Iron Oxide NPs Facilitated a Smart Building Composite for Heavy-Metal Removal and Dye Degradation

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ABSTRACT: Due to the growing population, drought, and the contamination of conventional water sources, the need for clean water is rising worldwide with high demand. The application of nanomaterials for water purification can provide a better water quality, by eliminating toxic metals and also decomposing organic contaminants. Exploitation of industrial coal-burned byproduct, fly ash, through nanomodification has been developed in this exertion for the treatment of wastewater along with heavy-metal remediation and dye degradation. The fly ash was sintered at 1000 °C with addition of hydrothermally synthesized iron oxide nanoparticles to make a cementitious composite (FA10C) using an alkali activator (NaOH + Na2SiO3) at ambient temperature. Chemical investigations of the fly ash and the FA10C composites were done by X-ray fluorescence techniques. Analysis of FA10C by X-ray diffraction, Fourier transform infrared, field emission scanning electron microscopy, energy-dispersive spectrometry, and dynamic thermal analysis/thermogravimetric techniques revealed that nanodimensioned rod-shaped mullite formation and its interlocking textures enhance the strength of the building composite. Furthermore, the cementitious composite (FA10C) has been used as an adsorbent to remove heavy metals (lead, chromium, cadmium, copper) and carcinogenic dyes (methylene blue, Congo red, and acid red-1) from their aqueous solutions. The mineralogical features of the composite FA10C and its adsorption capacities/efficiencies were studied by systematic investigation of different parameters, and the adsorption data have been analyzed using Langmuir isotherm. The experimental findings suggest that the iron oxide nanoparticles facilitated fly ash can be implemented as a substitute cementitious composite (greenhouse effect) in construction technology being an energy-saving, low cost, and eco-friendly process in adsorbent manufacturing.

1. INTRODUCTION

The waste product of coal combustion in thermal power plant as fly ash is a thoughtful alarming concern for the ecological purpose due to its lower utilization ratio in respect to its higher production about 750 Mt global annual production. The fly ash has been used in various fields, including soil amendments, zeolite synthesis, filling in road works, and lands, whereas the applications of fly ash as a key material of geopolymer concrete (cement, brick production) has been only about 20% in recent times. The consumption of fly ash was 60% in the United States and other countries; however, its aspect in civil engineering field is limited because of lower reactivity and inadequate strength gain, particularly when produced at room temperature. Diverse studies were conducted on temperature-dependent efficacy for the proper activation of fly ash with suitable binders for enhancing the mechanical strength and durability of concrete structure. Considering the huge amounts of fly ash generated, advancement of research is required to develop new environmentally benign applications to minimize the gap between generation and utilization.

On the other hand, environmental compliance requirements become gradually difficult to attain in both wastewater discharge and chemical handling. The rapid growth of an industrial society leads to a substantial upsurge in the demand for pure water. Industrial wastewater has a tremendously negative impact on the environment, i.e., it can cause soil contamination, and especially wastewater containing heavy metals results in severe environmental loss. Electroplating, battery, printed circuit board, and metal surface coating treatment are the principal sources of heavy-metal contamination, which affect the nature of the water, inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction, sometimes becoming toxic and even carcinogenic. The conventional methods for treating dye and heavy-metal adulterations are based on chemical coagulation and flocculation, reverse osmosis, activated carbon adsorption, ion exchange, solvent extraction, and adsorption; however, these technologies do not show significant effectiveness with economic advantages. Thus, utilization of industrial solid wastes for the treatment of wastewater could be helpful to not only the environment, in solving the solid waste disposal problem, but also the economy.
In this present work, the synthesized iron oxide (Fe₂O₃) nanoparticles (NPs) were characterized by ultraviolet–visible (UV–vis), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy-dispersive spectrometry (EDS) techniques and mixed with fly ash in a certain amount, which was further calcined at 1000 °C. The sintered particles were added with sodium hydroxide and sodium silicate solution to synthesize an alternative cementitious composite (FA10C) in ambient temperature. The characterization of FA10C was also evaluated by XRD, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and EDS techniques. Differential thermal analysis along the thermogravimetric activity of the unsintered mixtures has been investigated. The effects of FA10C on mechanical strength (compressive and split tensile) have been measured and further used for the dye degradation and heavy-metal removal from the contaminated water at different varying parameters by calculating the adsorption/degradation capacities.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Ingredients. Low-calcium class F dry fly ash and locally available sand (specific gravity, 2.52; water absorption, 0.50%; and fineness modulus, 2.38) were employed as the key ingredients for this study. Analytical-grade sodium hydroxide was supplied by Sigma-Aldrich. Commercial sodium silicate (specific gravity, 1.53 g/cc) was obtained from SRL Co. Ltd., India. Analytical-grade heavy-metal compounds (lead nitrate (Pb(NO₃)₂), MW = 331.21 g; cadmium nitrate (Cd(NO₃)₂), MW = 236.42 g; chromium(III) nitrate (Cr(NO₃)₃), MW = 238.01 g; copper nitrate (Cu(NO₃)₂), MW = 187.56 g) were acquired from Merck, Germany.

2.2. Synthesis and Characterization of Iron Oxide Nanoparticles. Ferric chloride (FeCl₃, 1 M) and urea (CH₄N₂O, 1 M) solutions were mixed gently under continuous stirring, and ammonium hydroxide (NH₄OH) solution was added dropwise until the pH was adjusted at 10.0. After that, the mixture was kept in a hydrothermal cell (Teflon-lined autoclave) and placed in an oven for 6 h at 100 °C. The remaining solution was washed several times with acetone and kept for drying at room temperature. The synthesized/as-grown iron oxide product was dispersed in deionized water, and optical characterizations with band gap were executed by a UV–vis spectrophotometer (UV-3101PC, Shimadzu). The crystallization-phase analysis was executed by a powder X-ray diffractometer (Bruker AXS, Inc., Model D8, WI). A field emission scanning electron microscope (Inspect F50 SEM, FEI Europe BV, The Netherlands) was used to characterize the morphological properties, and element composition of the synthesized materials was identified by an energy-dispersive X-ray spectrometry (EDS) system coupled to the FESEM.

2.3. Preparation of the Cementitious Composite. The fly ash (FA) was mixed with 5% iron oxide (Fe₂O₃) NPs by a ball-mixing machine for 2 h. The mixture (containing fly ash and Fe₂O₃) was then sintered at 1000 °C for 2 h and cooled at room temperature (FA10). The mortar sample was prepared by mixing the FA10, river sand, and binder. The FA10 to binder ratio was affixed at 0.48, and weight ratio of FA10 to sand was maintained at 1:3. The binder was prepared by using 10 M NaOH and Na₂SiO₃ solution at 1:2 gyrometric ratio. After thorough mixing, the mixture was poured into 20 mm × 20 mm × 20 mm cubes to prepare the cementitious composite (FA10C). After 48 h, the samples were removed and kept at room temperature for curing.

2.4. Characterization of the Cementitious Composite. The synthesized composite FA10C was crushed to a powder, sieved through a 50 μm sieve, and prepared for several characterization techniques. The chemical compositions of FA10C and fly ash were determined by X-ray fluorescence (AXIOSmAX, PANalytical, the Netherlands). The mineralogical composition of FA10C was assessed by X-ray diffraction (XRD; D8-FOCUS-type X-ray diffractometer). The scanning range was 10–80° 2θ at a scan speed of 0.5 s/step using Cu Kα radiation (40 kV and 40 mA), and phases were identified by JCPSD files. Fourier transform infrared (FTIR) spectra of FA10C were obtained using a Nicolet iS50 spectrometer (Thermo Scientific America) in the range of 400–4000 cm⁻¹. A field emission scanning electron microscope equipped with an energy-dispersive spectrometer (QUANTAX ESPRIT 1.9 software) was used to investigate the morphological behavior and elemental analysis, respectively. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) surface area analyzer (SA 3100, Beckman Coulter, Switzerland). The thermal reaction processes were measured using a dynamic thermal/thermogravimetric analyzer (DTG-60H, Shimadzu) for the mixture of fly ash and 5% Fe₂O₃ NPs sample in a N₂ gas atmosphere.

2.5. Strength Analysis. The mortar samples of cubical dimension (50 mm × 50 mm × 50 mm) and cylindrical dimension (100 mm diameter × 50 mm height) were tested for compressive strength and split tensile strength, respectively. The testing was performed at the age of 28 days and the results were compared to those of the conventional control mortar samples. The conventional control samples were made using ordinary portland cement, sand, and water. The ratios of cement to sand and cement to water were fixed at 1:3 and 1:0.4, respectively.

2.6. Effect on Heavy Metals (Pb²⁺, Cr³⁺, Cd²⁺, and Cu²⁺). 2.6.1. Adsorption and Desorption of Heavy Metals (Pb²⁺, Cr³⁺, Cd²⁺, and Cu²⁺). Initially, 1 g of dried FA10C was added to 25 mL of heavy-metal solution (1 M at pH 4.0) and continuously stirred at 200 rpm and 25 °C for 360 min using the inductively coupled plasma mass spectroscopy (ICP-MS), the adsorptions of metal ions were calculated by the following equation

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

where “qₑ” is the amount of metals adsorbed at equilibrium (mg/g), “C₀” and “Cₑ” are the initial and equilibrium concentrations of metals (mg/L), and “m” is the mass of FA10C (g), and “V” is the volume of the solution (L). The different carcinogenic heavy-metal (Pb²⁺, Cu²⁺, Cr³⁺, and Cd²⁺) solutions were made by dissolving their respective compounds (Pb(NO₃)₂, Cd(NO₃)₂, Cr(NO₃)₃, Cu(NO₃)₂) in distilled water distinctly. To study the effect of the pH of initial solution, the different pH values (2.0–7.0) were adjusted with diluted nitric acid (HNO₃) or sodium hydroxide (NaOH). The same mixing techniques were implemented at initial fixed pH (4.0) but varying shaking time (10–360 min) to see the influence of contact time on the adsorption of metals. To investigate the effect of temperature on the adsorption, a similar experiment was carried out at different temperatures (15, 25, 30, 35, and 45 °C), but the concentration of each heavy-metal solution was fixed at about 1 M at pH 4.0. The adsorption study was conducted after 360 min of contact time.
Desorption tests were also done on FA10C obtained from the previously described adsorption test. Two types of experiments were conducted to study the leaching characteristics of the metal ions in lead-containing specimens: (a) water treatment and (b) acid treatment. The contact time for each type was fixed at 3 h at 25 °C. The leaching efficiency ($\epsilon_L$) of metals (Pb²⁺, Cr³⁺, Cd²⁺, and Cu²⁺) was determined according to the following equation

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

where $C_e$ is the residual concentration (ppm) and $C_0$ is the initial concentration of the heavy-metal (Pb²⁺, Cr³⁺, Cd²⁺, and Cu²⁺) ions (ppm).

2.7. Dye Degradation Study. Methylene blue (MB), Congo red (CR), and acid red 1 (AR) dyes were employed for this experiment. Each dye solution of varying concentration was mixed with the FA10C samples under a UV lamp (KODAK, 40 W) under constant stirring at 25 °C. Absorbance spectra of the reaction mixtures were recorded at 663, 500, and 532 nm wavelengths for MB, CR, and AR after every 15 min time interval up to 3 h, respectively. The degradation efficiency was calculated using the formula

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\%$$

where “$A_0$” is the original absorbance of the solution before irradiation and “$A_t$” is the absorbance of the solution at $t$ time after irradiation. To investigate the effect of pH on adsorption, a series of each dye solution was prepared by adjusting pH (2−10) and optical density was measured after 180 min. An experiment was conducted for the various dosages of FA10C on dye degradation, varying the dosage from 0.1 to 2 g/L and keeping the initial concentration of each dye at 10 mg/L at constant pH 7.0.

2.8. Adsorption Isotherm. The equilibrium adsorption isotherm has an importance in the design of adsorption systems, which is conducted by the Langmuir isotherm in the present study. A Langmuir isotherm model is hired to evaluate the investigational data and to acquire the isothermal adsorption graphs and related parameters. The Langmuir isotherm model assumes that adsorption takes place at specific homogeneous surface within the adsorbent; there are no interactions between adsorbates, and the surface has equal affinity and energy.\(^{22,23}\) The Langmuir isotherm can be written in the form

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

where $q_e$ is the absorbed amount (mg/g); $C_e$ is the equilibrium concentration (mg/L); $q_m$ is the absorption capacity (mg/g); and $K_L$ is the Langmuir binding constant.

2.9. Statistical Analysis. For testing compressive and split tensile strengths, five samples of each category were tested and the experiment was repeated at least three times. Data were presented as average (over 12 samples) and ±SD (standard deviation).

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the Iron Oxide Nanoparticles. The formation of iron oxide particles can be described through the following probable chemical reactions. NH₄OH is responsible for the generation of hydroxyl ions (OH⁻) as well as controls the pH of the solution during the reaction process. FeOOH is formed by the reaction of FeCl₃ with NH₄OH. On heating, FeOOH further produces Fe²⁺ and OH⁻ ions, which consequently assist in the development of Fe₂O₃ ions.

$$\text{FeCl}_3 + \text{NH}_4\text{OH} \rightarrow \text{FeOOH} + \text{NH}_4^+ + \text{H}^+ + \text{Cl}^-$$

$$\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$$

The concentration of synthesized Fe₂O₃ increased with reaction time, which escorts the shape of desired nanodimensioned particles. Figure 1A exhibits the absorption spectrum of the as-
prepared iron oxide NPs solution. The onset of absorption maxima at 585 nm wavelength in the visible range was shown, indicating the formation of low-dimensional reddish Fe$_2$O$_3$ particles. In the UV/visible absorption progression, the outermost electrons absorb radiant energy and transit to high energy levels in any molecule/atom. In this procedure, the spectrum obtained owing to optical absorption can be analyzed to acquire the energy band gap of nanomaterial. The band gap of the as-prepared nanoparticles is determined by the relation
\[(αhν)^2 = αv_{υ} \nu \]
where “α” is a constant, “E” is the band gap of the material, and “α” is the absorption coefficient. Figure 1B represents the plot of $(αhν)^2$ versus energy (hν) to determine the band gap and it is found to be 2.86 eV for the synthesized nanoparticles.

XRD is a nondestructive method, which gives a clear idea about the nature of the composite material. It can give information about whether the material has crystalline or amorphous nature. Figure 1C depicts the typical crystallinity of the synthesized iron oxide NPs, where the reflection peaks matched with those of the Fe$_2$O$_3$ phase (JCPDS File no. 24-0072). Major characteristic peaks for the as-grown metallic iron oxide at 2θ values of 24.1°(012), 33.1°(104), 35.6°(110), 39.2°(006), 40.8°(113), 49.4°(024), 54.1°(116), 62.3°(214), and 63.9°(300) indicate that the nanoparticles are well crystalline. Figure 1D exhibits the morphology of the as-synthesized iron oxide NPs in an almost uniform spherical shape of nanodiameter.

The electron-dispersive spectroscopy (EDS) analysis of the particles specifies the presence of “Fe” and “O” elements in the pure as-grown iron oxide (Fe$_2$O$_3$) NPs. It is clearly shown that the materials are limited only iron and oxygen elements, in atomic percentages of 38.65 and 61.35%, respectively (Figure 1E).

3.2. Characterization of Composite Material. The chemical compositions of FA and FA10C obtained by XRF technique are represented in Table 1. It is shown that fly ash is mainly made of 64.48% SiO$_2$, 28.82% Al$_2$O$_3$, 2.57% Fe$_2$O$_3$, and little amount of oxides (CaO, MgO, Na$_2$O, K$_2$O, etc.). After geopolymerization, the content of sodium and the loss on ignition (L.O.I.) increased considerably as this process helps to incorporate sodium and hydroxyl group within the structure of geopolymer. The reduction of Al$_2$O$_3$ is observed in the FA10C sample compared to fly ash. The weight percentages of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ are about 56.45, 17.12, and 9.85 in FA10C, respectively. Calcium has an advance effect during the conversion of fly ash to geopolymer as the calcium provides additional nucleation sites for precipitation of dissolved species in the geopolymerization process. However, when the CaO content is high, the microstructural porosity decreases and the resulting formation of amorphous structure Ca−Al−Si gel strengthens the final product. The percentage increment of the Fe$_2$O$_3$ is observed from 2.57 to 9.85 as it was added externally before the calcination process.

The composition of the prepared FA10C was characterized by powder X-ray diffraction (XRD) study (Figure 2A). Several peaks at different positions in the XRD spectra confirm the presence of Mullite. The diffraction peaks at 2θ values of 16.43, 25.97, 26.26, 30.96, 33.22, 35.27, 40.87, 42.59, 57.56, and 60.71° represent the mullite structure with indices (110), (120), (210), (001), (220), (111), (121), (230), (041), and (331) and the peaks at 24.12, 35.61, and 49.41° represent the Fe$_2$O$_3$ NP structures with (012), (110), and (024) indices, respectively. The spectra are in close agreement with JCPDS card Nos. 15-0776 and 24-0072 for Mullite and Fe$_2$O$_3$, respectively. The presence of silica (quartz) is confirmed by the detection of peaks at 2θ values of 20.85° (100), 36.54° (110), and 75.67° (302) and matched with JCPDS file No. 331161.

In the FTIR spectra of FA10C (Figure 2A), the bands around 460 cm$^{-1}$ are identified due to in-plane Si−O bending and Al−O links; however, a minor peak at 822 cm$^{-1}$ is assigned to stretching modes of T−O (T: Si or Al) and corresponds to dissolve silicate/aluminosilicate species. The band at around 587 cm$^{-1}$ is due to the existence of Fe$_2$O$_3$ in the FA10C sample. The broad band (1622 cm$^{-1}$) is attributed to bending vibrations (H−O−H), and it is typical for polymeric configurations with aluminosilicate complex. The asymmetric and symmetric stretching vibrations ν (O−H) at 3433 cm$^{-1}$ suggest the presence of an amorphous silicate material or

| compound (%) | fly ash | FA10C |
|--------------|---------|-------|
| SiO$_2$      | 64.48   | 56.45 |
| Al$_2$O$_3$  | 28.82   | 17.12 |
| Fe$_2$O$_3$  | 2.57    | 9.85  |
| CaO          | 0.81    | 1.49  |
| MgO          | 0.36    | 0.32  |
| Na$_2$O      | 0.34    | 0.31  |
| K$_2$O       | 0.35    | 1.05  |
possibly hydrated aluminum silicates. Another broad band at 1069 cm⁻¹ is seen in this spectrum due to Si–O–Si asymmetric stretching vibrations of silica. The bands associated with mullite appear at around 560, 730, 822, and 1170 cm⁻¹, which correspond to alumina octahedra (AlO₆), alumina tetrahedra (AlO₄), Al–O vibrational modes of δ-alumina, and silica tetrahedra (SiO₄), respectively.

Scanning electron microscopy (SEM) image of the FA10C exhibits irregular rod-shaped mullite phases, along with spherical-shaped Fe₂O₃ NPs in Figure 3A. For a more detailed understanding of the individual component percentages in the composition of the FA10C, an energy-dispersive X-ray spectroscopy (EDXS) analysis was conducted, which indicates that the percents of aluminum, silicon, iron, and oxygen elements were 17.23, 28.3, 8.04, and 35.01%, respectively, as illustrated in Figure 3B. The surface characteristics of the FA10C samples were subsequently examined via BET. The surface area of the FA10C sample is about 60.75 m²/g, and the composite was mesoporous (~72%) in nature. The FA10C composite was used for adsorption and photocatalytic degradation due to its higher surface area.

Dynamic thermal analysis (DTA) of the FA (fly ash + Fe₂O₃) samples (Figure 4) shows a slow endothermic fall within the temperature range. This fall was attributable to the evaporation of volatile components, such as water, isopropyl alcohol, nitrogen dioxide, etc. As the fly ash is already a burned material, no such detectable change was observed in DTA. In Figure 4, the exothermic peak at high temperature was seen, which shows the probable evidence of mullitization. No change in weight loss is seen in thermogravimetric analysis (TGA) graph at higher temperature.

3.3. Activity of FA10C as a Building Materials. The mechanical strengths (compressive, split tensile) of the FA10C mortar samples were represented in tabular form (Table 2). The result shows that the maximum compressive and flexural strengths were obtained in the case of FA10C at 28 days compared to conventional mortar samples. The rod-shaped hard mullite was prepared in nanosize, which creates an interlocking textures in the FA10C matrices, which may be the key reason to increase the strengths of the composite.

3.4. Heavy-Metal Adsorption. The effect of pH, temperature, contact time, and initial concentration on the adsorption capacity of heavy-metal ions is shown in Figure 5. The adsorption of heavy-metal ions increases with increasing pH and molar concentrations of the initial solution (Figure 5A). At higher pHs, the H⁺ ion concentration is also sufficient in solution and adsorption capacity becomes higher as the adsorbent always has greater tendency to adsorb H⁺ ions. At higher molar concentration of the solution, the adsorption capacity of FA10C for every metal sufficiently increased and reached the saturation level above 6 M concentration (Figure 5D). At lower pH, the samples have poor adsorption capacities due to more H₃O⁺ availability in the solution as the adsorption capacities for metal ions are dropped by the competition with H₃O⁺.

The adsorption capacities of FA10C for each metal ion at pH 5 are significantly higher and saturated at pH ≥ 6, which is correlated to other studies. The adsorption capacity for Pb²⁺ is the highest (81.2 mg/g at pH 5) as FA10C has additional adsorption sites for Pb²⁺ than others, whereas the
lowest adsorption capacity was found for Cr³⁺ (24.6 mg/g at pH 5), which may be due to the presence of numerous unlike ions in its respective pH atmosphere. Figure 5B illustrates the effect of temperature on adsorption percentage. It can be noticed that the adsorption of each heavy-metal ion on FA10C increases with increasing temperature. The diffusion of the heavy-metals ions on the FA10C surface results in adsorption by ion-exchange phenomenon at higher temperature. Additionally, microcavities can be formed inside the composite by water vaporization at higher temperature, which may increase the adsorption capacity. The kinetic adsorption experiment is revealed in Figure 5C to calculate the equilibrium time dependence behavior of adsorption. The result demonstrates that the adsorption increased with increasing contact/shaking time, reached the maximum after 120 min, and became almost saturated after that. The nanodimensioned mullite is formed in FA10C during calcination at 1000 °C, resulting in the increase of the specific contact surface area of the composite and thus further leading to more adsorption sites with higher adsorption capacity. After the geopolymerization process, the matrix of FA10C may be introduced by nanosized pore structures, which leads to more efficacy for heavy-metal adsorption.

3.5. Heavy-Metal Desorption. Figure 6 illustrates the effect of water and acid treatment on the leaching efficiency at 24 and 48 h. The amount of metals extracted from the solution increased in conjunction with the experimental duration. The 24 h water treatment cannot remove Pb²⁺, Cd²⁺, and Cu³⁺ ions from the sample, where insignificant recovery rates up to 0.8, 0.3, and 0.2 were obtained, respectively. The desorption results indicate that the amount of heavy metals (Pb²⁺, Cd²⁺, and Cu³⁺) leached in the solution was smaller at water treatment for 24 h. The extraction is strongly enhanced when acidic conditions are employed.

The recovery of lead, copper, and cadmium at larger quantities was found, which can be recognized to an ion exchange between H⁺ and metallic cations or to dissolution of precipitated metals. The elements belonging to higher atomic number generally have lower free energy of hydration. The H⁺ ion can exchange the site of adsorbed metallic ions easily as it has the highest free energy of hydration. The amount of Cr³⁺ ions extracted was found to be the highest among the applied heavy metals. Having a 3⁺ charge, the net charge of chromium was not balanced after an ion exchange with Na⁺, resulting in an imbalance that destabilized the adsorption status, which assists in the detachment of Cr³⁺ from the sample and its redissolution into the solution. In addition, as the higher charged ions can perform ion exchange more easily, the Cr³⁺ leaching is the highest in amount to the solution.
3.6. Dye Degradation Analysis. The pH of the dye solution plays a pivotal role in the adsorption process. The variation of methylene blue, Congo red, and acid red 1 adsorption on FA10C over a broad range of pH is shown in Figure 7A. Experimental results show that, for the CR solution with lower pH (4.0), improved effectiveness of reduction and considerable efficiencies in higher pH (>7) were observed. Better efficiencies for the AR solution were shown at pH 3.0, and higher MB adsorption is found at pH 5.0. The adsorption of the dyes onto the adsorbent surface is mainly influenced by the superficial charge on the adsorbent as well as by the pH. The basic dyes produce cations (C+) and reduced ions (CH+) in water. The tendency for adsorption of the dyes (cations) is influenced by the increment of the negative charge density on the FA10C surface at the pH value near or above the zero point of the charge. In addition, by the protonation, in the acidic medium, the positive charge density can be found more on the dye molecules at lower pH, resulting in the lower enchanting. Adsorption of the organic substrate is generally considered to be an important parameter in determining photocatalytic degradation rates. Figure 7B shows that the amount of each dye adsorbed on the photocatalyst from aqueous solution increases quickly with time and equilibrium is established within 30 min. Therefore, when the adsorption reaches equilibrium, the amount of dyes adsorbed by FA10C is largest, which may be attributed to the synergistic effect of FA10C. The variation of dye degradation exhibits that the minimum 1.0 g/L dosage was considerable and sufficient for maximum dye degradation (Figure 7C). At lower concentrations, the dye removal efficiency was less as the required quantity of photoreactive elements was not present; thereby, the amount of OH radicals was also less. Hence, 1.0 g/L dosage was taken as an optimum value of FA10C and >90% degradation was credited to photocatalytic activity.

3.7. Langmuir Isotherm. The linear fitted curves for Langmuir isotherms and parameters depict that the isotherms data fit splendidly and the values of $R^2$ for the heavy metals/dyes are very close to 1 (Figure 8). The adsorption data fitted very well in the Langmuir model, with higher correlation coefficients. Considering the best fit with respect to the values of $R^2$ (0.9952, 0.9890, 0.9921, and 0.9917 for Pb, Cd, Cu, and Cr, respectively), the surface of the adsorbent is considered to be homogeneous. Similarly, the values of $R^2$ for MB, CR, and AR are 0.9963, 0.98787, and 0.99425, respectively, which support the statement of homogeneous surface of adsorbent for the monolayer of dye molecules. The monolayer adsorption is obtained and the process becomes highly favorable, which
confirms the homogenous adsorption and negligible interaction between adsorbed molecules.

4. CONCLUSIONS

Using iron oxide nanoparticles in fly ash has been suggested to diminish the multilization temperature. The mullite was synthesized in nano form at lower temperature and turned mullitization temperature. The mullite was used to improve the ecological footprint in construction field as cement causes massive CO₂ emission during its production, affecting the global climate negatively.

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Notes

The authors declare no competing financial interest.

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