



# Article Characterization of the Physical, Chemical, and Adsorption Properties of Coal-Fly-Ash–Hydroxyapatite Composites

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Abstract: (1) Hydroxyapatite (HAp), which can be obtained by several methods, is known to be a good adsorbent. Coal fly ash (CFA) is a commonly reused byproduct also used in environmental applications as an adsorbent. We sought to answer the following question: Can CFA be included in the method of HAp wet synthesis to produce a composite capable of adsorbing both heavy metals and dyes? (2) High calcium lignite CFA from the thermal power plant in Belchatów (Poland) was used as the base to prepare CFA-HAp composites. Four types designated CFA-HAp1-4 were synthesized via the wet method of in situ precipitation. The synthesis conditions differed in terms of the calcium reactants used, pH, and temperature. We also investigated the equilibrium adsorption of Cu(II) and rhodamine B (RB) on CFA-HAp1-4. The data were fitted using the Langmuir, Freundlich, and Redlich–Peterson models and validated using  $R^2$  and  $\chi^2/DoF$ . Surface changes in CFA–HAp2 following Cu(II) and RB adsorption were assessed using SEM, SE, and FT-IR analysis. (3) The obtained composites contained hydroxyapatite (Ca/P 1.67) and aluminosilicates. The mode of Cu(II) and RB adsorption could be explained by the Redlich-Peterson model. The CFA-HAp2 obtained using CFA, Ca(NO<sub>3</sub>)<sub>2</sub>, and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> at RT and pH 11 exhibited the highest maximal adsorption capacity: 73.6 mg Cu/g and 87.0 mg RB/g. (4) The clear advantage of chemisorption over physisorption was indicated by the Cu(II)-CFA-HAp system. The RB molecules present in the form of uncharged lactone were favorably adsorbed even on strongly deprotonated CFA-HAp surfaces.

**Keywords:** wet preparation method; chemical engineering; dye and heavy metals sorption; industrial wastewater treatment

# 1. Introduction

Dyes are widely used in the textile industry, as well as in the paper, leather, rubber, cosmetics, plastics processing, pharmaceutical, and food industries. Currently, 98,000 different dyes are available [1], which are divided into water-insoluble and water-soluble dyes. Water-soluble dyes include a large group of cationic basic dyes and anionic acid, direct, and reactive dyes [2]. Due to their good solubility, dyes end up in sewage and, ultimately, in natural sources of water in the environment. Dyes slow down photosynthesis and decrease oxygen content in water bodies. Dyes are also toxic to aquatic organisms, [1] as well as being genotoxic, mutagenic, and carcinogenic [3], and are characterized according to various toxicity levels [4]. However, mixtures of dyes often exhibit increased toxicity to aquatic organisms [5]. The high toxicity of dyes to humans, plants, and soil-based and aquatic organisms is caused by the high heavy-metal content in dyes [2,6]. These heavy metals pose a serious environmental problem. For these reasons, eco-friendly dyes with reduced toxicity are being developed [7].



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The water environment is particularly endangered by the presence of dyes that interfere with photosynthesis and lead to eutrophication [8]. Due to their good solubility, cationic dyes (e.g., rhodamine B) easily migrate in water. Dyes are removed from wastewater by chemical precipitation, coagulation, and electrocoagulation; adsorption and ion exchange; ultra- and nanofiltration; advanced oxidation; and various bioprocesses [9,10]. Organic and inorganic coagulants and electrocoagulation are widely used for the treatment of colored textile wastewater [11,12]. However, as with chemical precipitation, the use of such coagulants leads to the consumption of large amounts of reagents, increased wastewater salinity, and the formation of large amounts of sediments [10]. The treatment of wastewater to remove dyes is performed not only to decolorize the water but also to reduce chemical oxygen demands and the total organic carbon concentration. The degradation and mineralization of dyes and a reduction in the toxicity of sewage are possible with the use of electrochemical oxidation [13], catalytic ozonation [11], and other AOP techniques [14].

Adsorption is considered one of the most frequently used [10] and effective [15] methods for removing dyes from wastewater. The use of carbon sorbents for dye removal is widely known [9,16]. Low-cost sorbents and coated or composite magnetic particles [10] have also been studied for this application, as have natural and synthetic zeolites [17–20]. Due to the frequent coexistence of dyes and heavy metals in industrial wastewater, adsorbents that enable the removal of both types of pollutants are being sought. A review of the literature shows that these are very diverse materials, including chelating resins [21], low-cost waste-plant materials [22–24], nano-activated carbon [16], graphene oxide [2], nanocellulose/functionalized nanocellulose [25], clays and diatomaceous earth [26], fly ash [27], and zeolites [28]. Another group of highly effective dye-removing and heavymetal-removing [29–31] adsorbents [32–34] includes hydroxyapatites of natural and synthetic origin.

Hydroxyapatite (HAp), a calcium orthophosphate, is a thermodynamically stable substance with broad adsorption properties. The structure of HAp contains calcium cation and hydroxyl groups. Therefore, HAp is characterized by its ability to adsorb both cations and anions [35]. Currently, there are many different methods for obtaining HAp (dry, wet, sol–gel, fluxing, and mechanochemical methods), which allow one to obtain materials with the appropriate crystal structures, morphologies, and Ca/P ratios. The most widely used method for obtaining HAp is wet chemical precipitation [36,37]. The interest in modifying the structure of HAp stems from the fact that HAp is a simple and well-characterized chemical compound [38]. The possibility of combining other compounds, such as  $\beta$ -cyclodextrin [39], chitosan [40], proteins [37], and cellulose [41], with hydroxyapatite ceramics has led to the production of new composite materials characterized by the synergistic action of their components.

Various raw materials are used to produce HAps, and the possibility of using waste materials has been frequently explored. Biomaterials like oyster shells [32], eggshells [31], and bovine bones [33] have been successfully used as calcium substrates for synthesis using co-precipitation or hydrothermal methods. Power-plant byproducts—e.g., blast furnace slag [35,42] and steel slag [43]—are also good calcium substrates for the hydrothermal method. However, other byproducts, such as solid slag from bottom ash and fly ash from coal combustion [44,45]; and lignite, brown, and anthracite coal combustion [20], are useful sources of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> for the synthesis of zeolite. Furthermore, coal ash or steel slag containing SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO can be used to obtain zeolite–HAp nanocomposites [46, 47]. These methods for obtaining composites are based on hydrothermal synthesis under alkaline conditions.

Fluidized bed combustion fly ash is a byproduct that can be reused and, depending on its chemical composition and physical properties, applied as an agricultural fertilizer and construction material in aerated concrete or the production of synthetic lightweight aggregates [48,49]. Due to their high free CaO content (dependent on their origin), these ashes are chemical sequestering agents for  $CO_2$  removal [50] and can be used as mineral additives in cement pastes [51]. Fly ash is also recognized as a promising adsorbent for removing heavy

metals from multi-component systems [52]. The use of waste byproducts as secondary raw materials for the production of new materials in industrial and environmental applications is an important element of sustainability and the circular economy [53].

In this study, the subjects included four composites (CFA–HAp1–4) prepared via the HAp wet precipitation method under different reaction conditions using CFA from the Bełchatów power plant (Poland) as a substrate. The aim was to characterize the physical and chemical properties of the obtained materials as well as their abilities to adsorb Cu(II) and rhodamine B dye.

# 2. Materials and Methods

# 2.1. CFA Sample

The CFA was obtained from the storage ash heap of the Bełchatów power plant (Poland). Five primary samples of CFA (1 kg) were randomly taken from the surface layer of the heap at a depth up to 0.2 m. The primary samples were mixed to obtain a general sample of 5 kg. The laboratory sample (2.5 kg) was obtained from the general sample by coning and quartering. The laboratory CFA sample was covered with filter paper, dried under ambient conditions for 2 weeks, and then sieved on a 0.25 mm sieve. The CFA fractions that passed through the sieve constituted the research material applied to obtain the CFA–HAp composites.

#### 2.2. Synthesis of the CFA–HAp Composites

The CFA–HAp1–4 composite materials were synthesized via the in situ precipitation of HAp combined with CFA. The precipitation was carried out using wet methods differentiated by the pH and T conditions and the types and amounts of reagents, as described in Table 1. A suspension of CFA in deionized water (0.5 g in 1 cm<sup>3</sup>) was added to the reagent solutions. During each synthesis, the pH of the reaction mixture was adjusted over time through the addition of ammonia (25%). All mixtures were gently stirred for 1.5 h. The reagents were characterized by a Ca/P molar ratio of 1.67, which is the stoichiometric composition of HAp. Any white and gray CFA–HAp precipitates were removed from the solution via centrifugation at a rotation speed of 3000 rpm and then filtered and repeatedly rinsed with deionized water to adjust the pH to 7. The resulting composites were dried in an electric dryer at 120 °C for 24 h.

**Table 1.** Reagents and reaction conditions corresponding to the synthesis of each of the four CFA–HAp composites, as indicated.

CEA HAR	Reagents			Conditions	
Сга-пар	Туре	Concentration	Volume	pН	Temp.
CFA–HAp1	CFA CaCl <sub>2</sub> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0.5 g/cm <sup>3</sup> 0.5 mol/dm <sup>3</sup> 0.3 mol/dm <sup>3</sup>	40 cm <sup>3</sup> 0.5 dm <sup>3</sup> 0.5 dm <sup>3</sup>	9	60 °C
CFA–HAp2	CFA Ca(NO <sub>3</sub> ) <sub>2</sub> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0.5 g/cm <sup>3</sup> 0.5 mol/dm <sup>3</sup> 0.3 mol/dm <sup>3</sup>	40 cm <sup>3</sup> 0.5 dm <sup>3</sup> 0.5 dm <sup>3</sup>	11	room
CFA–HAp3	CFA Ca(OH) <sub>2</sub> H <sub>3</sub> PO <sub>4</sub>	0.5 g/cm <sup>3</sup> 0.5 mol/dm <sup>3</sup> 0.3 mol/dm <sup>3</sup>	40 cm <sup>3</sup> 0.5 dm <sup>3</sup> 0.5 dm <sup>3</sup>	9	room
CFA-HAp4	CFA Ca(NO <sub>3</sub> ) <sub>2</sub> (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	$0.5 \text{ g/cm}^3$ 0.5 mol/dm <sup>3</sup> 0.3 mol/dm <sup>3</sup>	40 cm <sup>3</sup> 0.5 dm <sup>3</sup> 0.5 dm <sup>3</sup>	9	room

#### 2.3. Batch Adsorption Test

The synthesized research materials were designated CFA–HAp1–4. In total, 0.5 g of each sample was weighed on an analytical balance. Then, 50 cm<sup>3</sup> of an aqueous solution of copper(II) nitrate(V) or rhodamine B ([9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride), hereafter referred to as Cu(II) and RB, respectively, was added to the glass flasks. Solutions with the following concentration ranges were used: 100–3000 mg/dm<sup>3</sup> for Cu(II) and 2–800 mg/dm<sup>3</sup> for RB. Before adding the composite to the solution, the pH was adjusted to a value of 11. The samples were then agitated on a shaker for 2 h at room temperature (20 °C), and the solutions were separated by filtration. Cu(II) and RB concentrations in the solutions before and after adsorption were measured, and the obtained data were used to determine the parameters of the adsorption isotherms. Samples of CFA–HAp1–4 at equilibrium with Cu(II) adsorbates were collected and then desorbed in distilled water at pH 2 under 2 h of agitation. The pH was corrected after the addition of the sample. The sorbents and solutions were retained for further studies to characterize the material properties.

Measurements of the Cu(II) concentrations in the solutions were conducted on a flame atomic absorption spectrometer (FAAS, Perkin-Elmer Model 3100, Waltham, MA, USA). The analytical line at 324.8 nm was selected, with a slit width of 0.7 nm. A hollow cathode lamp at 10 mA was used for Cu. The RB concentration in the solutions was determined using a UV–VIS spectrophotometer (JASCO, type V-670, Tokyo, Japan). The dependence of absorbance on the dye concentration was determined at a wavelength of 522 nm. Before measurement, the pH of the solutions was corrected.

## 2.4. Adsorption Equilibrium Modelling

The adsorption equilibrium capacity ( $q_e$ ) of the CFA–HAp1–4 was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where  $C_0$  (mg/dm<sup>3</sup>) and  $C_e$  (mg/dm<sup>3</sup>) are the Cu(II) and RB concentrations in the initial and equilibrated solutions, respectively; *m* (g) is the mass of CFA–HAp1–4 samples, and *V* (dm<sup>3</sup>) is the solution volume.

The adsorption of RB and Cu(II) on the CFA–HAp1–4 composites was studied using adsorption isotherms, whereby nonlinear Freundlich [54], Langmuir [55], and Redlich–Peterson [56] isotherms were generated. Modeling was performed using OriginPro 7.5. software. The fitting of the models to the experimental data was validated based on the values of the coefficient of determination ( $R^2$ ) and reduced chi-square statistic ( $\chi^2/DoF$ ).

#### 2.5. CFA–HAp Characterization Methods

The CFA–HAp1–4 composites were characterized both directly after synthesis and after Cu(II) and RB adsorption using the following methods.

Elemental analysis to determine the percentage of carbon, hydrogen, nitrogen, and sulfur in the composites was performed using an EA 1108 Elemental Analyser (former Carlo Erba, Italy; now Thermo Fisher Scientific, Waltham, MA, USA).

The chemical composition of the composites was also determined in the acid-digested samples. Silica content (SiO<sub>2</sub>) was determined according to the weight method, using hydrofluoric acid as an solvent. To determine the content of the remaining main components (Al, P, Fe, K, Mg, Ca, and Na), the CFA–HAp1–4 samples were dissolved in a mixture of concentrated sulfuric acid(VI), nitric acid(V), and hydrofluoric acid. The quantification was performed via flame atomic absorption spectrometry (FAAS) using a Perkin-Elmer model 3100 spectrometer.

The morphological and textural observations of the surface were carried out using a scanning electron microscope (SEM) with the VEGA 3 apparatus (TESCAN, Fuveau, France). SEM was also employed using a secondary electron (SE) detector X-ACT (Oxford Instruments, Abingdon, UK) to broaden the scope of the element content analysis. Fourier transform infrared (FT-IR) spectra were recorded on an Alpha spectrometer (Bruker, Billerica, MA, USA). The FT-IR spectra were employed a spectral range of 4000 to 400 cm<sup>-1</sup> at a resolution of 0.7 cm<sup>-1</sup>. FT-IR measurements were made on samples suspended in KBr discs.

The particle size distributions of CFA–HAp were determined via an Analysette 22 NanoTec plus laser particle sizer (Fritsch, Idar-Oberstein, Germany).

The specific surface area and total pore volume were determined via low-temperature nitrogen adsorption–desorption isotherms using a porosimeter model ASAP 2020 (Micromeritics, Norcross, GA, USA). Before measurements, the samples were degassed at 200 °C. The specific surface area was calculated via the Brunauer–Emmett–Teller method (BET) using adsorption data ranging from  $P/P_0 = 0.05$  to 0.25. The Barrett–Joyner–Halenda (BJH) method was employed to determine the total pore volume.

The point of zero charge pH (pH<sub>pzc</sub>) was determined using the pH suspension method. For measurements, we used a CP-501 pH meter (Elmetron, Zabrze, Poland). The pH<sub>pzc</sub> was determined by adjusting the 50 cm<sup>3</sup> pH of the 0.1 mol/dm<sup>3</sup> KNO<sub>3</sub> solution to a value between 2 and 13 (pH<sub>0</sub>). One gram of the composite was then added, and the final pH (pH<sub>f</sub>) was measured after 24 h of shaking on an laboratory shaker. The pH<sub>pzc</sub> was determined graphically ( $|\Delta pH| = |pH_f - pH_0|$  vs. pH<sub>0</sub>) as the abscissa value when the ordinate was equal to zero.

The pH was also measured in water extracts of CFA–HAp, obtained by shaking 1 g samples in 100 cm<sup>3</sup> of distilled water for 2 h at room temperature.

## 3. Results and Discussion

### 3.1. Physical–Chemical Characteristics of CFA–HAp Composites

In this experiment, high calcium lignite coal fly ash from the thermal power plant in Bełchatów (Poland) was applied to obtain CFA–HAp composites. The ash used in this study was classified as group C ash according to the American Society for Testing Materials (ASTM C618-05). Based on the manufacturer's information, the major components in the fly ash were oxides of SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> > 50% and CaO > 10%. The chemical composition of CFA from the Bełchatów power plant was SiO<sub>2</sub> 32.85–48.31%, Al<sub>2</sub>O<sub>3</sub> 15.08–24.02%, Fe<sub>2</sub>O<sub>3</sub> 3.56–7.04%, and CaO 19.58–31.60% [57–60]. The most common mineral composition of ash is quartz, mullite, anhydrite, anorthite, gehlenite, hematite, lime, the amorphous phase of calcium aluminosilicate glass, and unburned fuel [58–61]. The CFA from Bełchatów exhibited natural radioactivity, but the *f*1 and *f*2 activity indexes were below the respective limits of 0.79–0.90 and 118–150 Bq/kg [58,62].

The obtained composites were characterized through various methods; Table 2 presents the results. The chemical compositions of the CFA–HAp1–4 composites were very similar to each other. No significant differences were observed in the contents of the individual components. In terms of quantity, the dominant component in the composites was hydroxyapatite, as represented by a high content of CaO and P<sub>2</sub>O<sub>5</sub>. Based on this result, we calculated that the Ca/P molar ratio in the CFA–HAp1–4 was close to 1.67, which is a value characteristic of HAp [34,37]. The CFA component in the composites was represented by the presence of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in the composites ranged from 1.52 to 1.59. Fly ash of various origins and other power plant byproducts are the most popular solid wastes for the synthesis of zeolites [63]. The HAp-zeolite (Na-X) microcomposite can be easily synthesized from blast furnace slag, H<sub>3</sub>PO<sub>4</sub>, and NaOH [43]. The results of the elemental analysis are presented in Table 3. Carbon and sulfur originating from the CFA component were identified, along with the nitrogen that originated from the reagents and was added during synthesis.

Figure 1 shows the results of the FT-IR analysis of the four composites. Here, bands corresponding to the hydroxyapatite structure are visible in the spectra of all samples. These include bands attributed to the vibrations of the phosphate group  $PO_4^{3-}$ , such as the symmetrical stretching of P–O at 960 cm<sup>-1</sup>, the asymmetrical stretching of P–O at 1020–1080 cm<sup>-1</sup>, and the bending of O–P–O at 585–610 cm<sup>-1</sup>. The small half-width

 $(11-15 \text{ cm}^{-1})$  of the band with a maximum of 960 cm<sup>-1</sup>, characteristic of calcium phosphate, provides additional confirmation of the hydroxyapatite structure. At a wavenumber of 1458 cm<sup>-1</sup>, a band of low intensity corresponding to  $CO_3^{2-}$  is visible. Trace amounts of carbonate ions were detected, because hydroxyapatite composites can combine with  $CO_2$  from the air [64].

		Value				
N0.	Determination	CFA–HAp1	CFA–HAp2	CFA–HAp3	CFA-HAp4	
1.	pH <sub>PZC</sub>	6.43	6.03	7.16	6.12	
2.	pH of water extract	6.70	6.23	7.59	6.69	
3.	Bulk density, kg/m <sup>3</sup>	410	390	342	312	
4.	Moisture content, % ( $w/w$ )	3.10	3.25	3.58	3.21	
5.	Specific surface area, m <sup>2</sup> /g	17.40	18.53	18.02	17.95	
6.	Total pore volume, cm <sup>3</sup> /g	0.26	0.28	0.33	0.34	
7.	Average particle size, µm	36	41	32	37	
8.	Chemical composition, % (w/w): SiO <sub>2</sub> P <sub>2</sub> O <sub>5</sub> Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> K <sub>2</sub> O MgO CaO Na <sub>2</sub> O SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	13.80 42.5 8.79 6.04 2.16 1.55 43.7 0.62 1.57	12.81 41.7 8.43 5.92 2.53 1.21 42.3 0.56 1.52	13.20 43.23 8.57 5.64 2.72 1.42 44.42 0.70 1.54	14.21 42.63 8.94 6.13 2.02 1.63 43.96 0.73 1.59	

Table 2. Physical and chemical properties of the CFA-HAp composites.

Table 3. Elemental ar	alysis of the	CFA-HAp con	mposites (% $w/c$	w)
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	Composite				
Element	CFA–HAp1	CFA–HAp2	CFA–HAp3	CFA–HAp4	
Ν	0.9	2.3	2.8	1.5	
С	13.4	5.5	4.3	8.8	
S	0.06	9.6	14.1	5.0	
Н	0.5	1.4	6.8	5.3	

Based on the FT-IR spectra, the hydroxyapatite component in the composites can be classified into two groups: type B apatites (vibrations from  $CO_3^{2-}$  ions at a wavenumber of 1450 cm<sup>-1</sup>) and type AB apatites (with an additional band at a wavenumber of 1515 cm<sup>-1</sup>) [65]. The presence of CFA-derived components in CFA–HAp1–4 was not confirmed in the FT-IR spectra (Figure 1). The asymmetrical stretching vibration of bridging bands of Si–O–Si(Al) in CFA can be detected at 1050–1080 cm<sup>-1</sup> [66,67]. However, this is also a region with strong P–O absorption bands of the HAp component, which could mask the weaker-intensity bands from the Si–O–Si(Al) groups. Ultimately, the presence of the CFA component in the composite was confirmed by the results of the chemical composition analysis.

HAp powders with a Ca/P ratio of 1.67 tend to form small agglomerates, with grains of 30  $\mu$ m on average [68]. Fly ash particles present similar sizes: 15–45  $\mu$ m [69] and 22  $\mu$ m [70]. It was determined through laser analysis that the CFA–HAp1–4 composite grains are similar in size and fall within the average range of 30–40  $\mu$ m (Table 2).



Figure 1. FT-IR spectra of the CFA-HAp1-4 composites.

The BET specific surface area of CFA–HAp1–4 and the BJH total pore volume were not notably variable, with values in the range of 17.40–18.53 m<sup>2</sup>/g and 0.26–0.34 cm<sup>3</sup>/g, respectively. Generally, depending on the type of procedure used to obtain HAp, the porosimetry parameters of HAp can be diverse (e.g., 12.5–22.9 m<sup>2</sup>/g [71], 26.34–86.15 m<sup>2</sup>/g, and 0.12–0.51 cm<sup>3</sup>/g) [72]. Similarly, depending on its origin, coal fly ash can also have varied parameters (e.g., 12.1 m<sup>2</sup>/g [73], 16.2 m<sup>2</sup>/g and 0.031 cm<sup>3</sup>/g [74], 17.4 m<sup>2</sup>/g [52], 35 m<sup>2</sup>/g and 0.042 cm<sup>3</sup>/g [75], and 39.3 m<sup>2</sup>/g and 0.171 cm<sup>3</sup>/g) [70].

The pH<sub>PZC</sub> of synthetized CFA–HAp1–4 occurs from pH 6.03 to 7.16 (Table 2). This result could be caused by the presence of both components, CFA and HAp, whose pH<sub>PZC</sub> values vary greatly. The pH<sub>PZC</sub> of CFA was found to be 8.1 [66], 10.70 [76], and 12.17 [77], depending on its origin and composition. The pH<sub>PZC</sub> of HAp occurs in a wide range, including 3.0 [78], 4.6 and 5.8 [33], 6.22–6.64 [79], and 7.9 [80], and strongly depends on the synthesis conditions and precursor types. However, the pH<sub>PZC</sub> of CFA is in the alkaline region, whereas the pH<sub>PZC</sub> of HAp is in the acidic region, and the pH<sub>PZC</sub> of CFA–HAp1–4 is a result of the properties of both materials. The water extracts of the composites in this study were neutral, with pH in the range of 6.23–7.59. These extracts did not affect the changes in the pH values of the solutions in the sorption experiments.

## 3.2. Cu(II) and RB Adsorption Equilibrium

To characterize the ideal adsorption system, it is necessary to determine which mathematical description of the adsorption equilibrium best fits the experimental data. For this purpose, adsorption isotherms are used. These isotherms are considered a valid method for comparing the adsorption properties of materials. The results for matching the isotherm models of Cu(II) and RB adsorption onto CFA–HAp1–4 are presented in Tables 4 and 5.

Based on the highest values of  $R^2$  and the smallest values of  $\chi^2/DoF$  as indicators of the best match, we determined that the Langmuir model, which calls for coverage with an adsorbate monolayer, does not adequately describe Cu(II) adsorption in the case of all four composites. The equilibrium of Cu(II) adsorption onto the CFA–HAp2–4 composites was characterized by the Redlich–Peterson isotherm, which is an empirical model of a mixed adsorption mechanism that does not represent an ideal monolayer covered by an adsorbate. The Freundlich model had the best match in the case of equilibrium adsorption onto CFA–HAp1, and the Redlich–Peterson model is almost reduced to Freundlich model ( $K_{RP}/a_{RP} \approx K_F$  and  $1 - B \approx 1/n$ ). The Redlich–Peterson model was also used to predict the adsorption of RB, the cationic dye, onto CFA–HAp1–4.

Freundlich Isotherm							
Composite $R^2$ $\chi^2/\text{DoF}$ $\frac{K_{F,}}{(\text{mg/g})(\text{L/mg})^{1/n}}$ $n$							
CFA–HAp1	0.989	3.99	6.9	4.1			
CFA–HAp2	0.910	113	16.5	4.7			
CFA–HAp3	0.948	40.9	9.8	3.9			
CFA-HAp4	0.980	9.4	14.9	5.6			
		Langmu	ir Isotherm				
Composite $R^2$ $\chi^2$ /DoF $K_L$ , dm <sup>3</sup> /mg $q_{max}$ , mg/g							
CFA–HAp1	0.889	39.7	$9.10^{-3}$	44.4			
CFA–HAp2	0.923	97.6	$9.2 \cdot 10^{-2}$	73.6			
CFA–HAp3	0.830	134	$8.7 \cdot 10^{-3}$	65.9			
CFA-HAp4	0.933	30.6	0.1	45.3			
Redlich-Peterson Isotherm							
Composite	<i>R</i> <sup>2</sup>	$\chi^2/\text{DoF}$	$K_{RP}$ , dm <sup>3</sup> /g	$a_{RP}$ , (dm <sup>3</sup> /mg) <sup>B</sup>	В		
CFA–HAp1	0.989	4.99	$1.4 \cdot 10^4$	$2 \cdot 10^3$	0.7		
CFA–HAp2	0.964	56.8	14.8	0.42	0.9		
CFA–HAp3	0.959	40.2	14.6	1.03	0.8		
CFA-HAp4	0.993	3.9	11.8	0.70	0.9		

Table 4. Parameters of the isotherm models of Cu(II) adsorption on the CFA-HAp composites.

Table 5. Parameters of the isotherm models of RB adsorption on the CFA-HAp composites.

Freundlich Isotherm						
Composite	$R^2$	$\chi^2$ /DoF	<i>K<sub>F</sub>,</i> (mg/g)(L/mg) <sup>1/n</sup>	n		
CFA–HAp1	0.882	34.7	1.12	1.5		
CFA–HAp2	0.869	50.93	1.47	1.5		
CFA-HAp3	0.837	12.4	0.86	1.9		
CFA–HAp4	0.880	17.3	0.98	1.7		
		Langmu	ir Isotherm			
Composite $R^2$ $\chi^2$ /DoF $K_L$ , dm <sup>3</sup> /mg $q_{max}$ , mg/g						
CFA–HAp1	0.939	18.0	$6.22 \cdot 10^{-3}$	73.0		
CFA-HAp2	0.922	30.3	$7.82 \cdot 10^{-3}$	87.0		
CFA-HAp3	0.932	5.1	$8.64 \cdot 10^{-3}$	27.0		
CFA–HAp4	0.958	6.1	$7.02 \cdot 10^{-3}$	42.0		
Redlich-Peterson Isotherm						
Composite	$R^2$	$\chi^2/{ m DoF}$	$K_{RP}$ , dm <sup>3</sup> /g	$a_{RP}$ , (dm <sup>3</sup> /mg) <sup>B</sup>	В	
CFA-HAp1	0.996	5.1	0.48	$2.42 \cdot 10^{-4}$	0.8	
CFA-HAp2	0.989	9.6	0.74	$3 \cdot 10^{-3}$	0.75	
CFA-HAp3	0.975	3.1	0.26	$4 \cdot 10^{-3}$	0.85	
CFA–HAp4	0.998	0.8	0.47	$6.1 \cdot 10^{-3}$	0.79	

Despite offering a worse fit to the experimental data, the Langmuir model was used to determine the maximum adsorption capacity. Based on the values of the  $q_{\text{max}}$  constant, which are presented in Tables 4 and 5, the following series of adsorption abilities of the CFA–HAp composites were determined:

- Cu(II): CFA-HAp2 > CFA-HAp3 > CFA-HAp4  $\approx$  CFA-HAp1,
- RB: CFA-HAp2 > CFA-HAp1 > CFA-HAp4 > CFA-HAp3.

The CFA–HAp2 (Cu(II)  $q_{max} = 73.6 \text{ mg/g}$  and RB  $q_{max} = 87.0 \text{ mg/g}$ ) showed the best adsorption properties in terms of having the highest capacity. Figures 2 and 3 graphically illustrate the model matches for the studied composites. The CFA–HAp2 composite was obtained using fly ash, Ca(NO<sub>3</sub>)<sub>2</sub>, and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> in an alkaline environment at room temperature.



Figure 2. Freundlich (a), Langmuir (b), and Redlich–Peterson (c) isotherm of Cu(II) adsorption on Table 2 composite.

The obtained dye-removal effects were promising compared to the abilities of CFA and HAp. Using 1 g of HAp, the adsorption capacities for various dyes was characterized, including 29.5 mg of methylene blue [16], 49.1 mg of brilliant green [81], 85.51 mg of carmine [30], and 125 mg of reactive yellow [31]. This comparison is, naturally, an approximation due to the various properties of the dyes and different experimental conditions of the pH-dependent process. The adsorption capacity of RB onto CFA was 4.25 mg/g at pH 1 and decreased along with the pH: the adsorption capacity was 2.4 mg/g at pH 12 and was about 2.75 mg/g at pH 11 [82]. These capacities were much lower than those obtained for the CFA–HAp composites. The closest comparison can be made with the mineral and organic materials presented in Table 6. Given these results, the adsorption capacities of the CFA–HAp composites appear promising.



Figure 3. Freundlich (a), Langmuir (b), and Redlich–Peterson (c) isotherm of RB adsorption on the CFA–HAp2 composite.

Adsorbent	Adsorption Capacity mg/g	рН	Ref.
CFA-HAp composites	27–87	11	present study
CFA	2.4-4.25	1–12	[82]
CFA magnetic spheres–SiO <sub>2</sub> –polyaniline	41.49	11	[83]
montmorillonite	17.1	-	[84]
magnetic ZnFe <sub>2</sub> O <sub>4</sub> nanocomposite	12.1	7	[85]
	36.7	4	[9/]
Araucaria angustijoid sterile bracts	24.6	8	[86]
	3.44	2	[07]
exnausted corree ground powder	0.814	10	[87]
acid-modified banana peel	9.522	2	[88]
activated carbon from almond shell	255.39	-	[89]

Table 6. Comparison of the adsorption capacities of various adsorbents for RB.

To compare the ability of the obtained composite to remove heavy metals with that of other materials such as CFA or HAp, the  $q_{\rm max}$  of CFA–HAp2 was represented as 1.16 mmol Cu/g. As shown in Table 7, the adsorption capacity determined for unprocessed CFA varied from 0.039 to 0.894 mmol/g. HAp with a typical composition was characterized by a greater adsorption capacity of 0.494–1.43 mmol/g. Making a direct comparison is difficult, however, because the cited data were obtained from studies conducted in slightly

acidic environments, whereas, an alkaline environment was applied in our adsorption– precipitation studies. The Langmuir adsorption capacities obtained for raw CFA at pH 9 were 7.5 mg Cu/g [90] and 8.1 mg Pb/g [70].

		Adsorptio		
Adsorbate	Adsorbent	mg/g	mmol/g	– Ret.
Cu(II)	CFA-HAp composites	44.4–73.6	0.699–1.16	present study
Cu(II)	FA from fluidized bed combustion FA from fixed bed combustion	8.54 5.09	0.134 0.080	[91]
Cu(II)	CFA	56.8	0.894	[92]
Pb(II)	FA from pulverized coal combustion	8.1	0.039	[70]
Pb(II)	FAs from coal-biomass combustion	34.8 28.9	0.168 0.139	[93]
Cu(II)	НАр	31.4	0.494	[94]
Cu(II)	HAp-coated limestone	90.90	1.43	[95]
Zn(II)	Mg–HAp	62.11	0.950	[96]
Zn(II)	HAp nanopowder	57.504	0.880	[97]
Pb(II)	synthetic HAp commercial HAp	166.67 142.86	0.804 0.689	[33]
Cd(II)	synthetic HAp commercial HAp	138.89 125	1.24 1.11	[33]
Cd(II)	НАр	119	1.06	[98]

Table 7. Comparison of the adsorption capacity of CFA and HAp for heavy metals.

The sorption experiment was carried out under alkaline conditions, during which the HAp was stable and did not leach out [98], which is a beneficial characteristic. Additionally, textile wastewaters are often alkaline [99,100]. These conditions can also prevent the potential leaching of copper from the CFA part of the composites [101]. As is known, fly ash is characterized by a diverse content of toxic elements present in water-soluble and acid-soluble fractions, some of which are mobile under certain environmental conditions (e.g., 2.6% Cu, 3.4% Zn, 23.2% Ni, and 24% Co) [102,103]. Moreover, alkaline conditions can favor the elution of certain elements, such as Se, Mo, and Sr [101]. However, the degree of leaching depends not only on the pH but also on the individual composition and origin of the ash [101,104]. Taking this factor into account, further research on CFA–HAp composites that includes tests for leaching of elements is needed.

The speciation of RB is strongly dependent on pH [105,106]. As shown in Figure 4, under acidic conditions, the cationic form predominates. Under neutral conditions, the carboxyl group dissociates, and the molecule becomes a zwitterion with a positive and negative charge. In an alkaline environment, RB assumes the closed uncharged form of lactone. Below pH 5, favorable adsorption is indicated as a result of electrostatic interactions between the RB cation and the deprotonated sorbent surfaces, as well as by ion exchange between the RB cation and the protonated sorbent surfaces [82,84,86,87,105,106]. At higher pH, the mechanism for the adsorption of the zwitterion RB particles involves complexing a lone nitrogen pair with a metal hydroxyl group on the adsorbent surface via hydrogen bonding through a water bridge [84]. In a highly alkaline environment, the interactions are limited but not inhibited [84,87] and, in some cases, do not affect the adsorption efficiency of RB [83].

At pH 11, the surface of the CFA–HAp1–4 composites was strongly deprotonated due to the composites  $pH_{PZC}$  being 6.12–7.16 (Table 2). Based on this result and RB speciation, it can be assumed that there was no cation exchange or electrostatic attraction between the negatively charged surfaces of CFA–HAp1–4 and the uncharged dye molecule. Although the surfaces of the hydroxyapatites [107] and aluminosilicates [108] are characterized by

the presence of numerous hydroxyl groups, strong deprotonation inhibits the formation of hydrogen bonds. For this reason, we considered a different basis for RB adsorption onto the composites. In the RB lactone structure, the carbonyl group is characterized by reactivity. Since the double band is polar, and the carbon is slightly positive, the carbonyl group can interact with strongly negatively charged groups on the CFA–HAp1–4 surfaces, leading to an addition reaction. This hypothesis, however, requires further research. Moreover, as previously shown, the adsorption is mixed. The *B* coefficient in the Redlich–Peterson model takes values close, but not equal, to 1. This result suggests that in addition to chemisorption, interactions of a physical adsorption nature also occur. These may be  $\pi$ – $\pi$  interactions between the adsorbate molecules.



Figure 4. The speciation of RB: cation (A), zwitterion (B), and lactone (C).

In alkaline environments, the hydrolysis of Cu(II) leads to the formation of the following hydroxo-Cu(II) complexes: Cu(OH)<sub>4</sub><sup>2–</sup>, Cu(OH)<sub>3</sub><sup>–</sup>, Cu(OH)<sup>+</sup>, and Cu(OH)<sub>2</sub>. However, at the applied concentration range, Cu(OH)<sub>2(s)</sub> dominates [109,110]. Previous studies reported the adsorption of divalent metal ions in the form of hydroxides from an alkaline solution on aluminosilicates, representing the CFA component [111,112]. According to the described mechanism, Cu(OH)<sub>2</sub> can interact with three-coordinated aluminium ions, forming Lewis acid centers.

In the case of HAp, the mechanism for removing heavy metals has a dual nature [96,113,114] that involves (i) dissolution–precipitation (releasing Ca and binding metals from the solution through the ion exchange process) and (ii) surface complexation that leads to the formation of chemical bonds between the adsorbent and adsorbate. Depending on the research conditions, the authors reported the predominance of dissolution–precipitation [94] or chemisorption [78]. The removal of Cu(II) on CFA–HAp1–4 was extended by a desorption test carried out in an acidic environment (pH 2). Figure 5 presents the results of this test. It was determined that only a small part of the Cu(II) adsorbate was weakly associated with the surfaces of the composites. A much greater portion of the adsorbate was Cu(II), which was permanently bound with the surface of the composites and did not desorb. These results confirm the mixed, chemical, and physical nature of adsorption determined from optimal fitting with the Redlich–Peterson model. The results obtained for weak desorption confirm previous reports on the permanent binding of heavy metal ions (Pb, Cu) by HAp [113]. Attempts to remove Cu(II) from CFA–HAp1–4 indicate the permanent binding of a large portion of the adsorbate to the surface of the composite.

#### 3.3. Characteristics of CFA–HAp2 Composite with Cu(II) and RB Adsorbates

The surface of the CFA–HAp2 composite was observed using SEM, and the elemental contents of the micro areas were established (Figure 6a). For comparison, the samples of this composite after Cu(II) and RB adsorption were also measured (Figure 6b,c). Covering the CFA–HAp2 surface with Cu(II) adsorbates confirmed the signal in the SE spectrum, which did not appear in the analysis of the composite surface before the adsorption process. When comparing these spectra, the it was found that the spectrum of CFA–HAp2 was characterized by an intense Ca spectral signal, which was less pronounced in the CFA–HAp2–Cu(II) spectrum, which corresponds to the calculated elemental content in the micro areas of the selected surface. The composite sample with RB adsorbates was characterized by a significant change in surface morphology. There was also a strong chlorine signal in

the spectrum that could indicate the presence of a dye molecule adsorbed in the form of undissociated lactone.



Figure 5. The amount of Cu(II) desorbed from CFA-HAp1-4 under acidic conditions.



**Figure 6.** SEM surface micrograph, SE spectra, and contents of identified elements for the CFA–HAp2 composite: (a) before adsorption, (b) after Cu(II) adsorption, and (c) after RB adsorption.

The CFA–HAp2 composite with Cu(II) and RB adsorbates were subject to FT-IR analysis. The spectra are charted in Figures 7 and 8, and the numbered bands are listed in Tables S1 and S2 (from Supplementary Materials). In the CFA–HAp2 spectra, after Cu(II) and RB adsorption, a significant change in the wavenumber value for the OH<sup>-</sup> group was caused by the adsorption of water from solution. The phosphate(V) group bands appear practically unchanged. A comparison of the spectra after Cu(II) adsorption and desorption (Figure 7b) indicates the invariability of the wavenumber values after desorption. This result confirms the strong connection of the Cu(II) adsorbate with the CFA–HAp2 surface and its lack of susceptibility to desorption.

In comparing the spectra before and after the RB adsorption process bands characteristic of C–H binding are revealed. The C–H stretching mode peak at 2924 cm<sup>-1</sup> demonstrates that the dye was adsorbed onto the surface of the composite. Adsorption of the RB molecule took place on the CFA–HAp2 surface, as confirmed by the visible bathochromic shift of the spectrum maximum for the dye (towards longer wavelengths).



**Figure 7.** Comparison of FT-IR spectra of CFA–HAp2 samples: (**a**) before and after Cu(II) adsorption; (**b**) after Cu(II) adsorption and desorption.



Figure 8. FT-IR spectra of CFA-HAp2 before and after RB adsorption and for RB dye alone.

# 4. Conclusions

CFA was successfully used as a substrate in the synthesis of HAp, which yielded a composite. Composites with similar physical and chemical properties can be produced using a low-temperature wet precipitation method under alkaline conditions based on various reagents. The adsorption properties of composites towards Cu(II) and RB are diverse, and the most effective adsorbent was the composite produced using fly ash,  $Ca(NO_3)_2$ , and  $(NH_4)_2$ HPO<sub>4</sub> in an alkaline environment (pH 11) at room temperature.

The adsorption of hydroxo-Cu(II) complexes and RB dye in the form of lactone is most accurately described by the Redlich–Peterson isotherm, which indicates a mixedmodel process. The clear advantage of chemisorption over physisorption was indicated in the Cu(II)–CFA–HAp system, where many Cu(II) adsorbates were not susceptible to desorption in the acidic environment. The RB molecules in a lactone-uncharged form were favorably adsorbed even by strongly deprotonated CFA–HAp surfaces.

The presence of composite-bound adsorbates was confirmed by analyzing the elemental contents on the surface (SE) alongside spectral analysis (FT-IR). The synthesized coal-fly-ash–hydroxyapatite composites should be investigated further as materials for removing heavy metals and dyes from industrial alkaline wastewater.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/min11070774/s1. Table S1: Types of vibrations, bands, and intensities for the FT-IR spectra of CFA–HAp2 before adsorption (black), CFA–HAp2 after Cu(II) adsorption (red), and CFA–HAp2 Cu(II) desorption (blue); Table S2: Types of vibrations, bands, and intensities for the FT-IR spectra of CFA–HAp2 before adsorption (black) and CFA–HAp2 after the adsorption of RB (red) and for RB dye alone (blue).

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