

Original Article

Synthesis of novel ZSM-22 zeolite from Taiwanese coal fly ash for the selective separation of Rhodamine 6G



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ABSTRACT

The present study reveals the potential of coal fly ash (CFA) as the environmental pollutant adsorbent. The conventional approach of alkali fusion followed by hydrothermal treatment of Taiwan based coal fly ash resulted in new and novel zeolite material ZSM-22. The composition, morphology, chemical structure, and the surface properties of as-prepared zeolite were investigated using BET, SEM, FT-IR, XRD, and XRF. The specific surface area (S_{SA}) of the zeolite is enhanced from 1.28 m²/g to 30.21 m²/g with a drop in Si/Al ratio of 3.1 to 2.4 suggesting the improvement of crystallinity. Further, the application of zeolite on the adsorption of the cationic dye Rhodamine 6G (R 6G) from aqueous solution in a batch process was investigated. Besides, the effect of parameters such as the effect of time, temperature, pH, dosage, agitation speed, kinetics, and isotherms on the removal of dyes was studied. The results indicate that adsorption of dye is more significant at pH = 6indicating the zeolite surface is positively charged. The proficient sorption efficacy of R 6G onto ZSM-22 followed pseudo-second-order kinetic model and fits well with the Langmuir adsorption isotherm with maximum specific removal of 195.3 mg/g. Moreover, the possible adsorption mechanism for the selective separation of dye using CFA is mainly due to the electrostatic interactions and the hydrogen bonding. Finally, the key takeaways of the present research are that zeolite ZSM-22 is a prospective candidate as an adsorbent for the separation of dye molecules.

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1. Introduction

To date, rapid urbanization has been associated with the industrial revolution and the synchronized generation of toxic and hazardous pollutants. From the various toxic releases, the dye industry an integral part of daily life contributes a higher portion of pollution to the water bodies. More than 100,000 commercial dyes are already in use generating 700,000 tons, upon which 15% being discharged into the environment as waste [1]. Further, organic dyes are more frequent in manufacturing papers, plastics, cosmetics, and so on [2]. Thus, organic dyes are more prevalent in the effluents from these industries, which have become detrimental effects on the ecological balance and the aquatic environments. Besides, waste streams containing dyes which are recalcitrant molecules, impervious to anaerobic digestion, do not alter with oxidizing agents, and hence complex treatment procedures [3]. One among them is R 6G is a fresh peach of synthetic monocationic xanthene dye primarily used as a colorant, in the manufacture of textiles [4]. The colored effluents in water sources not only create aesthetic problems especially rhodamine dyes could lead to subcutaneous tissue borne sarcoma, which is highly carcinogenic, and neurotoxic [5]. This prompted exhaustive research on the best possible (in terms of cost and the eco-friendly natured) pathways for trace detection, faster removal, and significant degradation of organic dyes. Among the different strategies such as electrochemical separation, adsorption, coagulation, and membrane filtration, adsorption has been attractive and favorable due to the cost-effective mechanism. Several adsorbents used to remove R 6G from aqueous solution include activated carbon [6], shells of palm [7], and almond [8], graphene derived materials [9], metal-organic frameworks [10], clay minerals [11], magnetic silica nanoparticles [12], but no signs of mesoporous materials/zeolites derived from the CFA.

In recent times, mesoporous materials are the new addition to the field of adsorption study. Since the advent of mesoporous materials, they proved the distinctiveness and wide stretch of applications including drug delivery, ecology, nanotechnology, sensing, adsorption, and separation etc. [3]. Several mesoporous materials are already available and utilized to the full extinct in the field of adsorption. However, the zeolites synthesized from the CFA possess unique features and show significant adsorption tendencies in treating the effluent streams. The uniqueness arises, as the CFA contains silica (50%-70%) and alumina (16%-30%) either in the crystalline (quartz, mullite, and haematite), or amorphous phase (glass phase), a structure resembling honeycomb possessing higher porosity, and surface area [13]. These inimitable physio-chemical features indent CFA a close semblance to the natural volcanic material and front-line substitute/precursor of zeolite particles [14]. Secondly, the ascending energy demands invoked excessive utilization of coal, thereby releasing massive volumes of CFA (750 Mt annually) [15] which is just land disposed or left untreated generates airborne particulates both contaminating soils and water bodies. To date, CFA is limited to building materials, while some conventional applications include its utilization as filler material for reclamation of low lying land, filling of mines, road construction

and ceramic industry etc. [16]. Hence, transmuting CFA into zeolites could be an attractive option mitigating the growing ecological concerns, and reducing the stress to the coal-based energy industry. The traditional approach of zeolite preparation from CFA is hydrothermal synthesis involving the alkaline agents. The variable parameters such as the solid to liquid mass ratio, type of CFA, reaction temperature, pressure, residence time, activation period, alkaline agents hold the key in yielding different zeolite materials and the associated Physico-chemical properties. Many zeolites were synthesized and put into conventional product base since the decades; however, the exploration of few zeolites such as nanorod zeolite ZSM-22 from CFA is highly underrated and explored possibility till date. Further, the synthesis of ZSM-22 is mainly derived either in the presence or absence of the structuredirecting agents [17], but no attempt has been made to synthesize from the CFA. Mostly, the ZSM-22 is used as a catalyst during the isomerization reaction. On the other hand, very few attempts and explorations were made on the Taiwanese based CFA in synthesizing conventional commercial zeolites.

Hence, the present research is primarily focused on the synthesis of ZSM-22 zeolite from Taiwanese CFA and proposing the use as an adsorbing medium to the toxic cationic R 6G. To the best of our knowledge, the two key unique aspects of the research were to enlighten the potentiality of Taiwanese CFA in preparing ZSM-22 zeolite and introducing the zeolite to the adsorption deviating from conventional catalysis. The proposed research approach has not been compiled elsewhere and has a great scope of future research.

2. Materials and experimental details

The CFA used for zeolite synthesis in the study was sourced from the outlet of the electrostatic precipitator of Taiwan Power Company in the city of Taichung, Taiwan. The elemental and the mineralogical composition of the CFA are reported in Table 1. The chemicals sodium hydroxide, sodium chloride, hydrochloric acid, sodium aluminate, cationic dye R 6G, and the other reagents are purchased from Sigma–Aldrich Taiwan. All the reagents and chemicals are of analytical grade with no further purification required. The water used is deionized throughout the experimental study. UV–vis spectroscopy was performed using a PerkinElmer Lambda 850 spectrophotometer for the adsorption studies of R 6G onto CFA based zeolite (ZSM-22) at 530 nm.

2.1. Synthesis of zeolite

Initially, the raw CFA is sieved with a mesh size of 75 μ m, followed by the calcination at 800 °C for 4 h in an electric furnace to reduce the unburnt traces of the carbon left in the raw feedstock. A repetitive washing removed the impurities of the CFA with deionized water and drying at 70 °C for 24 h, and the dried CFA is now ready for the zeolite synthesis. To prepare the zeolite, the pretreated CFA combined with NaOH (mass ratio of 1:2) and fused at 500 °C for 1 h, otherwise known as dissolution step. The choice of the parameters is after several combinations such as maintaining a constant temperature of 120 °C, Si:NaOH ratio (1:2), and varying fusion

Table 1 – Chemical composition of coal fly ash and zeolite ZSM–22 (wt.% dry basis).					
Major oxides	Raw CFA	Standard	Zeolite ZSM – 22/TON		
SiO ₂	63.45	_	58.86		
Al_2O_3	20.44	-	26.22		
Fe ₂ O ₃	4.79	\geq 70 (Class - F)	6.48		
CaO	4.39	\leq 10	4.55		
K ₂ O	1.29	-	0.41		
TiO ₂	1.84	-	1.37		
CuO	0.02	-	0.03		
MgO	0.97	50 Max	0.87		
MnO	0.07	-	0.07		
NiO	0.02	_	0.007		
ZnO	0.02	_	0.03		

temperature (400 °C, 500 °C, and 600 °C). From all these combinations the S_{SA} was calculated to be; 400 °C=24.45 m²/g, 500 °C = 32.1 m²/g, 600 °C = 13.20 m²/g. This confirms that the increase in temperature decreases the surface area of the synthesized zeolite, and hence the optimal temperature of 500 °C has been chosen for the present study.

Further, the alkaline reagent added to the CFA acts as an activator reagent during fusion, and the OH- in alkali agent contributes to the dissolution of Si⁴⁺ and Al³⁺ in CFA particles [18]. Besides, the crucible used for the fusion of CFA and NaOH is Nickel (Ni), and the choice of this universally accepted crucible is to avoid any secondary chemical reactions and mainly due to their higher resistance to dilute alkalis (NaOH). The fused mixture was cooled then to ambient temperature, milled, transferred to a beaker containing 100 mL of water, and 20% sodium aluminate. The reason ascribed to the addition of sodium aluminate is to increase the concentration in the liquid phase and to fine-tune the Si/Al ratio [19] so as to obtain pure phase zeolites. The slurry was agitated mechanically using a magnetic stirrer at 400 rpm for 24 h, under ambient conditions to form a homogenized aluminosilicate gel. Finally, the mixture was then transferred to the 100 mL PTFE bottles which were hermetically sealed so as to ensure the homogeneity, and avoid inference of external factors, and then crystallized under static temperature conditions 120 °C for 24 h. The solution was then filtered with Whatman filter paper and washed several times with deionized water for a near neutral pH. Finally, the newly formed crystalized gel (ZSM-22) was then aged for 24 h at 150 °C to impart the strength and optimize the morphological features.

3. Results and discussion

3.1. XRF characterization

The chemical composition of the raw CFA and the zeolite ZSM-22 were determined using the X-ray fluorescence spectrometer (Bruker 5i Tracer) and confirms the classification of CFA as class F (See Table 1). From Table 1 it is clear that raw CFA possessing sufficient composition of the SiO₂ and Al₂O₃ favors the synthesis of zeolites. The calculated molar ratio of selected raw CFA (silica (63.45) to alumina (20.44)) is 3.10, which favors the H-type zeolites [20]. The role of molar ratio is

critical in the structural framework of the zeolite that influences the morphology and physico-chemical features of final zeolite. After, the alkali fusion and hydrothermal treatment, the newly formed zeolite have the molar ratio (SiO₂ (58.86), Al₂O₃ (28.22)) of 2.44. The results of XRF especially the lowering of the Si/Al ratio as a result of hydrothermal treatment promote the crystallinity, crystal growth and affected the morphology of the zeolites from CFA.

3.2. Powder X-ray diffraction (XRD)

Crystallographic data of both the raw CFA (red color) and the zeolite (ZSM-22, blue color) were obtained using X-ray Diffractometer (Bruker Advanced-D825A) over a 20 range between 0 and 60° , and the step scan size of 0.01° (See Fig. 1.). From the XRD diffractogram of CFA, the intense peaks at 26.57° [21], 44.49° [22] denotes the major composition of the CFA is quartz (SiO₃), mullite (2Al₂O₃.SiO₃) [23] and less intense peak at around 39.01° was reported as hematite (Fe₂O₃) [24]. The patterns of the X-ray diffractogram is in compliance with XRF, conforming the selected CFA is rich in Si and Al. Upon hydrothermal treatment of CFA resulted in the disappearance of the aforementioned quartz and mullite peaks, and appearance of new high intensity peaks at $2\theta = 24.21^{\circ}$, 32.17° , 33.31° , 35.73° , 42.72° confirms the formation of zeolite ZSM-22 [25]. The disappearance of peaks is mainly due to the alkali agent (NaOH) that converts the quartz and mullite rich phases to soluble silicate and aluminates, also known as crystallinity determination step. Further, the crystallinity level of indexed as ZSM-22 has sheets of 10-rings with indexing cell parameters $a = 13.86 A^{\circ}$, $b = 17.41 A^{\circ}$, and $c = 5.04 A^{\circ}$ [26].

3.3. FTIR analysis

The structural aspects of the CFA and the zeolite (ZSM-22) was monitored by the infrared spectroscopic analysis using FTIR (PerkinElmer Spectrum One) containing DTGBr detector and KBr as split beamer in the range of 400–4000 cm⁻¹. The detailed information on the spectral bands of raw CFA and the zeolite ZSM-22 are shown in Fig. 2. Further, the spectral bands



Fig. 1 – Mineralogy of CFA and ZSM-22 by XRD analysis.

were alienated into Fig. 2a, b, c for a clear vision of peaks at respective frequencies. Based on Fig. 2a, b, c (red), FTIR spectra of CFA samples presents T-O (Si, Al) asymmetric stretching peak at 1055 cm⁻¹, broad peak at 550 cm⁻¹ confirms the CFA is rich in quartz [21]. The second major compound of CFA, mullite is represented by a weak peak at 800 cm⁻¹ [27]. From Fig. 2, it is seen that the intensity of the peaks is higher in the range of 400–600 cm⁻¹, especially the bands at 420 cm⁻¹ (T–O bending vibrations) [27], 493 cm⁻¹ (presence of various aluminosilicates) [28], and 600 cm⁻¹, Cience of various at 1098 cm⁻¹, 1608 cm⁻¹, 1641 cm⁻¹, 2853 cm⁻¹, 2934 cm⁻¹ represents Si–O–Si asymmetric stretching [30], H–O–H bend of water [28], presence of carbon and C–H vibrations [31].

On the other hand, the FTIR spectra of ZSM-22 (Fig. 2a, b, c blue) show the disappearance of intense CFA bands, and lead to new set of peaks conferring the formation of zeolite. It is reported by [32], that the asymmetric stretching modes of zeolites are more prevalent in the range of 950-1250 cm⁻¹. From Fig. 2a, the noticeable shift of CFA peak at 1053 cm^{-1} towards the low frequency zone, confirms the zeolite formation. Besides, the sharp stretch at 440 $\rm cm^{-1}$ and weak bend at 659 cm^{-1} denotes the internal deformation of O-T-O [33], and changing shape of Al–O–H bonds [34]. Further, the bending peak at 966 cm^{-1} signifies the asymmetric bending of Si–O bonds. In addition, the peaks at 1413 cm⁻¹, 1475 cm⁻¹, 2359 cm⁻¹, 2924 cm⁻¹, and 3750 cm⁻¹ attributes to bending vibrations of trapped O-H-O in silica matrix [35], bending vibrations of C–H [36], O–H stretching [37], and symmetric stretching of silanol groups, non-acidic and fairly strong O-H bonds [36]. These peaks denote the formation structural rearrangement of CFA in order to form ZSM-22.

3.4. SEM analysis

The morphological features of CFA and the zeolite ZSM-22 were obtained using Ultra-High-Resolution Thermal Field Emission Scanning Electron Microscope (JEOL, JSM-7610F Plus) SEM analysis (see Fig. 3). From the SEM analysis, it is seen that the CFA particles are spherical, with a glassy smooth surface (Fig. 3a–c). Upon alkali fusion and hydrothermal treatment, some portions of spheres and agglomerates have turned to cubical crystal structures Fig. 3d with relatively smaller particle size in comparison to the raw CFA. While, the remaining

portion of the crystallized intergrowth sample display needle like microstructure (particle size $< 1 \mu m$) (Fig. 3e and f), and similar instance was reported by [38]. The surface morphology is strongly influenced by the alkaline agent NaOH and higher temperatures forcing the dissolution of Si and Al of CFA. The subsequent hydrothermal treatment fastens the nucleation resulting exclusive crystal assembly i.e., needles [39]. Thus, the surface morphology of the crystal structure is dependent on two critical aspects namely, crystallization step and the phase transition step. During the crystallization structural reorganization happens, whereas, the phase transition involves the movement of matter from high free energy to low free energy position inside the crystal structure. The added advantage of being a needle structure is that zeolite can have a fibrous quality similar to asbestos [40]. This means that the structure of zeolite is essentially non-crossing one-dimensional. Further, fibrous zeolites contain at least 8-ring channels, still more preferred at least 10-ring channels. Contrarily, needle-shaped are fragile [41], and shorter life time due to pore blockage due to its structural morphology.

3.5. Textural properties

The textural analysis defines the quality of zeolites, and helps to assess the inherent features such as specific surface area (S_{SA}), pore-volume, and pore-diameter. The conventional N₂adsorption based surface area pore size analyzer (Micrometrics, ASAP 2060) was used in the present study. The detailed information related to the S_{SA} (BET method), pore volume and the diameter of raw CFA and the ZSM-22 zeolite were obtained via built software ASAP 2060 and presented in Table 2. From the table it is seen that the S_{SA} of the zeolite ZSM-22 has increased to a great extent 30.21 m^2/g , with a pore volume of 0.1152 cm³/g in comparison to the raw CFA 1.28 m²/ $\,$ g, and 0.0009 cm³/g. Further, the confined surface area of zeolite ZSM-22 despite hydrothermal treatment is attributed to restricted entrainment of the N2 molecules, and molecular door effect which is quite similar to the Na-A and Linde Type A (LTA) [42]. Further, the adsorption isotherm of zeolite (ZSM-22) has a close resemblance of Type IV (see Fig. 4a) featuring a type H3 hysteresis loop, due to capillary condensation at interparticle mesoporous as established by the International Union of Pure and Applied Chemistry (IUPAC). Moreover, Fig. 4b presents the relation between pore volume and pore



Fig. 2 – FTIR spectrum of coal fly ash and the Zeolite ZSM-22.



Fig. 3 – SEM micrographs of CFA (a,b,c) and ZSM-22 (d,e,f) by SEM.

diameter with a cylindrical pore geometry and a pore volume of $0.1152 \text{ cm}^3/\text{g}$ and similar values were reported by [43].

3.6. Effect of pH

The influence of pH at optimum conditions of 0.05 g adsorbent dosage, 2 h contact time at room temperature (303 K), under variable pH ranging between 2 and 10 by the addition of acid (0.1 N HCl) or alkali solvent (0.1 N NaOH) was studied. The solution pH plays a key role during the adsorption which influences the binding sites of the sorbent molecules, and ionization [44]. From Fig. 5, the adsorption capacity tends to increase up to pH = 6 with maximum uptake of dye of 79 mg/g. The increase in uptake capacity is ascribed to the accessibility of the vacant adsorption sites on the sorbent molecule. Contrastingly, in the alkaline medium i.e., pH > 7, a declining trend of adsorption capacity with the rising pH value was observed. This phenomenon is associated with the excess Na⁺ ions, and are responsible for screening effect decreasing the ionic interaction between cationic dye and anionic zeolite [45]. In summary, the synthesized anionic zeolite ZSM-22 highly favors the acidic pH for the effective adsorption of cationic dye when compared to the alkaline medium.

Table 2 – Si/Al and BET results of the CFA and the zeolite ZSM-22.					
Sample	Si/ Al	BET surface area (m²/g)	SA _{ext} (m²/ g)	V _{micro} (cm³/ g)	
Raw CFA	3.10	1.28	0.029	0.0009	
ZSM - 22	2.24	30.21	23.99	0.1152	

3.7. Point of zero charge

The real effect of pH and its profound influence on adsorption mechanism was explained via isoelectric point of the adsorbate surface. It is known that the pH of the solution is highly influential in the adsorption process, and can alter the surface charge of the adsorbent, ionization extent, and morphology of dye molecule [46]. The existence of multiple oxides of Si and Al in zeolite contributes to the reaction with dyes. Whereas, the acid and alkaline functional groups have no contribution towards the pH [47]. From Fig. 5 it is seen that the zero-point discharge of the CFA was found to be 6.89, signifying the positively charged anionic adsorbent surface that readily accepts the cations and vice versa. As mentioned in the previous sections, the newly formed zeolite ZSM-22 possesses anionic binding sites i.e., H⁺ ions in the acidic medium compete with cationic dye R 6G to interact for optimal adsorption process.

3.8. Adsorption mechanism

In general, the adsorption mechanism comprises of electrostatic interaction, hydrogen bonding, ion exchange, coordination, acid-base interaction, In the present study, the cationic dye R 6G was adsorbed onto the surface of ZSM-22 mainly due to electrostatic interaction, and the hydrogen bonding shown in Fig. 6. These electrostatic interactions are the resultant of strong covalent bonding and more prevalent during the chemisorption process. The occurrence of electrostatic interactions is mainly due to the silanol groups (Si-OH) existence. Moreover, the increase in the dye uptake with pH, suggesting the existence of more Si-O⁻ (deprotonated silanol) probing electrostatic interactions towards the cationic dyes [48]. Further, hydrogen bonding is more



Fig. 4 – Spectra of a) N₂ adsorption-desorption isotherms and b) BJH pore size distribution of synthesized zeolite ZSM-22.



Fig. 5 – Effect of pH on the adsorption of R 6G onto ZSM-22.

prevalent due to the interactions of silanol and amine functional groups of zeolite and dye molecule respectively. Thus pH holds the key in regulating the dissociation of the functional groups on the active sites of adsorbents. For acidic pH i.e., pH < 7, electrostatic interactions are predominant between the cationic adsorbate (R 6G) and anionic adsorbent (ZSM-22), thus augmenting the uptake of dye adsorption process [49]. Hence, in the present study, the adsorption is mainly due to electrostatic interactions and hydrogen bonding.

3.9. Adsorption dosage

Adsorption dose is a vital parameter that determines the overall economy of the process. To study the effect of dose on R 6G adsorption, 8 different dosages ranging between 0.05 and 0.40 g were selected and the adsorption trails were carried at room temperature under pH = 6. It is seen from Fig. 7, a declining tendency of the adsorption capacity with the increasing adsorbent dosage was observed, attributed to the

existence of concentration gradient between the dye molecule and the adsorbent [50]. Further, the increase in the dosage leads to the blockage of active pores of the adsorbent that leads to the fall in the uptake capacity. Besides, increasing dose, decreases capacity due to a greater number of active sites of adsorbent that remain purely unsaturated [51]. In the present scenario, it is clear that the lower adsorbent dosage i.e., 0.05 g is suitable and has a higher adsorption capacity of the dye molecules.

3.10. Agitation speed

Agitation speed is another crucial parameter governing the adsorption process. The agitation speed highly influences the solute distribution in bulk solution, thereby altering the formation of boundary film. In the present study, the agitation speed is varied in the range of 100–500, maintaining pH = 6, and adsorption dose of 0.05 g. From Fig. 8, it is clear that the dye uptake increased from 50 mg/g to 70 mg/g with the agitation speed up to 200 rpm. It is well known that the agitation speed assist in the proper mix of solute and solvent that helps to form the external boundary layer, and promoting film transfer coefficient along with the adsorption capacity [52]. However, further increasing the agitation speed beyond 200 rpm the adsorption capacity reports a downtrend phenomenon. The declining pattern of q_e at higher agitation speed was due to the experience of centrifugal force by the dye molecules causing the release of bound molecules that are attached to the surface of the adsorbent [53]. In summary, it is visible that the lower agitation speed favors the highest dye uptake, and beyond 200 rpm the desorption is more prevalent than adsorption. Hence, the choice of agitation speed in the present study was chosen to be 200 rpm.

3.11. Effect of contact time

The change of R 6G adsorption onto ZSM-22 at variable adsorption times are shown in Fig. 9. It is seen from Fig. 9, the rapid absorption phenomenon during the time interval of 0-60 min, followed by the slow adsorption from 60 to 180 min and no significant changes thereafter. The rapid adsorption at the initial stage i.e., 0-60 min is ascribed to the higher



Fig. 6 - Adsorption mechanism of R 6G onto ZSM-22.



Fig. 7 – Effect of dosage on the adsorption of R 6G onto ZSM-22.

35 30 100 200 300 400 500 Speed (rpm) Fig. 8 – Effect of agitation speed on the adsorption of R 6G onto ZSM-22.

concentration of R 6G, and availability of vacant sites on the adsorbent [54]. As time progress, from 60 to 180 min, the dye uptake seems to be very low. The slow adsorption is because, the majority of the vacant sites are filled with R 6G and limit the further transfer of ions on the surface, and hence the degree of adsorption is very mild [55]. Finally, after 180 min, the adsorbent is occupied by the R 6G and hence, no further adsorption is possible, representing an equilibrium state. Therefore, the maximum time for the adsorption of R 6G onto ZSM-22 is fixed as 60 min and the same has been used in further experimentation.

3.12. Adsorption isotherms

Adsorption isotherm studies help to identify the most suitable equation fit that defines the physico-chemical specifications of adsorbent and its surface properties. The relation between

the adsorption capacity of zeolite (ZSM-22), and the concentration of the dye at equilibrium was studied by Langmuir, and Freundlich isotherms, shown in Fig. 10. The hypothesis of the Langmuir isotherm includes a monolayer coverage of adsorbate molecule at the specific homogenous sites of adsorbent, the presence of homogeneous sorption sites with equivalent energy on the adsorbent surfaces and the absence of any interaction between the adsorbed molecule [56]. The standard non-linear form of Langmuir hypothesis is shown in Eq. (1).

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_e, q_m (mg/g) denotes the equilibrium and maximum adsorption capacities, K_L is the Langmuir constant R_L, C_i is the initial concentration of adsorbate. In the present study, the Langmuir adsorption capacity (q_{\max}) is 195.3 mg/g and the Langmuir constant is 0.0150.





Fig. 9 – Effect of agitation time on the adsorption of R 6G onto ZSM-22.



Fig. 10 — Nonlinear adsorption isotherms analysis under variable concentrations.

Freundlich isotherm illustrates the multi-layer adsorption on the heterogeneous surface with the possibility of reversibility [57]. The Freundlich constants comprising $K_f(mg/g)$, and n serves as an indicator of the relative adsorption capacity i.e., 2 < n < 10: good, 1 < n < 2: moderately difficult and n < 1: poor. The linearized Freundlich isotherm is shown in Eq. (2)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

The non-linear Freundlich isotherm is shown in Eq. (3)

$$q_e = K_f C_e^{1/n} \tag{3}$$

where, n is the magnitude that categorizes the adsorption process. In the current study, the value of n = 2.831 is well within the range of 1 < n < 10, and both the isotherms have best r^2 values. However, the closeness of q_e (exp) and q_e (cal) suggests the homogeneous adsorption via Freundlich

isotherms. Further, the summary of R 6G adsorption using various adsorbents is presented in Table 4. From the table it is very clear that the zeolite ZSM-22/TON from the CFA possess near neutral characteristics and offers higher sorption capacity (195.3 mg/g) than the materials showcased in Table 4. Summarizing and comparing the two correlation coefficients (r^2), Langmuir isotherm with ($r^2 = 0.9933$) is highly suitable to analyze the adsorption of R 6G onto the ZSM-22 zeolite. Besides, various adsorption parameters such as correlation coefficients r^2 , K_f, K_h, n, q_{max}, values are presented in Table 3.

3.13. Adsorption kinetics

Adsorption kinetics holds the key in designing and operational procedures in industries. Kinetics are the governing factors of the adsorption process and determines the type of adsorption, i.e., either physical or chemical. The kinetic models include first, pseudo-first-order, second [58], and pseudo-second-order [59] reactions shown in Eqs. (4)-(7).

$$LnC_t = LnC_i - k_1t \tag{4}$$

$$\log(q_e - q_1) = \log q_e - \frac{k_{PFO}}{2.303}t$$
(5)

$$\frac{1}{C_t} = \frac{1}{C_i} + k_2 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_{\text{PSO}}q_e^2} + \frac{1}{q_e} \tag{7}$$

where k_{1} , k_{PFO} , k_{2} , and k_{PSO} are the rate constants for the first, pseudo-first, second, pseudo-second-order kinetic models respectively; t is the time. C_i and C_t are the concentrations at the initial time and the time t, while $q_{\rm t}$ and $q_{\rm e}$ are the amount of dye adsorbed at the time t and equilibrium respectively. The aforementioned values of the rate constants, concentrations, and correlation coefficients are presented in Table 5. Fig. 11 displays the kinetic sorption of ZSM-22 zeolite for the adsorption of R 6G under various temperatures ranging between (303 K-323 K). From Table 5, it is evident that the experimental and the calculated sorption capacities tend to rise with the increase in the temperature. Further, the kinetic data fit well with the pseudo-second-order indicating the chemisorption [60] of R 6G onto the ZSM-22. However, both the pseudo-first and second-order kinetics fit well and are in close approximation; but pseudo-second-order fits well and has a better value of regression $r^2 = 0.99$ in comparison to PSO $r^2 = 0.95$.

Table 3 – Equilibrium modeling of data for the removal of R 6G using ZSM - 22.				
Isotherm	Parameter	Value		
Langmuir	q _m (mg/g) K _L (L/mg) r ²	195.3 0.0150 0.9933		
Freundlich	K _f (mg/g) n r ²	20.48 2.831 0.9269		

Table 4 — Summary of the literature on the separation of R 6G by various adsorbents.						
Adsorbent	pН	Adsorption capacity (mg/g)	Reference			
Activated carbon	7	44.70	[6]			
Palm shell powder	4	19.65	[7]			
Almond shell	8	32.60	[8]			
Hexadecyl functionalized magnetic silica nanoparticles	9	35.60	[12]			
H-0.2	10	36.60	[64]			
Graphene oxide	-	23.30	[9]			
Graphene sand composite	7	55.00	[65]			
Fe ₃ O ₄ modified with humic acid	6	161.8	[66]			
Nanoscale metal—organic framework NMIL-100(Fe)	6.1	88.62	[10]			
Clay minerals	7	111.0	[11]			
γ-Fe ₂ O ₃ /N-rGO composite	-	44.30	[61]			
α-Fe ₂ O ₃ /rGO composite	7	8.360	[67]			
Zeolite ZSM-22/TON	6	195.3	This work			

Table 5 — Kinetic modeling of data for the separation of R 6G using ZSM - 22.								
Adsorbent	Temp. (K)	q _{e,exp} (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			q _{e1,cal} (mg/g)	k1 (1/min)	r ²	q _{e2,cal} (mg/g)	k ₂ (g/mg min)	r ²
Zeolite	303	80	76.5	0.1014	0.9559	81.5	0.0019	0.9925
	313	91.8	87.9	0.1188	0.9493	93.3	0.0021	0.9907
	323	102.2	98.3	0.1495	0.9519	103.6	0.0023	0.9908

3.14. Effect of temperature

The impact of the adsorption temperature on the R 6G removal efficacy is presented in Fig. 12a. It is clear that the removal efficiency is improved with the increasing temperature from 303 to 323 K at constant adsorbate concentration of 300 mg/L maintained at pH = 6. As can be seen from Table 6, the increase in the temperature from 303 to 323 K resulted in the enhanced adsorption capacity of 72 mg/g to 93 mg/g. The increasing uptake concerning temperature indicates the endothermic nature of the reaction, attributed to the enhanced mobility of ions and stability of the active sites [61]. Further, based on the temperature studies, the thermodynamic analysis was performed to evaluate Gibbs free energy (ΔG^{0}), change in entropy (ΔS^{0}), and deviations of enthalpy (ΔH^{0}). The respective equations for evaluating the aforementioned thermodynamic parameters are shown in Eqs. (8)–(11).

$$\Delta G^{0} = - \operatorname{RT} \ln K_{c} \tag{8}$$

$$K_{c} = \frac{C_{Ae}}{C_{e}} \tag{9}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{10}$$

$$\ln K_{\rm c} = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$
(11)

where R is the universal gas constant, T is the absolute temperature, K_c is the distribution constant, and the values of ΔH^0 , ΔS^0 were determined from the intercept and slope of the plot between lnK_c Vs 1/T (See Fig. 12 b) as per the van't Hoff equation. The positive value of ΔH^0 denotes the endothermic nature [62] of the dye adsorption on to the surface of ZSM-22. Whereas, the negative values of ΔG^0 , ΔS^0 indicates the viability and impulsive nature of the adsorption, and increase in entropy as a result of adsorption. It is known that the adsorption favors the high temperatures due to the ΔH^0 , ΔS^0 are greater than zero.



Fig. 11 – Nonlinear kinetic studies fitted to pseudo-first-order and pseudo-second order models.



Fig. 12 – a) Effect of temperature on the adsorption of R 6G onto ZSM-22 b) Van't Hoff plot for the adsorption of R 6G onto ZSM-22.

Table 6 – Thermodynamic assessment on adsorption of R6G onto ZSM-22.					
Temp. (K)	∆G° (kJ/mol)	∆H° (kJ/mol)	∆S° (kJ/mol K)		
303	-0.0915	15.06	0.05		
313	-0.6281				
323	-1.0906				



Fig. 13 – Desorption of R 6G using various eluents.

3.15. Desorption studies

Desorption and regeneration experiments give useful insights about the possibility of the recovery and reusability of the adsorbent. Adsorption of R 6G was carried out for 300 ppm, 30 ml of dye solution with 0.05 g of the ZSM-22 zeolite, for a predetermined time of 1 h, at room temperature, maintaining acidic pH = 6. Once the adsorption studies were completed the solution is dried in a furnace at 60 °C to recover the sediment. Further, desorbing agents 0.1 N HCl, 0.1 N H₂SO₄, 0.1 N NaOH, and 100% ethanol, were chosen as eluents, for the desorption experiments of R 6G loaded ZSM-22. The choice of the eluents is to evaluate the desorption capacity under various environments, i.e., acidic, basic, and organic to choose the best possible mechanism. From Fig. 13, it is clear that the alkaline eluent NaOH yields a higher desorption percentage of 78.85% followed by HCl (63.06%) > H₂SO₄ (54.65) > Ethanol (15.85%). The reason ascribed for the better desorption capacity for the alkaline medium i.e., NaOH in the present study is because the surface of the adsorbent acquires negative charge in the presence of NaOH, resulting in the repulsion with anionic dye molecules followed by the detachment of dye molecules [63]. Further, the remaining portion of the adsorbent (ZSM-22) actively participated in the adsorption mechanism that shows the dominance of chemisorption over adsorption, also confirms with higher ΔH^0 from the thermodynamic studies. A summary of the researchers about the desorption studies of R 6G using various adsorbents is presented in Table 6.

4. Conclusion

The present study deals mainly synthesizing the nanorod structured zeolite ZSM-22 from CFA using conventional hydrothermal synthesis approach. The newly synthesized zeolite ZSM-22 has been tested its utility in the adsorption of anionic dye R 6G. The surface area of ZSM-22 has been greatly improved to 32.1 g/m² when compared to the raw CFA of 1.2 g/ m². The adsorption studies revealed the successful separation of R 6G dye molecule on the surface of ZSM-22 with a maximum adsorption capacity of 195.3 mg/g. Moreover, the thermodynamic techniques revealed the type of reaction is highly endothermic and spontaneous. A pseudo-second order reaction fits well, while the Langmuir approach pronounced the adsorption to be monolayer. Further, alkaline agent NaOH has been chosen as the best selective desorption eluent to reuse the adsorbent for the successive cycles. In summary, it is very clear and evident that the CFA based zeolite ZSM-22 emerges as a successful and new entry to the zeolite data base for the selective sorption of cationic dyes from effluent streams.

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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