. Moreover, the formation of external boundary layers in the bulk solution via solute distribution, thereby enhancing the mass transfer coefficient [60] is majorly attributed to the agitation speed [61]. Hence, the influence of agitation speed (100-500 rpm) on the adsorption of R 6G and Cr (VI) onto the zeolite AlPO<sub>4</sub>-5 is studied and presented in Fig. 7b. From the figure, it can be seen that the optimal agitation speed for the efficient adsorption of R 6G increased with increased speed toll 200 rpm (83.14 mg/g). This is due to the fact that increased turbulence, the boundary layer thickness around the sorbent molecule is decreased, thus increasing external film diffusion rate and the uptake rate [62]. Contrarily, with the increasing agitation speed, the adsorption phenomenon was decreasing in case of Cr (VI), and also lower agitation speeds favors higher adsorption, i.e., 58.3 mg/g at 100 rpm. Beyond the optimal speed, there observed a declining pattern of the adsorption tendency for both the R 6G and Cr (VI). This is due to the dominant centrifugal force on the solutes and the solvent mixture reducing the binding capability of adsorbate (R 6G, Cr (VI)) on the adsorbent surface (AlPO<sub>4</sub>-5) [63]. Thus, the optimal agitation speed is fixed to be 200 rpm for R 6G adsorption, and 100 rpm for the Cr (VI) separation from the aqueous stream and the same conditions were used in the entire study.

#### 3.11. Effect of contact time

With regards to the designing batch mode adsorption systems, another vital aspect to be assessed is the contact time. In the present study, the contact time is varied between 0 and 300 min in order to evaluate the adsorption capacity of the AlPO<sub>4</sub>-5 zeolite towards the R 6G dye and the Cr (VI) metal (Fig. 7c). From the figure, the optimal adsorption capacity of the zeolite for the R 6G dye molecule was 120 min, and for Cr (VI) metal ions it was 180 min. Further, the pace of the adsorption was classified into three stages as rapid (0–60 min, R 6G dye; 0–40 min, Cr (VI), slow or linear (60–120 min; R 6G; 40–180 min), and attainment of equilibrium (180–300 min, R 6G; 180–300 min, Cr (VI)). The brisk adsorption during the initial time span was due to the vacant sites on the adsorbent surface, thus the adherence of the adsorbates were higher. Increasing the intact time, the less availability of vacant sites [64], and

multi layered lumping of adsorbates onto adsorbents, an indication of primary saturation resulting slow or linear adsorption [65]. Finally, attainment of the equilibrium, i.e., unavailability of binding sites forces the new entrants (R 6G, Cr (VI)) to flush away without binding to surface, shown as a flat line. Thus, the optimal contact time of adsorption of R 6G dyestuff, and Cr (VI) metal onto AlPO<sub>4</sub>-5 was fixed as 120 min and 180 min respectively, and the same conditions were maintained throughout the study.

#### 3.12. Isotherm studies

To design the better adsorption system, it is necessary to have the knowledge of the surface properties of the adsorbent and the adsorption behavior. Further, the equilibrium relationship among the adsorbent and the bulk liquids is established only through the adsorption isotherms. In the present study, the batch adsorption reactions of R 6G, Cr (VI) onto AlPO<sub>4</sub>-5 were evaluated using two parameter isotherm models namely Langmuir, Freundlich respectively Fig. 8 (a,b). The respective Langmuir and Freundlich isotherm model equations are presented below as Eqs. (3)–(4) and, the selection of these models is justified by the correlation coefficient ( $r^2$ ) values.

Langmuir isotherm model : 
$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$
 (3)

Freundlich isotherm model : 
$$q_e = K_f C_e^{1/n}$$
 (4)

From the equations  $q_e (mg/g)$ ,  $q_m (mg/g)$  were the equilibrium and the maximum adsorption capacities, and  $C_e (mg/L)$  is the equilibrium final concentration. The constants  $K_L$  (L/mg),  $K_f$  (L/mg) relates to the Langmuir and Freundlich energy of adsorption, and n is adsorption intensity as a function of heterogeneity.

#### 3.12.1. Langmuir isotherm model

As known that the Langmuir isotherm models deals with the monolayer adsorption phenomenon also known as saturated monolayer capacity. This isotherm helps in identifying the determinate number of identical binding sites for the adsorbate on to surface of adsorbent [66]. In addition, all the vacant sites are expected to be equivalent with a homogeneous adsorbent surface, i.e., each vacant site is occupied by one adsorbate molecule. Moreover, the adsorbate energies were assumed to remain constant of the surface. Fig. 8 shows the adsorption Langmuir isotherm plot of R 6G, and Cr (VI) adsorption onto AlPO<sub>4</sub>-5. From Table 3, the correlation values shows a higher degree of linearity, i.e, 0.9987 (R 6G), and 0.991 (Cr (VI)) respectively. Moreover, the applicability



Equilibrium modeling of data for the removal of R 6G, and Cr (VI) onto AlPO<sub>4</sub>-5.

Isotherm	Parameters	R 6G	Cr (VI)
Langmuir	$q_m (mg/g)$ $K_t (L/mg)$	208.61 0.0078	97.32 0.0166
Freundlich	$r^2$	0.998	0.991
	$K_f(mg/g)$	12.35	13.87
	n	2.37	3.26
	$r^2$	0.919	0.924

of the model was justified by the excellent parity of the experimental and the calculated values with q<sub>m</sub> reported to be 208.61 mg/g (R 6G), and 97.32 mg/g (Cr (VI)). Furthermore, the fitness factor (K<sub>L</sub>) determines the feasibility of the adsorption phenomenon, i.e., K<sub>L</sub> > 1 (unfavorable), K<sub>L</sub> = 1 (linear),  $0 \le K_L \le 1$  (favorable), and K<sub>L</sub> = 0 (irreversible). The K<sub>L</sub> values of R 6G, Cr (VI) adsorption using AlPO<sub>4</sub>-5 is 0.0078, 0.0166 from the Langmuir isotherm model confirms the adsorption reaction is highly favorable, monolayer and possibly chemisorptive in their surface interactions.

# 3.12.2. Freundlich isotherm model

It is an important two-parameter isotherm model that defines the experiential relation among the solid/liquid equilibrium with heterogeneous multilayer binding of ions/molecules on the surface with distinct energy distributions [67]. Freundlich model is highly reliable by relating the exponential adsorbent surface sites to the adsorption capacity, and equilibrium adsorbate concentration. The key parameters of this model K<sub>f</sub> (Freundlich adsorption capacity), and "n" defines the measure of feasibility, and the intensity of adsorption. This means n > 1 favors adsorption, n < 1 unsuitable, n = 1 linear tendency. Fig. 8 presents the Freundlich isotherm model of R 6G, Cr (VI) onto the AlPO<sub>4</sub>-5 surface that shows deviations from the experimental observations. Table 3 confirms the deviations through regression correlation r<sup>2</sup> values of 0.9194 (R 6G), and 0.9275 (Cr (VI)). Also, the value of  $K_{\rm f}$  reported to be 12.35 mg/g (R 6G), and 13.87 mg/g (Cr (VI)), respectively. The value of "n" was in case of R 6G adsorption was 2.37, and for Cr (VI) it was 3.26 suggests the positive trend towards the adsorption. However, the values of regression is better for Langmuir compared to the Freundlich suggesting the mode of adsorption was inclined to monolayer, and Langmuir isotherm model is considered as better fit. Further, Table 4 showcases the comparison pertaining to the adsorption of R 6G and Cr (VI) via different adsorbent materials.



Fig. 8. Non-linear adsorption isotherms analysis of R 6G, and Cr (VI) onto zeolite AIPO<sub>4</sub>-5.

#### Table 4

Summary of the literature on the separation of R 6G, and Cr (VI) by various adsorbents.

Adsorbent	рН	Adsorption capacity (mg/g)	Reference
R 6G			
Fe <sub>3</sub> O <sub>4</sub> -composited biochar	7	9.42	[75]
Graphite SERS substrate	2	212.72	[76]
Ceria nanoparticles (CeO <sub>2</sub> -NPs)	9.1	87.25	[77]
Polyaniline/ZnS nanocomposite	8	80.62	[78]
Ti, AI, Al mixed nanoparticles	9	142.9	[79]
Zeolite ZSM-22/TON	6	195.3	[19]
Zeolite AlPO <sub>4</sub> -5	7	208.61	This Work
Cr (VI)			
Natural clintophile zeolite	2	5.37	[80]
Na-P from CFA	2	31.13	[81]
Zeolite X from CFA	13	1.51	[82]
Zeolite A from CFA	6	42.67	[83]
Metakaoline based geopolymer	5	95.3	[84]
Zeolite AlPO <sub>4</sub> -5	2	97.32	This Work

#### 3.13. Dye adsorption kinetic studies

The solid-liquid equilibrium does not provide the detailed information related to the reaction pathway, reaction rate, whereas, adsorption kinetics clearly describe solute adsorption reaction pathways onto solid surface. Further, the movement of the solute molecules across the boundary to attain equilibrium is greatly relied upon the physico-chemical properties of the solid adsorbent. Moreover, the efficacy of this solute transfer requires understanding of exchange rate between the bulk liquid and solid adsorbent [68]. Thus, kinetic models help to evaluate the retention time/rate of adsorption process and the potential rate limiting step of the adsorption process. Further, evaluating kinetic models requires several adsorption control mechanisms, such as chemical reactions, diffusion control or mass transfer coefficients [69]. Besides, these kinetic models help to identify the type of adsorption (physiosorption or chemisorption), choose the optimal parameters (solute adsorption, residence period of solution interface etc.) during the adsorption phenomenon [70]. Thus, in the present study pseudo-first-order, pseudo-second-order kinetic models were adopted to test the adsorption tendency of the R 6G dye, Cr (VI) metal onto the AlPO<sub>4</sub>-5 adsorbent surface [71]. The temperature dependent adsorption studies were evaluated from the following non-liner kinetic model equations (Eqs. (5)-(6)) listed below

$$Pseudo-first-order\ kinetics:\ q_t = q_{e1}(1-exp(-k_1t)) \eqno(5)$$

$$Pseudo-second-order \ kinetics: \ q_t = \frac{q_{e2}^2 k_2 t}{1+q_{e2} k_2 t} \eqno(6)$$

where  $q_e$  (mg/g), and  $q_t$  (mg/g) are the quantities of the R 6G dye, and Cr (VI) adsorbed onto AlPO<sub>4</sub>-5,  $k_1$ ,  $k_2$  are the rate constants of pseudo-first-order, pseudo-second-order kinetic models respectively. Table 5 provides the detailed summary and comparison of experimental, and the calculated (pseudo-first and pseudosecond order kinetic model data) adsorption data of R 6G and Cr (VI) onto AlPO<sub>4</sub>-5. Fig. 9 (a–c) portrays the comparative kinetic analysis of R 6G uptake on AlPO<sub>4</sub>-5 surface, and 9 (d–f) showcase the Cr (VI) affinity towards the adsorbent. The adsorption of R 6G Fig. 9(a– c), and Cr (VI) Fig. 9 (d–f) onto AlPO<sub>4</sub>-5 increased with the increase in temperature, and the kinetic values are best fitted to pseudosecond order compared to pseudo-first order confirming the rate limiting step is chemisorption [25]. This phenomenon of chemisorption is mainly due to the sharing of electrons between the adsorbate and adsorbent, thereby creating strong covalent or ionic bonding.

#### 3.14. Influence of solution reaction temperature

Solution reaction temperature is another crucial parameter in assessing the adsorption potential of the adsorbent. Thus, a series of experiments were performed analyzing the influence of temperature on the sorption process of the R 6G dyestuff, and the Cr (VI) metal onto the freshly prepared AlPO<sub>4</sub>-5 zeolite. All the other critical optimal parameters of R 6G dye solution, and Cr (VI) metal solution (pH, contact time, agitation speed, adsorbent dosage, and initial dye concentration) were maintained optimal, and the temperature was varied between 303 and 323 K, respectively (as shown in Fig. 10a). From the figure it was evident that the rising temperature increases the adsorption capability of both the R 6G, and Cr (VI). This was ascribed to the intense mobility of the dye molecules as well as the metal ions towards the active temperature adsorption sites [72]. Also, the enlargement of pore size at higher temperatures enhanced the surface activation of the adsorbent and affinity of dye molecules and metal ions towards AlPO<sub>4</sub>-5. Further, the insights of the thermodynamic parameters, such as Gibbs free energy  $\Delta G^{\circ}$ , enthalpy  $\Delta H^{\circ}$ , and entropy  $\Delta S^{\circ}$ , clearly elucidates the internal energy shifts, and the swiftness of the adsorption reaction. The aforementioned thermodynamic aspects were evaluated from a set of well-established equations (Eqs. (7)-(10)) as follows:

$$\Delta G^{o} = -RTlnK_{c} \tag{7}$$

$$K_{c} = \frac{C_{Ae}}{C_{e}}$$
(8)

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \tag{9}$$

$$ln K_c = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{10}$$

where R is the universal gas constant (J/mol K), T is the absolute temperature (K), K<sub>c</sub> is the distribution constant,  $\Delta$ H<sup>o</sup> is the change in enthalpy,  $\Delta$ S<sup>o</sup> is the change in entropy (shown in Fig. 10b). A detailed summary of the experimental findings on the thermodynamic aspects were provided in Table 6. The positive value of  $\Delta$ H<sup>o</sup> in case of R 6G, Cr (VI) implies endothermic nature of the adsorption reaction, during which the adsorbate species had to displace more

#### Table 5

Kinetic modeling of data for the separation of R 6G, and Cr (VI) onto AlPO<sub>4</sub>-5.

Adsorbate	Temp (K)	$q_{e, exp} (mg/g)$	Pseudo-first-order model		Pseudo-second-or	der model		
			$q_{e1, cal} (mg/g)$	k1 (1/min)	r <sup>2</sup>	$q_{e2, cal} (mg/g)$	k <sub>2</sub> (g/mg min)	r <sup>2</sup>
R 6G	303	84.18	83.85	0.028	0.966	84.69	0.0650	0.996
	313	92.55	91.21	0.035	0.978	91.89	0.0045	0.998
	323	98.98	96.70	0.049	0.969	98.62	0.0044	0.994
	303	57.01	60.29	0.014	0.964	58.16	0.021	0.992
Cr (VI)	313	66.25	67.30	0.016	0.975	66.10	0.002	0.997
	323	73.58	72.38	0.023	0.988	74.01	0.003	0.995



Fig. 9. Non-linear kinetic studies on the sorption of R 6G (a-c), and Cr (VI) (d-f) onto AlPO<sub>4</sub>-5.



Fig. 10. (a) Effect of temperature on the adsorption of R 6G dye, Cr (VI) onto AlPO<sub>4</sub>-5 zeolites, (b) van't Hoff plot for the adsorption of R 6G dye, and Cr (VI) onto the AlPO<sub>4</sub>-5 zeolite.

#### Table 6

Thermodynamic assessment on adsorption of R 6G, and Cr (VI) onto AlPO<sub>4</sub>-5.

Adsorbate	T (K)	$\Delta G^{o} (kJ/mol)$	ΔH <sup>o</sup> (kJ/mol)	$\Delta S^{o}$ (J/mol K)
R 6G	303	-0.3717	4.3	15.4
	313	-0.5408		
	323	-0.6817		
Cr (VI)	303	-1.6103	2.4	13.3
	313	-1.7816		
	323	-1.8681		

than one water molecule for their adsorption and this resulted in endothermicity of the adsorption phenomenon. Besides,  $\Delta S^{\circ}$  is a measure of width of the "saddle point of energy" over which the reactant molecules must pass as activated complexes. The positive value of  $\Delta S^{\circ}$  for both R 6G, and Cr (VI) reflects the increased randomness at the solid/solution interface with structural changes in the adsorbate and adsorbent. In addition, the positive values of  $\Delta S^{\circ}$  indicates the affinity of the adsorbent towards the adsorbate species, and also corresponds to the increasing degrees of freedom of the adsorbed species. Further, Gibb's free energy  $\Delta G^{\circ}$  is an indication of spontaneity of a chemical reaction and therefore is an important criterion. From the Table 6 it can be seen the values of  $\Delta G^{\circ}$  tends to decrease for both the R 6G dye, Cr (VI) metal, with the increasing temperature indicating the adsorption process is more favorable at higher temperatures and spontaneous. The reason ascribed is due to the mobility of the adsorbate ions/molecules



Fig. 11. Desorption of adsorbent from solutions a) R 6G, and b) Cr (VI) using various eluents.



Fig. 12. Reusability studies of the adsorbent AIPO<sub>4</sub>-5 in case of a) R 6G solution, and b) Cr (VI) solution.

in the solution increase with the rising temperature. Summarizing the facts of the thermodynamic studies, the adsorption phenomenon of the R 6G and Cr (VI) was spontaneous, endothermic in nature with an increased affinity towards the AlPO<sub>4</sub>-5.

#### 3.15. Desorption studies

Desorption studies are of particular importance which allows to monitor the mechanistic aspects of solute transfer. In general, desorption studies were related to intensify the process economy and helped to regenerate the adsorbent material. Prior to the desorption, adsorption tests were carried out considering 30 mL of 300 ppm R 6G solution, and 30 mL of 300 ppm Cr (VI) solution separately, adding 0.05 g (R 6G), 0.1 g Cr (VI) adsorbent, while maintaining the other optimal conditions. After the adsorption, R 6G, and Cr (VI) solutions were dried in a furnace at 333 K for 24 h and the recovered sediment of R 6G, and Cr (VI) which are ready for the desorption experiments. Different eluents for the recovery of adsorbent from R 6G, and Cr (VI) sediments were NaOH, HCl, H<sub>2</sub>SO<sub>4</sub>, and ethanol; NaCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, NH<sub>4</sub>OH, DI water, and NaNO<sub>2</sub>. The choice of the eluents is to check the suitability and high recovery and of wide range comprising alkaline, acid, organic and inorganic solvents respectively. Fig. 11 (a,b) presents a clear outline of the desorption capacity of eluents to recover adsorbent AlPO<sub>4</sub>-5 from R 6G, and Cr (VI) sediments. The highest desorption from the R 6G, and Cr (VI) sediments were possible through an alkaline eluent NaOH (R 6G-89.4%, Cr (VI)- 91%). The reason ascribed for higher desorption towards the alkaline medium lost negative ions gained by the adsorbent surface thereby generating repulsive forces and detaching the R 6G dye molecule, and Cr (VI) ions [73]. Thus, NaOH had been chosen the best eluting agent to the maximum desorption of adsorbent both from the R 6G , Cr (VI) adsorption sediments.

#### 3.16. Regeneration studies

From the economic, environment, and sustainable standpoints, reusability of adsorbent holds the key deciding the practical utility, and formulating commercial scale applications [74]. To evaluate the efficacy of the adsorbent (AlPO<sub>4</sub>-5) towards the sorption of R 6G, and Cr (VI), five adsorption-desorption were performed. The results are shown in Fig. 12 (a,b). To start with, the adsorption experiments were performed mixing 0.05 g of adsorbent in 30 mL of 300 ppm R 6G dye solution, maintained at pH = 7, under ambient temperature conditions (303 K) for an optimal time period of 120 min. In the case of the Cr (VI) adsorption 0.1 g of the adsorbent was added to 30 mL of 300 ppm Cr (VI) dye solution maintained at pH = 2, in the room temperature 303 K, for a residence period of 180 min. From Fig. 12a, it is clearly seen that the desorption efficiency of the adsorbent after three successive cycles was decreased from 85.67% to 55.64% in the case of R 6G dye. Whereas, the desorption efficiency rapidly declined from 61.24% to 17.55% in the case of the Cr (VI) solution after two successive cycles Fig. 12b. During each cycle, the eluted sorbent was repeatedly washed with deionized water to scrub off the residual desorbing solution and made available for the next cycle. Thus, from

this regeneration studies it is clear that, the reusability of the zeolite AlPO<sub>4</sub>-5 was promising towards the dye separation and found effective even after three cycles, however, zeolite AlPO<sub>4</sub>-5 is effective up to two cycles in case of Cr (VI) metal solution.

#### 4. Conclusions

The motive of the current study was to synthesize a mesoporous molecular sieve framework (AlPO<sub>4</sub>-5) from CFA, and test the utility as adsorbing medium of R 6G dye, and Cr (VI) from liguid phase. The research once again proved the importance of alkali fusion followed hydrothermal analogy vastly improved the surface area from 6.27 m<sup>2</sup>/g (raw CFA) to 219.31 m<sup>2</sup>/g (AlPO<sub>4</sub>-5) near to 40 folds. Further, the uptake of R 6G and Cr (VI) strategies confirmed the monolayer adsorption with a best fit to Langmuir isotherm reported maximum uptake of 208.61 mg/g (R 6G) and 97.32 mg/ g (Cr (VI)). Further, the pseudo-second order kinetics fits well, compared to the pseudo-first order, and the thermodynamic analysis revealed the spontaneity, and endothermicity of the adsorption reaction. Finally, desorption capacity was on topnotch with basic medium eluent (NaOH) for both R 6G and Cr (VI) sorption phenomenon. Lastly, the as-synthesized AlPO<sub>4</sub>-5 zeolite showed promising performance in reusability studies up to three successive cycles (R 6G) and relatively low, i.e., two cycles Cr (VI). Summarizing the research, there has been a success in handling the toxic trio of CFA, R 6G, Cr (VI) contaminations via converting CFA to CFAZ's (AlPO<sub>4</sub>-5) adsorbent. Thus, addition of AlPO<sub>4</sub>-5 to the existing zeolite database was one objective but the synthesizing from CFA without structural directing agent was another advantage, and the positive boost up in utilizing CFAs, effectively.

# **CRediT** authorship contribution statement

Anjani R.K. Gollakota: Conceptualization, Methodology, Writing - original draft. Venkata Subbaiah Munagapati: Conceptualization, Data curation. Krushna Prasad Shadangi: Editing, validation. Guda Mallikarjuna Reddy: Editing. Jet-Chau Wen: Validation. Chi-Min Shu: Supervision, Conceptualization, Resources, Validation.

# **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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