A Mineral By-Product from Gasification of Poultry Feathers for Removing Cd from Highly Contaminated Synthetic Wastewater

Zygmunt Mariusz Gusiatin [1],*, Jurate Kumpiene [2], Sylwia Janiszewska [3], Sławomir Kasiński [1] [ID]**, Mariusz Pecio [4], Robert Piec [4]** [ID] **and Maja Radziemska [5]** [ID]

[1] Department of Environmental Biotechnology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, Sloneczna 45G, 10-719 Olsztyn, Poland; slawek@kasinski.pl

[2] Waste Science and Technology, Lulea University of Technology, 97187 Lulea, Sweden; jurate.kumpiene@ltu.se

[3] REMEA Sp. z o.o., Powazkowska 44c, 01-797 Warsaw, Poland; sjaniszewska@remea-group.com

[4] The Main School of Fire Service, Slowackiego 52/54, 01-629 Warsaw, Poland; mpecio@sgsp.edu.pl (M.P.); rpiec@sgsp.edu.pl (R.P.)

[5] Institute of Environmental Engineering, Warsaw University of Life Sciences, Nowoursynowska 159, 02-776 Warsaw, Poland; maja_radziemska@sggw.edu.pl

* Correspondence: mariusz.gusiatin@uwm.edu.pl; Tel.: +48-8952-341-86

Abstract: Ash from poultry feather gasification was investigated as an adsorbent for Cd removal from synthetic wastewater under a range of operational conditions: initial pH (2–8) and salinity (8–38 mS/cm) of wastewater, ash dosage (2.5–50 g/L), Cd concentration (25–800 mg/L) and contact time (5–720 min). The ash was highly alkaline and had low surface area and micropores averaging 1.12 nm in diameter. Chemical/mineralogical analysis revealed a high content of P_2O_5 (39.9 wt %) and CaO (35.5 wt %), and the presence of calcium phosphate, hydroxyapatite and calcium. It contained only trace amounts of heavy metals, BTEX, PAHs and PCBs, making it a safe mineral by-product. Cd adsorption was described best with Langmuir and pseudo-second order models. At pH 5, an ash dosage of 5 g/L, 40 min contact time and 100 mg Cd/L, 99% of Cd was removed from wastewater. The salinity did not affect Cd sorption. The maximum adsorption capacity of Cd was very high (126.6 mg/g). Surface precipitation was the main mechanism of Cd removal, possibly accompanied by ion exchange between Cd and Ca, coprecipitation of Cd with Ca-mineral components and Cd complexation with phosphate surface sites. Poultry ash effectively removes high concentrations of toxic Cd from wastewater.

Keywords: poultry waste; adsorption; heavy metal; sorption isotherms; kinetics; instrumental analyses

1. Introduction

Heavy metals are commonly found in industrial wastewater from mining, electroplating, metallurgy and chemical plants [1]. They pose a threat to the environment due to their toxicity, non-biodegradability, persistence and bioaccumulation at low concentrations [2]. Apart from As, Cr, Hg and Pb, Cd has the most serious effects on living organisms and the environment. It is thought that the largest anthropogenic source of Cd released to aquatic environments is the smelting of non-ferrous metal ores [3]. Moreover, this metal is used to make Ni-Cd batteries, pigments, phosphate fertilizers, alloys and metal plating [4]. About 17,000 tons of Cd is used in industry annually, of which only 5% is recovered [5]. In wastewater from the chemical and metallurgical industries, Cd concentrations range from 0.1 to 100 mg/L [6]. In battery industry effluent, Cd concentrations are over 100 mg/L [7]. There are also technological reasons why heavy metals need to be removed from wastewater, as they can interfere

with biological wastewater treatment and biochemical stabilization of sewage sludge. Heavy metal concentrations in treated wastewater are tightly regulated, due to the negative effect of these metals on the environment. Under Polish law, permissible metal concentrations in treated wastewater depend on the type of metal and the industry. For Cd, these values range from 0.05 (glass industry) to 0.4 mg/L (most industries) [8].

For legal, environmental and technological reasons, more efficient technologies have been implemented to eliminate heavy metals from wastewater. Adsorption before biological treatment of wastewater is one of the most useful of these technologies, and due to its simplicity, low cost and high efficiency, it is more attractive and effective than conventional methods such as precipitation, coagulation, solvent extraction or reverse osmosis [9]. Those other methods are very often ineffective when Cd concentrations in wastewater are very high. The effectiveness of metal adsorption depends on the adsorbent type. Up to now, a variety of adsorbents have been tested for adsorption of Cd, including plant-based adsorbents, agricultural products and industrial waste [9–11]. Zeolites, clay minerals, activated carbons and nanomaterials are among the most popular metal adsorbents [12], and increasing attention is being given to the use of adsorbents from waste to implement the principles of a circular economy in wastewater treatment.

The poultry industry is rapidly developing around the world. In 2018, the European Union (EU) produced 15.2 million tons of poultry meat. About 70% of EU production of poultry meat came from Poland (16.8%), the United Kingdom (12.9%), France (11.4%), Spain (10.7%), Germany (10.4%) and Italy (8.5%) [13]. Worldwide, about 96 million tons of poultry meat is produced annually, including about 85 million tons of chicken meat, 5.6 million tons of turkey meat and 4.4 million tons of duck meat [14]. The expansion of poultry production around the world has increased generation of different poultry wastes, i.e., viscera, feet, head, bones, blood and feathers. Feathers are one of the most resistant slaughterhouse wastes and constitute up to 10% of all waste generated by the poultry industry [15]. This means that about 8.5 million tons of chicken feathers, 0.6 million tons of turkey feathers and 0.4 million tons of duck feathers are generated annually.

Feathers are not directly used for industrial applications on a large scale due to their specific properties. Nevertheless, there are attempts to directly use poultry feathers or their components in pollutant adsorption. In order to use feathers directly as an adsorbent, they need to be pretreated with water, detergent and alcohol and then dried [16]. Keratin, a protein present in feathers, is used to prepare special composites for wastewater decoloration [17] or to remove heavy metals and metalloids from water or wastewater, such as Co [18], As [19], Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb [20].

Considering the growing interest in thermal waste treatment technologies, an interesting alternative for waste management is converting feathers or poultry litter into energy by thermochemical processes, such as gasification [15,21]. Although thermal treatment of feathers is limited by their high water content, they can be successfully gasified in fixed-bed gasifiers [22]. In order to implement a circular economy, greater attention should be given to the proper disposal and use of the ash that is a by-product from gasification of poultry feathers. So far, poultry-feather ash is considered waste and the proper method for its management has not been proposed. An attractive method for managing this by-product could be using it as an adsorbent for heavy metals or an amendment for metal contaminated soils. Despite significant progress made in using mineral adsorbents for metal removal from water and wastewater, ash from gasification of poultry feathers has not been fully characterized and tested as a metal sorbent. There is only one paper indicating successful metal removal from an aqueous solution using chicken bone ash [23]. The ash was prepared in laboratory conditions, without detailed characterization. Most existing studies have evaluated the adsorption characteristics of heavy metals with the use of fly ash from coal combustion [24,25], chemically modified coal fly ash [26,27] and fly ash and bottom ash from wood pellet thermal power plants [28]. The type of feedstock affects the chemical composition and physical properties of fly ash and its adsorption performance [29]. Park et al. [28] have found that fly ash from wood pellet thermal power plants consisted of inorganic compounds such as $CaSiO_3$, P_2O_5 and K_2O, whereas bottom ash showed properties similar to biochar

from organic biomass. Moreover, not all fly ashes can be used as adsorbents due to their impacts on the environment and human health. For example, municipal-solid-waste incinerator fly-ash contains large quantities of metals/metalloids, chlorides and organic pollutants and is considered a hazardous waste [30]. Since the characteristics of ash from coal, wood or municipal solid waste can be different than those of poultry feathers, it is of critical importance to determine the characteristics and the sorption capacity of poultry-feather ash for further development of management of this by-product via its utilization in water and wastewater treatment technologies.

For this reason, the present study was designed with two aims in mind: first, to provide a detailed characterization of poultry-feather ash from a real installation for thermal waste conversion with regard to its potential use as a new adsorbent by examining its physical, chemical and mineralogical composition, using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis, and its important organic and inorganic contaminants. Second, to assess the effectiveness of the ash for treating synthetic wastewater highly contaminated with Cd under various operational parameters (pH, salinity, adsorbent dosage, contact time and initial metal concentration) by performing batch adsorption experiments. Additionally, with the results of Cd removal and the characterization of the ash after adsorption, the main process mechanisms were inferred.

2. Materials and Methods

2.1. Adsorbent

Ash from gasification of poultry feathers was used as a metal adsorbent. The ash came from an industrial-scale plant located in Warmia and Mazury Province (Poland). The feathers were dewatered in a screw press to a final moisture content of 50%, then gasified in a fixed bed gasifier at 1000–1200 °C with a small quantity (up to 10%) of poultry processing waste (bones, beaks and claws). The rate at which the feathers were dispensed to the gasifier was 1200 kg/h, and the height of the bed was 50% of the gasifier. Before the adsorption experiments, the ash was milled in a RETSCH SM-100 cutting mill to obtain ≤0.5 mm particles. The appearance of the ash before and after milling is shown in Figure 1. For preservation, the ash was kept in plastic bags to minimize contact with moisture.

(**a**)   (**b**)

Figure 1. Ash from gasification of poultry feathers, shown before milling (**a**) and after milling (**b**).

2.2. Preparation of Synthetic Wastewater

Synthetic wastewater was prepared by dissolving a known weight of cadmium nitrate salt ($Cd(NO_3)_2 \cdot 4H_2O$) in distilled water (1 g/L), and then by diluting the stock solution with distilled water to a concentration of 100 mg Cd/L (pH 5.5, electrical conductivity 5.9 mS/cm). The solutions with Cd concentrations lower than 100 mg/L that were required for the experiment were prepared by direct dilution of the working solution. To examine the effect on Cd adsorption capacity of different salinity levels in the synthetic wastewater, $NaNO_3$ was used. The pH in the synthetic wastewater was adjusted

with 0.1 M HNO$_3$ or 0.1 M NaOH. All reagents were of analytical-grade and were purchased from Sigma-Aldrich (Poland).

2.3. Batch Adsorption Experiments

The experiments on Cd removal with poultry ash were performed at 25 °C in 50 mL falcon tubes. The effects on Cd sorption of five operational conditions were studied: wastewater pH, adsorbent dosage, contact time, metal concentration and wastewater salinity. The experimental conditions for Cd adsorption were adapted from suitable references [31–35]. The setup for Cd sorption with the ranges of the operational conditions is presented in Figure 2. For each experiment, 20 mL of synthetic wastewater and 0.1 g of poultry ash (except for the adsorbent dosage experiment) were used. The experiments were conducted in triplicate.
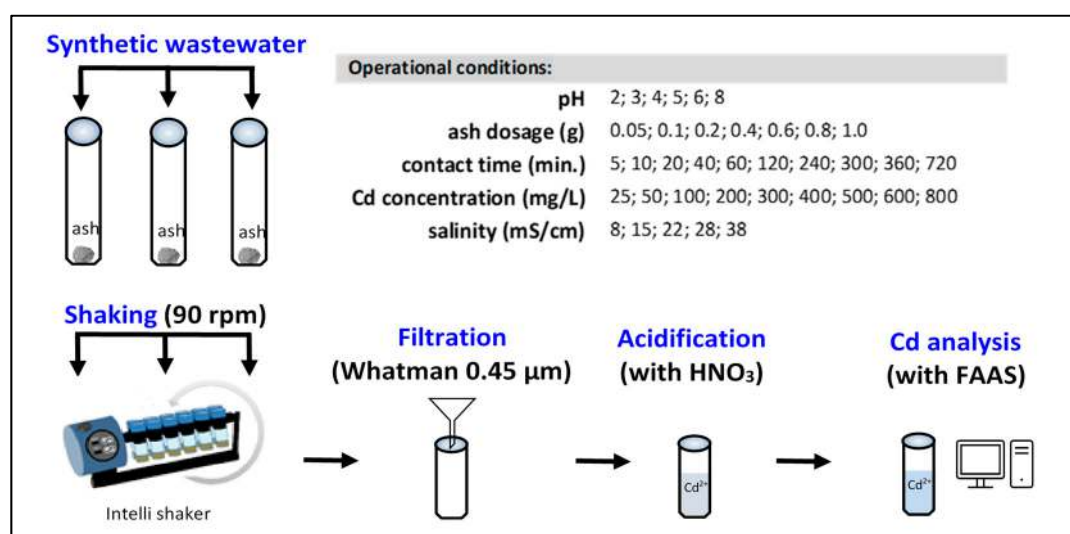

Figure 2. Batch experiments for investigating Cd adsorption onto poultry ash under different operational conditions.

2.4. Calculations and Models

The amount of Cd adsorbed onto ash (q$_{exp}$) and the efficiency of Cd removal (E) were calculated using the following formulas:

$$q_{exp} = \frac{(C_0 - C_e)}{m} \times V \tag{1}$$

$$E = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

where m is the mass of adsorbent (g), V is the volume of synthetic wastewater (L), C$_0$ is the initial Cd concentration in wastewater (mg/L) and C$_e$ is the equilibrium Cd concentration in the supernatant (mg/L).

Adsorption kinetics models: To predict the rate at which Cd would be removed from aqueous solutions, three models were used:

Pseudo-first-order model:

$$q_t = q_e\left(1 - e^{k_1 t}\right) \tag{3}$$

Pseudo-second-order model:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

Intraparticle diffusion model:

$$q_t = k_i\, t^{1/2} + C_i \tag{5}$$

where: q_e is the amount of Cd adsorbed at equilibrium (mg/g), q_t is the amount of Cd adsorbed at a specific contact time (mg/g), k_1 is a rate constant (1/min), k_2 is a rate constant (g/mg/min), h is the initial adsorption rate (mg/g/min), k_i is the intraparticle diffusion rate constant (mg/g/min$^{1/2}$), C_i is constant related to the thickness of the boundary layer (mg/g) and t is the contact time (min) [26].

Equilibrium adsorption models: To evaluate and compare the adsorption capacities of Cd and to provide some insight into adsorption mechanisms, the following models were used:

Freundlich model:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

Langmuir model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

Temkin model:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{8}$$

where: C_e is the equilibrium concentration of adsorbate (mg/L), K_F is the Freundlich isotherm constant related to adsorption capacity (L/g), n is the surface heterogeneity factor, q_m is the maximum monolayer coverage capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg), C_0 is the initial metal concentration (mg/L), R_L is the separation factor, K_T is the equilibrium binding constant (L/mg), b is the Temkin isotherm constant, B is a constant related to heat of sorption (J/mol), R is the gas constant (8.314 J/mol/K) and T is the temperature (298 K) [36,37].

2.5. Analytical Methods

Physical analyses: The Brunauer-Emmet-Teller (BET) specific surface area was determined by fitting the BET equation to the linear portion of the BET plot; the pore size distribution was calculated on the basis of the desorption plot of the N2 adsorption-desorption isotherm using the Barret-Joyner-Halenda method (Micrometrics ASAP 2000, USA). The morphology of ash was examined with a LEO 1430VP scanning electron microscope (SEM; Carl Zeiss).

Chemical analyses: The pH of ash was determined in distilled water extracts (1:10 *w/v*) using a pH-meter (HI 221). The electrical conductivity (EC) in synthetic wastewater before and after adsorption onto ash was measured with the use of a HANNA HI 8733 conductivity meter. To determine mineral and volatile matter contents, the ash was combusted in a muffle furnace at 750 °C for 2 h (uncovered ceramic crucibles) and at 950 °C for 6 min (covered ceramic crucibles), respectively. Detection of functional groups in the ash was performed with Fourier transform infrared (FT-IR) spectroscopy. The ash samples were scanned at 4000–700 cm^{-1} using an FTIR spectroscope (Nicolet 6700, Thermo Scientific) equipped with a Smart Multi-Bounce HATR™. The chemical composition of the ash was analyzed with a Quantax 200 energy dispersive X-ray spectrometer (EDS) equipped with an XFash 4010 detector (Burker AXS). Total oxide content in ash was measured with a Spectro X-Lab 2000 Energy Dispersive X-ray fluorescence (XRF) spectrometer. A mineralogical analysis of the ash was performed with an X'Pert Pro diffractometer with an X'Celerator Scientific detector (Malvern Panalytical) at an angular range of 5–120° (2Theta).

Contaminant analysis: Total metal concentrations were measured with a flame atomic absorption spectrometer (FAAS; Varian, AA28OFS). The concentration of the sum of BTEXs (benzene, toluene, ethylbenzene, xylenes and styrene) was measured with an Agilent 7694E headspace analyzer connected with an Agilent 6890 gas chromatograph coupled with an Agilent 5973 mass spectrometer. For analysis of the sum of nine PAHs (naphthalene, phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzofluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene), ash samples were extracted with a dichloromethane and acetone mixture (1:1 *vol/vol*) at 100 °C and 100 atm in a MARSXpress oven (CEM Corporation), then evaporated and dissolved in acetonitrile. The PAHs analyses were performed with an Agilent 1200 HPLC. For analysis of the sum of six PCBs (PCB28, PCB52, PCB101, PCB153, PCB138 and PCB180), the ash samples were extracted with a hexane and acetone mixture

(1:1 *vol/vol*) at 100 °C and 100 atm in a MARSXpress oven (CEM Corporation, Stallings, NC, USA), then evaporated and dissolved in isooctane. The concentration of PCBs was measured with an Agilent 6890N gas chromatograph with an ECD detector.

2.6. Statistical Analysis and Quality Control

The adsorption experiments were conducted in triplicate, and the mean and standard deviation are presented. To test the statistical significance (defined as $p < 0.05$) of differences between the means of Cd removal in different treatments, Tukey's honest significant difference test was used (Statistica 13.3, TIBCO Software Inc., Palo Alto, CA, USA).

The fit of the adsorption and kinetics models to the Cd adsorption data was analyzed by calculating the sum of squared errors (SSE):

$$SSE = \sum \frac{\left(q_{exp} - q_m\right)^2}{q_{exp}^{\,2}} \tag{9}$$

where q_{exp} is the measured amount of adsorbed Cd in the experiment (mg/g), and q_m is the amount of adsorbed Cd calculated with the adsorption isotherm or kinetics model (mg/g).

3. Results and Discussion

3.1. Ash Characterization

The poultry ash was a strongly alkaline (pH 12.9) mineral by-product (98.9% mineral matter and 1.02% volatile matter). The analysis of the surface morphology of poultry ash showed that the ash particles had a relatively narrow range of size, from less than 0.2 to more than 30 μm. Most of the particles were irregular in shape, with the presence of aggregate-like structures that could be carbonaceous in nature (Figure 3a,b) and microflake structures (Figure 3c,d).
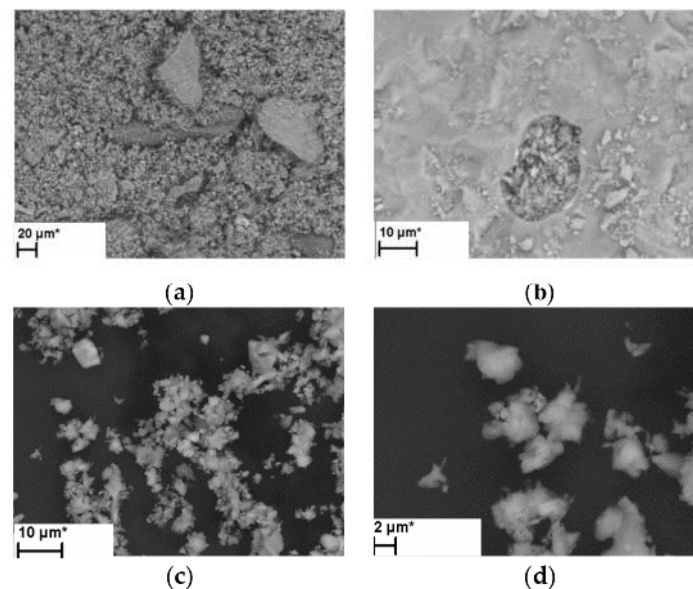

Figure 3. SEM micrographs of powdered poultry ash at different magnifications: (**a**) 500×, (**b**) 2,000×, (**c**) 20,000×, and (**d**) 50,000×.

The microflake structures could indicate phosphorous-rich morphotypes, as poultry litter contains phosphorus. For comparison, coal fly ash is composed mostly of small and spherical particles (so called cenosphere particles) [38,39]. In poultry litter ashes, the particle composition ranges from coesite relics (2 mm) to micrometric morphotypes rich in phosphorous [40]. The composition of these morphotypes can vary, as they can contain different elements, such as P, Si, Ca, K and Mg. Indeed, their composition

depends on the composition of the thermally processed feed and on the processes that take place during thermal processing of waste, such as transformations of the substances present in the feed, interactions between melting particles and later vitrification during cooling [41].

Table 1 summarizes the physical properties, the chemical composition and the content of organic and inorganic pollutants in the poultry ash. The ash sample had a poorly developed BET surface of 1.1966 m^2/g and low total pore volume and total area in pores. The ash contained mostly micropores, with an average diameter of 1.179 nm. Mesopores and macropores were small in number, and they had heterogeneous diameters that ranged from 1.179 to 73.968 nm. For comparison, municipal solid waste incineration fly ash had an average pore size of 20.607 nm [42]. The surface area of the poultry ash was similar to that of fly ashes of various origins: 5.14 m^2/g for bottom coal ash from a power plant [10], 1.52 m^2/g for coal fly ash [43], 7.99 m^2/g for fly ash from the pulp and paper industry [44] and 1.83 m^2/g for municipal solid waste incineration fly ash.

Table 1. Physicochemical characteristics of ash from gasification of poultry feathers.

Physical Property			Chemical Composition			Contaminants		
Type *	Unit	Value	Type	Unit	Value	Type	Unit	Value
SA	m^2/g	1.19	P_2O_5		39.9	Cd		0.0
TPV	cm^3/g	0.0023	CaO		35.5	Cr		1.8 ± 0.5
TAP	m^2/g	0.618	SiO_2		10.9	Cu		2.4 ± 0.09
			Na_2O		3.5	Ni		0.0
			MgO	wt%	2.2	Pb	mg/kg	0.0
			K_2O		2.2	Zn		0.3 ± 0.03
			Al_2O_3		1.5	$\sum$BTEXs		<0.1
			Fe_2O_3		0.7	$\sum$PAHs		<0.1
						$\sum$PCBs		<1

* Non-standard abbreviations: surface area (SA), total pore volume (TPV) and total area in pores (TAP).

Raw feathers are rich in organic carbon (due to the presence of keratin) and they contain some macroelements, such as nitrogen, phosphorus, potassium, manganese, iron, sulphur, calcium and chlorine [45]. The contents of individual elements in ash depend on the type of feathers, the species of bird, and on the type of food intake [45]. With the XRF analysis, three major mineral compounds were found in the poultry ash: P_2O_5, CaO and SiO_2. SiO_2 is typically produced at high temperatures during the combustion process [46]. The high content of P_2O_5 and CaO resulted from the mineral composition of the raw feathers. In addition, bones added to the feathers can be a source of calcium carbonates and calcium phosphates [45]. During thermal processing of feathers at high temperature, the organic fraction of feathers is easily removed, and the percentage of the mineral fraction is increased [40,45]. In addition, gaseous phosphorus oxides can be released from organic-P compounds at c.a. 500 °C, and these substances may condense on the ash surface, and thus contribute to the content of P_2O_5 in ash [41].

The XRF results are corroborated by the XRD analysis (Figure 4). In the XRD analysis, the presence of three main mineralogical components was confirmed, i.e., calcite ($CaCO_3$), calcium phosphate ($Ca_4P_2O_9$) and calcium hydroxide phosphate ($Ca_5(PO_4)_3OH$), known as hydroxyapatite. The presence of hydroxyapatite is related to the high contents of Ca and P in ash. In contrast to calcite or calcium phosphate, hydroxyapatite has a crystalline structure, and its crystallinity increases with the temperature of thermal waste processing. Our results are similar to those of other reports on the mineralogical composition of ash from waste biomass. Fahimi et al. [40] found that P- and Ca-, or K- and Si-rich crystalline and amorphous phases were the main constituents in poultry litter ash. Hydroxyapatite and potassium sodium calcium phosphate ($KNaCa_2(PO_4)_2$) predominated in ash from meat and bone meal [47].
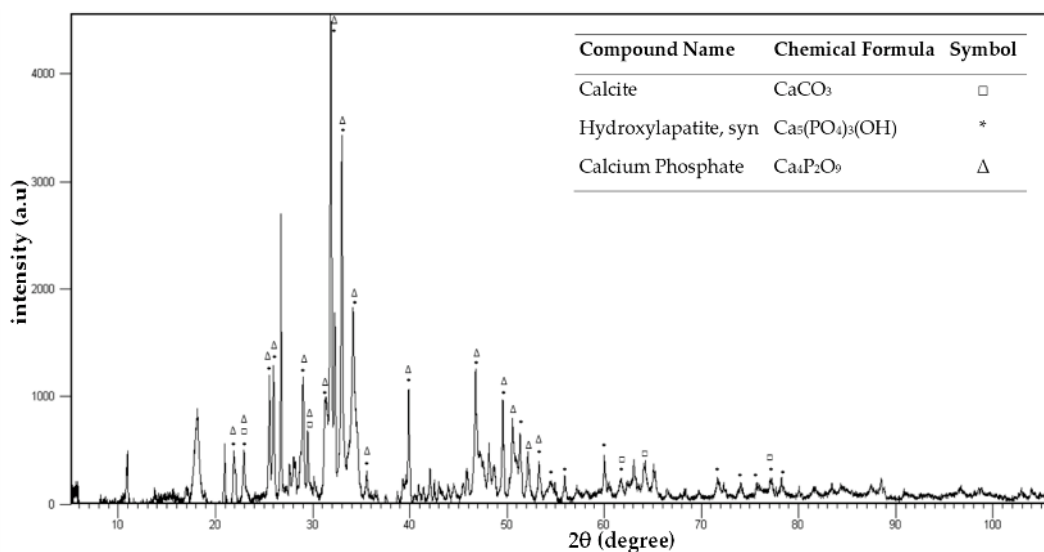
Figure 4. Diffraction pattern of poultry ash.

The FTIR spectrum of ash (Figure 5) contained a high intensity peak at 1052 cm^{-1}, attributable to a Si-O-Si asymmetric stretching vibration. A weak peak at 961 cm^{-1} could indicate phosphate band or Si-O groups [48]. The peaks at 1430 cm^{-1} and 876 cm^{-1} could be evidence of the presence of calcite [47,49]. A peak at 3643 cm^{-1} could be due to OH- groups in the hydroxyapatite, whose presence was confirmed with XRD, or these groups in portlandite (Ca(OH)$_2$), whose presence was not confirmed with XRD [47].
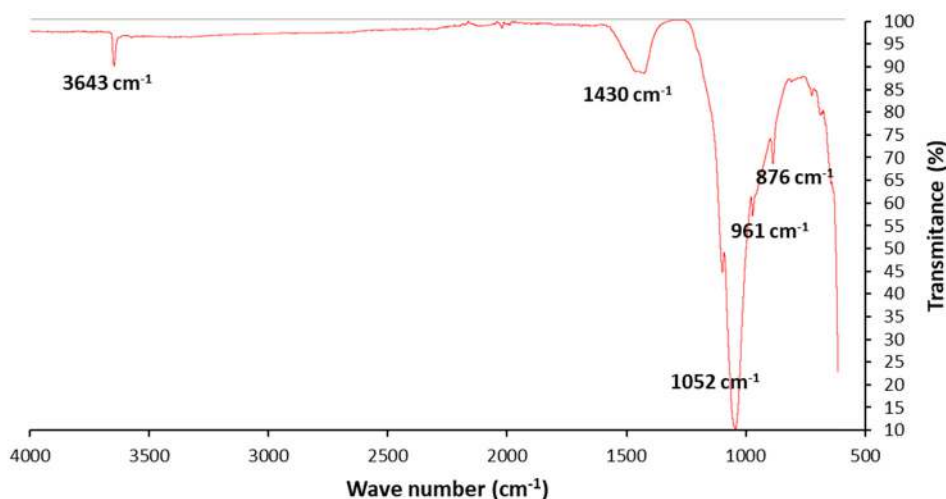

Figure 5. Fourier transform infrared (FTIR) spectrum of poultry ash.

The poultry ash contained only trace amounts of three heavy metals (Cr, Cu and Zn) and BTEXs, PAHs and PCBs. The ash did not contain toxic Cd and Pb. Thus, the ash is an environmentally safe mineral by-product. In contrast, Fahimi et al. [40] found much higher metal concentrations, especially those of Zn and Ni, in ash from incineration of poultry litter. Unlike the feathers that were the main feed for gasification in the present study, poultry litter is a mix of bedding material, manure and feathers, which can result in higher levels of heavy metals in the waste, and subsequently, in the ash.

3.2. Effect of Operational Conditions on Cd Sorption onto Poultry Ash

3.2.1. Initial pH in Wastewater

The effect of the pH of the synthetic wastewater on Cd adsorption was studied at pH values ranging from 2 to 8, and the results are shown in Figure 6.
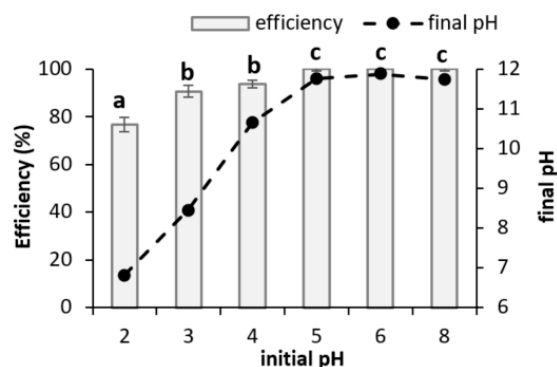

Figure 6. Adsorption efficiency of Cd removal as a function of wastewater (Cd concentration = 100 mg/L, adsorption time = 24 h and ash dosage = 5 g/L). Error bars represent standard deviations (*n* = 3). Different letters above bars indicate significantly different efficiencies with different initial pH values (ANOVA followed by Tukey's honest significant difference test, $p < 0.05$).

The efficiency of Cd removal onto poultry ash was already high at pH 2 (76.7%), and nearly complete Cd removal was obtained at pH 5 (99.8%). When the pH in the synthetic wastewater was increased to 8.0, no further changes in Cd removal efficiency were observed. Therefore, pH 5 was chosen as optimum. Our results correspond well with those reported for chicken bone ash [38]. Those authors demonstrated that, at three pH values (1.5, 3 and 5.6), Cd, Pb, Ni and Zn were completely removed from an aqueous solution.

The initial pH has an important effect on the charges in the active sites on the adsorbent surface and on the form of the metal in the solution. Usually, metal sorption at low pH is reduced, due to electrostatic repulsion between the metal and positively charged sites on the adsorbent surface, and/or metal competition with H^+ ions [32,50]. In the cited study, Cd was present predominantly as Cd^{2+} within the tested pH range (2–8) [51]. In the present study, the poultry ash had a strongly alkaline pH (12.9) and the point of zero charge for the ash (PZC) was 13.1. This means that the surface of the poultry ash was positively charged and mechanisms other than electrostatic attraction were involved in Cd adsorption [52].

When wastewater comes into contact with an alkali adsorbent, alkali metals are released [53]. As a result, the final pH of the solution can be substantially higher than the initial pH, as the alkali metals buffer the initial acidity [54]. In the present study, with an initial pH of 2.0, the final pH of the wastewater increased to 6.8, and with an initial pH of 5.0, the final pH was 11.8 (Figure 5). A considerable increase in the pH of the solution (to around 11) was also reported during adsorption of heavy metals, including Cd, onto red mud [31]. The alkali metals in wastewater can compete with H^+ ions and heavy metals for the active sites on an adsorbent [53]. The results obtained here suggest that poultry ash can be suitable for treatment of acidic wastewater, e.g., mine drainage or other industrial wastewaters.

3.2.2. Adsorbent Dosage

It is important to determine the amount of the ash that is needed for designing the optimum treatment system. The influence of poultry ash dosage on cadmium adsorption is illustrated in Figure 7.
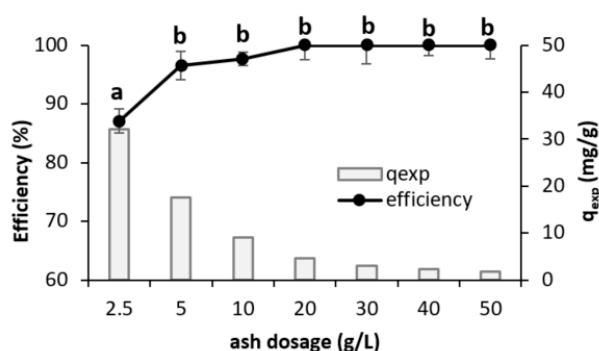
Figure 7. Efficiency of Cd adsorption and adsorption capacity as functions of ash dosage (Cd concentration = 100 mg/L, adsorption time = 24 h, pH 5). Error bars represent standard deviations (*n* = 3). Different letters above bars indicate significantly different efficiencies with different ash dosages (ANOVA followed by Tukey's honest significant difference test, *p* < 0.05).

Cd was effectively removed with low dosages of poultry ash, which makes this adsorbent an attractive choice for treatment of wastewater highly contaminated with metals. The efficiency of Cd adsorption increased as the ash dosage was increased from 2.5 (87.1%) to 5 g/L (97%). At higher ash dosages (10-50 g/L), Cd was completely removed from the wastewater. As the adsorbent dosage was increased, the adsorption capacity of the poultry ash decreased sharply; from 32 (at 2.5 g/L) to 1.8 mg/g (at 50 g/L). At high metal concentrations, it is common to observe such a decrease in metal adsorption capacity per gram of adsorbent as the dosage is progressively increased, and this can mean that not all of the active sites on the adsorbent surface were used for metal adsorption [28,53]. Taking into account the efficiency of Cd removal and its equilibrium concentration in the solution, it can be seen that an ash dosage of 5 g/L is sufficient for optimal Cd removal.

3.2.3. Salinity

In the present study, the effect of salinity in wastewater was simulated with the use of sodium nitrate ($NaNO_3$) at concentrations from 0.01 to 0.05 M, which corresponded to electrical conductivities from 8 to 38 mS/cm, respectively. Within the tested range, the $NaNO_3$ had little or no effect on Cd sorption onto the ash (Figure 8a). The adsorption capacity varied from 17.2 (at 0.01 M $NaNO_3$) to 18.4 mg/g (at 0.05 $NaNO_3$), but these differences were not statistically significant (*p* > 0.05, Tukey's honest significant difference test).

In general, salinity can diminish metal sorption due to competition between Na^+ and heavy metal ions for sorption sites. This is especially noticeable at high salt concentrations in solutions [54]. The presence of Na^+ increases or expands the electrically diffused double layer and decreases electrostatic attraction between metal ions and the adsorbent surface [55]. The results obtained in the present study suggest that a maximum wastewater salinity of ca. 40 mS/cm (0.05 M $NaNO_3$) does not disturb Cd sorption onto poultry ash. This information can be useful guidance for the application of poultry ash for treating saline wastewater. The changes in the electrical conductivity of the wastewater before and after adsorption onto ash indicate that, at higher salt concentrations than those that were tested, Na competition with metal ions for sorption sites should continue to increase (Figure 8b). Jiang et al. [54] have shown that the metal adsorption capacity of biochar and activated carbon was reduced when the Na_2SO_4 concentration exceeded 0.1 M. In the present study, the maximum salt concentration in the wastewater was 0.05 M.

In addition, the presence of anions in wastewater can diminish metal sorption due to the formation of ion pair complexes with metals. Metal sorption can be inhibited by anions that form sufficiently stable complexes. The degree to which an anion inhibits sorption of a cation depends on the constant of stability. Bivalent anions (e.g., CO_3^{2-} and SO_4^{2-}) can have a greater inhibitory effect on metal sorption than monovalent anions (e.g., Cl^- and NO_3^-) [56,57].
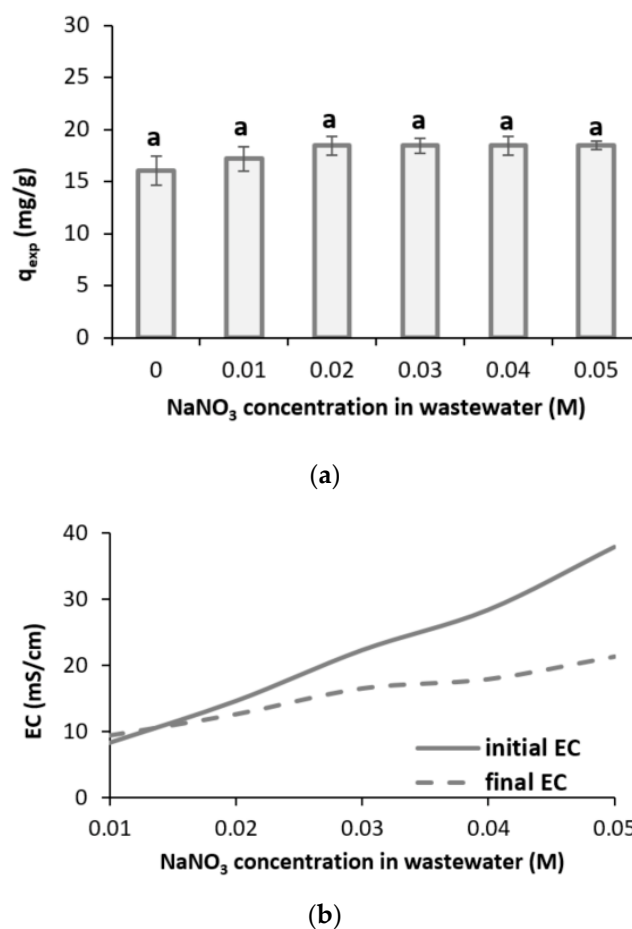
(a)

(b)

Figure 8. Effect of wastewater salinity (as electrical conductivity, EC) on Cd adsorption onto poultry ash: (**a**) adsorption capacity, (**b**) changes in initial (before adsorption) and final (after adsorption) salinity in wastewater (Cd concentration = 100 mg/L, adsorption time = 24 h, pH = 5). Error bars represent standard deviations (*n* = 3). Different letters above bars would indicate significantly different adsorption capacities at different concentrations of $NaNO_3$ in wastewater (ANOVA followed by Tukey's honest significant difference test, $p < 0.05$).

3.3. Initial Cd Concentration and Adsorption Isotherms

Cd adsorption onto ash increased rapidly as the initial metal concentration in wastewater was increased (Figure 9a). Increasing Cd concentration increases the driving force to overcome resistance to mass transfer between the ash and wastewater, resulting in increasing metal sorption. With increasing initial metal concentrations, the binding sites on the adsorbent are gradually occupied by metal until saturation occurs [26]. Our observations are consistent with reports on Cd adsorption onto different adsorbents, e.g., pretreated rice straw and rice husk [55], chicken-manure-derived biochars [58] and coal fly ash [27]. In order to analyze the relationship between the amount of Cd adsorbed and the equilibrium Cd concentration, three adsorption isotherm models were used: the Freundlich, Langmuir and Temkin models.

The fit of these models to the experimental data and the adsorption isotherm constants are shown in Figure 9b and Table 2, respectively. The R^2 and SSE values indicated that the Langmuir model provided a better fit to the data than the Freundlich and Temkin models. The Langmuir model has been found to be suitable for Cd adsorption onto different adsorbents by many authors [28,32]. In this study, poultry ash showed a very high maximum monolayer capacity for Cd adsorption of 127 mg/g. This means that poultry ash can be a comparable substitute for, or even a more effective replacement for other mineral adsorbents, such as ashes of other origins (Table 3).
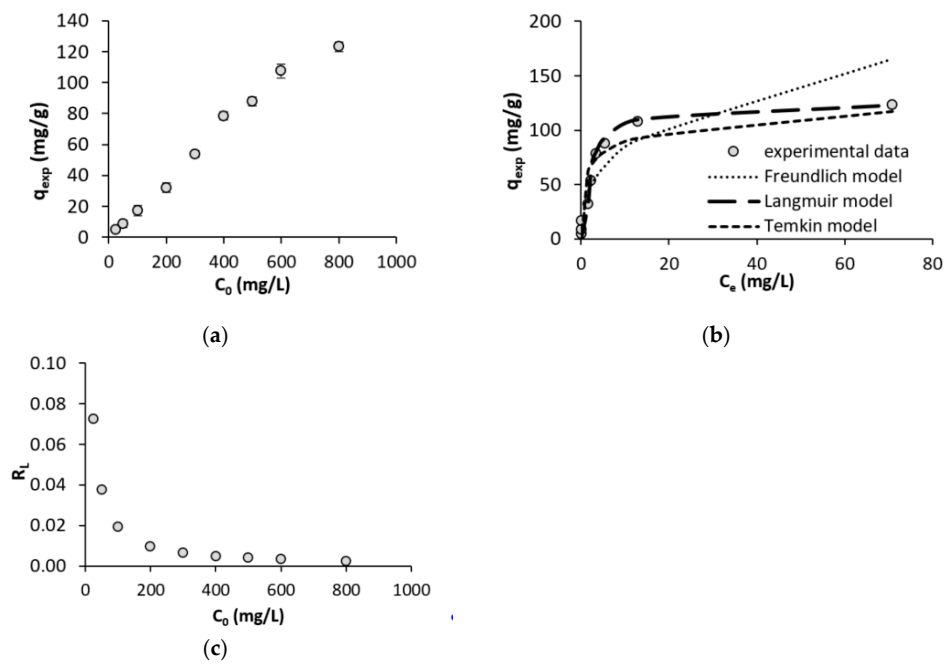
(a)

(b)

(c)

Figure 9. Sorption of Cd onto poultry ash: (**a**) q_{exp} vs. initial Cd concentration, (**b**) q_{exp} vs. equilibrium Cd concentration and (**c**) separation factor (RL) vs. initial Cd concentration.

Table 2. Comparison of adsorption isotherm parameters for Cd adsorption onto poultry ash (ash dosage = 5 g/L, adsorption time = 24 h, pH = 5).

Adsorption Model	Parameters	Unit	Value
Freundlich	K_F	L/g	37.2
	n	–	2.85
	R^2	–	0.8494
	SSE	–	3.2
Langmuir	q_m	mg/g	126.6
	K_L	L/mg	0.51
	R^2	–	0.9961
	SSE	–	0.8
Temkin	B	mg/L	14.454
	K_t	J/mol	47.6086
	R^2	–	0.8798
	SSE	–	3.8

Table 3. Comparison of the Langmuir equilibrium capacities for selected mineral sorbents of Cd under specific adsorption conditions.

Adsorbent	Adsorption Conditions	Adsorption Capacity (mg/g)	References
Bottom ash	1 g/L, pH 6, 60 min, 30 °C	13.7	[10]
Modified coal fly ash	2 g/L, pH 5, 120 min, 25 °C	69.3	[26]
Geopolymers	4 g/L, pH 5, 400 min, 25 °C	33.98–67.83	[32]
Fly ash from wood pellets	2 g/L, pH 5, 24 h, 25 °C	142.9	[28]
Bottom ash from wood pellets		23.3	
Coal fly ash	3 g/L, pH 6, 20 min, 30 °C	78.14	[27]
Zeolite from coal fly ash	10 g/L, 90 min, 25 °C	74.074	[59]
Cedar leaf ash	10 g/L, 30-45 min, pH 5, 20 °C	4.33–7.85	[33]
Modified oil shale ash	5 g/L, pH 7, 15 min, 20 °C	12.05	[60]
Hydroxylapatite	2.5 g/L, pH 5, 180 min, 20 °C	111.1	[61]
Bagasse fly ash	10 g/L, pH 6, 150 min, 30 °C	1.24	[62]
Poultry ash	5 g/L, pH 5, 24 h, 25 °C	126.6	this study

In this study, the separation factor (RL) was used to predict the affinity of Cd for poultry ash [63]. Throughout the entire tested range of initial Cd concentrations in wastewater (25–800 mg/L), the RL values were far below 1.0, indicating favorable conditions for Cd sorption onto the ash (Figure 9c).

3.4. Contact Time and Adsorption Kinetics

Sorption time is a crucial parameter affecting metal removal from wastewater, and technological and economical aspects of the adsorption process. At an initial Cd concentration of 100 mg/L, its adsorption onto poultry ash increased rapidly with time. The amount of absorbed Cd plateaued, and equilibrium sorption was obtained with adsorption times of 5–40 min. After 40 min contact time, the amount of adsorbed Cd was 18.4 mg/g (Figure 10), which corresponded to a removal efficiency of 99%. According to other reports, with the use of high initial Cd concentrations (ranging from 50 to 200 mg/L) and other adsorbents, the equilibrium of metal adsorption was obtained at various times, e.g., 20 min with modified coal fly ash [27], 60 min with bottom ash [50] or 90 min with zeolites from coal fly ash [59].
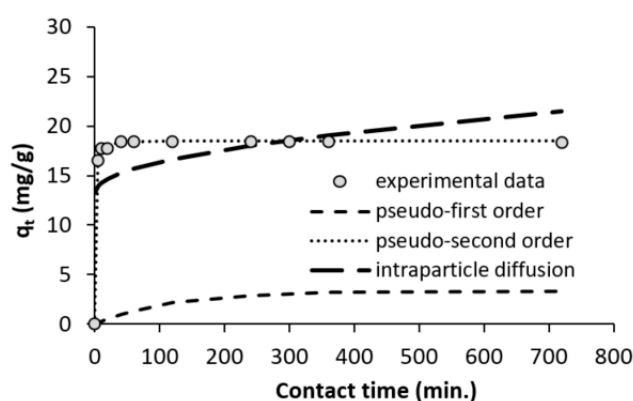

Figure 10. Adsorption kinetics of Cd adsorption onto poultry ash (ash dosage = 5 g/L, Cd concentration = 100 mg/L, pH = 5).

Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were fitted to the Cd sorption data to determine the major parameters governing the sorption kinetics and for insight into the mechanisms of Cd adsorption. The fits (expressed with the R^2 coefficient) of the pseudo-first order and intraparticle diffusion models were markedly lower than that of the pseudo-second-order model (Table 4). The R^2 value for the pseudo-second-order model was equal to 1, indicating that Cd sorption onto poultry ash was well described by this model. Many other papers also indicate that the kinetics of sorption of Cd onto different adsorbents is successfully described with the pseudo second-order model (e.g., [26,55,64]). With the use of a pseudo-second-order model, it can be assumed that chemisorption (as precipitation and adsorption onto ash solids) was the main mechanism of Cd removal from the wastewater. The high pH of ash and the high Cd concentration in the wastewater (100 mg/L) could facilitate formation of hydroxides on the adsorbent surface [27,58,61]. In this study, the presence of calcium phosphate, hydroxyapatite and calcite in the ash, as confirmed by the XRD analysis, could be responsible for Cd precipitation. Cd has a tendency to concentrate in the solid phases, forming amorphous precipitates of low crystallinity in neutral and basic solutions [65]. In the present study, the presence of Cd precipitates on the poultry ash surface was confirmed with SEM-EDX micrographs (Figure 11).

Zheng et al. [61] have found that, in addition to precipitation, ion exchange and physical adsorption were also responsible for Cd removal from an aqueous solution by carbonate hydroxylapatite derived from eggshell waste. Ion exchange was more pronounced at lower pH, when both hydrogen and metal cations can replace Ca cations on the adsorbent surface [61].

In the study presented here, the ash surface composition changed after Cd adsorption (Figure 12), which suggests an ion exchange mechanism was responsible for Cd removal. Ca loss was highest, while losses of S, P and K were lower.

Table 4. Comparison of kinetic parameters of Cd adsorption onto poultry ash (ash dosage = 5 g/L, Cd concentration = 100 mg/L, pH = 5).

Kinetic Model	Parameters	Unit	Value
Pseudo-first order	q_e	mg/g	3.33
	k_2	1/min	0.0124
	R^2	–	0.8125
	SSE	–	6.8355
Pseudo-second order	q_e	mg/g	18.55
	k_2	g/mg/min	0.121
	R^2	–	1.000
	SSE	–	0.002
Intraparticle diffusion	C_i	mg/g	0.3046
	k_i	mg/g min$^{1/2}$	13.305
	R^2	–	0.2166
	SSE	–	0.1539
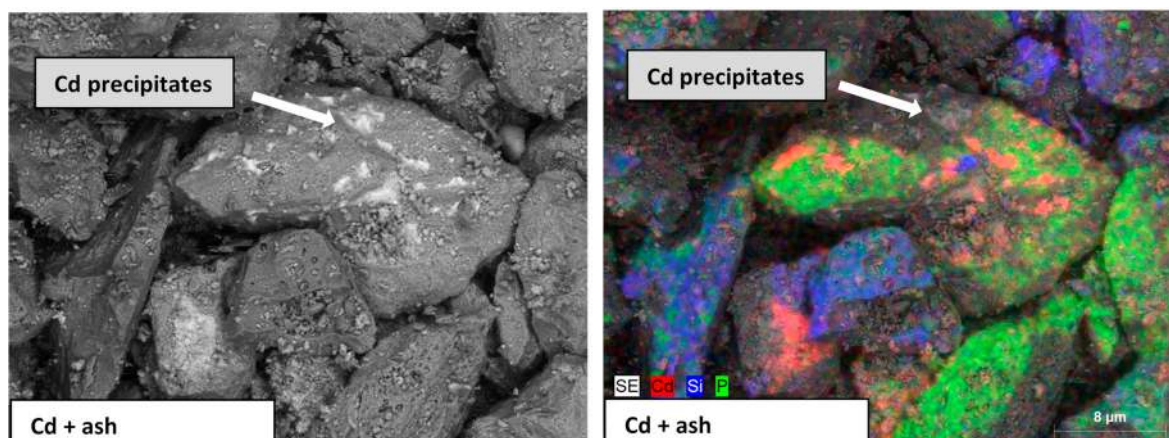
Figure 11. SEM micrographs of poultry ash after Cd adsorption.

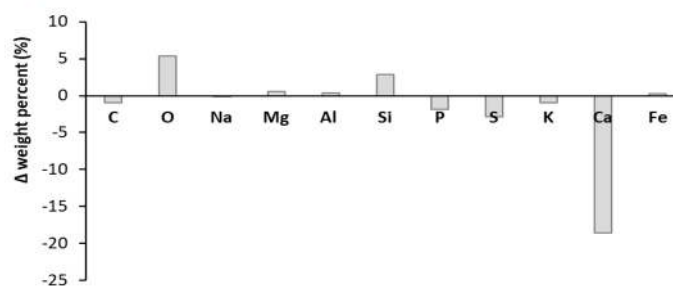| wt %	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe
Ash	1.1	30.7	1.6	1.1	1.8	4.4	8.3	3.1	1.6	45.5	0.8
Ash+Cd	0.12	36.11	1.51	1.61	2.16	7.29	6.43	0.27	0.61	26.95	1.03

Figure 12. Changes in the elemental composition of poultry ash. Δ weight percent indicates the difference in the content of an individual element before and after Cd adsorption. A positive Δ weight percent value indicates an increase in the wt% content of a given element, whereas a negative value indicates a decrease in its wt% content.

Xu et al. [66] have found that two main mechanisms are responsible for the sorption of Cd onto hydroxyapatite: Cd complexation with surface functional groups of hydroxyapatite, such as phosphate surface sites ($\equiv$POH), to form metal surface species like $\equiv$POCd$^+$ and coprecipitation of Cd with Ca to form hydroxyapatite, which was implied by significant changes in Ca and phosphate concentrations during sorption. Ca can coprecipitate with Cd to a much greater extent than with other cations because Ca and Cd have similarly large ionic radii, 0.99 Å and 0.97 Å, respectively.

Thus, ion exchange between Cd and Ca, coprecipitation of Cd with Ca present in some mineral components of ash, and Cd complexation with POH groups can all play roles in the overall process of Cd removal from wastewater.

4. Conclusions

Water and wastewater contamination with heavy metals, including toxic Cd, is a cause of great environmental concern. Thus, there have been many approaches that aim to develop cheaper and more efficient adsorbents for metal removal. The present study has shown that the use of ash from the gasification of poultry feathers for this application is not only a means of utilizing this waste product, but also an effective method for removing Cd from highly contaminated wastewater. This is due to the chemical properties of the ash rather than its physical characteristics. The ash has high alkalinity, a high content of P_2O_5 and CaO, and contains calcium phosphate, hydroxyapatite and calcite, which affect the optimum conditions for adsorbing Cd onto ash and the mechanisms by which this takes place. Under optimal operational conditions, which include a pH of wastewater, an ash dosage of 5 g/L, a relatively fast contact time to obtain equilibrium and an initial Cd concentration of 100 mg/L, Cd was almost completely removed. Within the tested salinity range, this parameter had little or no effect on Cd removal. Cd adsorption onto poultry ash occurred via a pseudo-second-order mechanism, which may involve chemical processes such as surface precipitation, ion exchange, coprecipitation with Ca-mineral components and complexation with phosphate surface sites. Among these mechanisms, surface precipitation seemed to predominate, is indicated by SEM-EDS analysis. As the Langmuir model provided the best fit to the experimental data, Cd adsorption onto the ash may take place via the monolayer process and the ash may have a very high maximum adsorption capacity (126.6 mg/g).

These results are useful for proper management of waste and waste by-products from the poultry industry. Poultry ash can be an attractive alternative to mineral sorbents used in remediation of metal-contaminated media, especially those with a low pH. An application that could be further explored is the use of the ash as an adsorbent of multi-inorganic contaminants in real industrial wastewater and restoration of chemically degraded soil.

References

1. Yang, J.; Hou, B.; Wang, J.; Tian, B.; Bi, J.; Wang, N.; Huang, X. Nanomaterials for the removal of heavy metals from wastewater. *Nanomaterials* **2019**, *9*, 424. [CrossRef]
2. Hussain, A.; Alamzeb, S.; Begum, S. Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children, District Mardan, Pakistan. *Food Chem.* **2013**, *136*, 1515–1523. [CrossRef]

3. Friberg, L.; Elinder, C.; Kjellstrom, T. *Cadmium. Environmental Health Criteria 134*; World Health Organization: Geneva, Switzerland, 1992.

4. Kumar, R.; Chawla, J.; Kaur, I. Removal of cadmium ion from wastewater by carbon-based nanosorbents: A review. *J. Water Health* **2015**, *13*, 18–33. [CrossRef]

5. Kuchekar, S.R.; Patil, M.P.; Aher, H.R.; Gaikwad, V.B.; Han, S.H. Adsorptive removal of cadmium (II) ion from industrial wastewater by natural adsorbent. *J. Mater. Environ. Sci.* **2019**, *10*, 1117–1122.

6. Vullo, D.L.; Ceretti, H.M.; Daniel, M.A.; Ramirez, S.A.M.; Zalts, A. Cadmium, zinc and copper biosorption mediated by *Pseudomonas veronii* 2E. *Bioresour. Technol.* **2008**, *99*, 5574–5581. [CrossRef] [PubMed]

7. Manjula, D.M.; Oviyaa Sri, M. Heavy metals removal from industrial wastewater by nano adsorbent prepared from cucumis melopeel activated carbon. *J. Nanomed. Res.* **2017**, *5*, 00102. [CrossRef]

8. Ordinance of the Minister of Environment (OME). Ordinance of the Minister of Environment on the conditions for wastewater discharge to water and ground and on pollutants in water environment. *J. Law* **2014**, *1800*, 1–42. (In Polish)

9. Padmaja, M.; Bhavani, R.; Pamila, R. Adsorption of Cadmium from Aqueous Solutions Using Low cost Materials-A Review. *Int. J. Eng. Technol.* **2018**, *7*, 26–29. [CrossRef]

10. Sukpreabprom, H.; Arqueropanyo, O.A.; Naksata, W.; Sooksamiti, P.; Janhom, S. Single and binary adsorption of Cd (II) and Zn (II) ions from aqueous solutions onto bottom ash. *Korean J. Chem. Eng.* **2015**, *32*, 896–902. [CrossRef]

11. Joseph, L.; Jun, B.M.; Flora, J.R.; Park, C.M.; Yoon, Y. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere* **2019**, *229*, 142–159. [CrossRef]

12. Chakraborty, R.; Asthana, A.; Singh, A.K.; Jain, B.; Susan, A.B.H. Adsorption of heavy metal ions by various low-cost adsorbents: A review. *Int. J. Environ. Anal. Chem.* **2020**, 1–38. [CrossRef]

13. Eurostat. 2019. Available online: https://ec.europa.eu/eurostat/web/products-eurostat-news/-/DDN-20190325-1 (accessed on 2 October 2020).

14. Reddy, N.; Santosh, M.S. Recovery and Applications of Feather Proteins. In *Protein Byproducts: Transformation from Environmental Burden into Value-Added Products*; Dhillon, G.S., Ed.; Academic Press: Oxford, UK, 2016; pp. 255–274.

15. Kwiatkowski, K.; Krzysztoforski, J.; Bajer, K.; Dudyński, M. Bioenergy from feathers gasification–Efficiency and performance analysis. *Biomass Bioenergy* **2013**, *59*, 402–411. [CrossRef]

16. de la Rosa, G.; Reynel-Avila, H.E.; Bonilla-Petriciolet, A.; Cano-Rodriguez, I.; Velasco-Santos, C.; Martínez-Hernández, A.L. Recycling poultry feathers for Pb removal from wastewater: Kinetic and equilibrium studies. *Proc. World Acad. Sci. Eng. Technol.* **2008**, *1*, 185–193.

17. Chen, B.; Yan, L.; Liu, X.; Worral, J.L. Poultry keratin based decolorants for dyeing wastewater treatment. *J. Bioresour. Bioproduct.* **2016**, *1*, 30–35.

18. Nodoushan, M.H.S.; Ehrampoush, M.H. Study of Co (II) adsorption from aqueous solution using protein granules produced from chicken feather. *Environ. Health Eng. Manag. J.* **2015**, *2*, 193–197.

19. Khosa, M.A.; Wu, J.; Ullah, A. Chemical modification, characterization, and application of chicken feathers as novel biosorbents. *RSC Adv.* **2013**, *3*, 20800–20810. [CrossRef]

20. Zhang, H.; Carrillo, F.; López-Mesas, M.; Palet, C. Valorization of keratin biofibers for removing heavy metals from aqueous solutions. *Text. Res. J.* **2019**, *89*, 1153–1165. [CrossRef]

21. Dalólio, F.S.; da Silva, J.N.; de Oliveira, A.C.C.; Tinôco, I.D.F.F.; Barbosa, R.C.; de Oliveira Resende, M.; Coelho, S.T. Poultry litter as biomass energy: A review and future perspectives. *Renew. Sustain. Energy Rev.* **2017**, *76*, 941–949. [CrossRef]

22. Dudyński, M.; Kwiatkowski, K.; Bajer, K. From feathers to syngas–technologies and devices. *Waste Manag.* **2012**, *32*, 685–691. [CrossRef]

23. Ghiaci, M.; Dorostkar, N.; Gil, A. Chicken bone ash as an efficient metal biosorbent for cadmium, lead, nickel, and zinc from aqueous solutions. *Desal. Water Treat.* **2014**, *52*, 3115–3121. [CrossRef]

24. Asokbunyarat, V.; van Hullebusch, E.D.; Lens, P.N.; Annachhatre, A.P. Coal Bottom Ash as Sorbing Material for Fe (II), Cu (II), Mn (II), and Zn (II) Removal from Aqueous Solutions. *Water Air Soil Pollut.* **2015**, *226*, 143. [CrossRef]

25. Asl, S.M.H.; Javadian, H.; Khavarpour, M.; Belviso, C.; Taghavi, M.; Maghsudi, M. Porous adsorbents derived from coal fly ash as cost-effective and environmentally friendly sources of aluminosilicate for sequestration of aqueous and gaseous pollutants: A review. *J. Clean. Prod.* **2019**, *208*, 1131–1147. [CrossRef]

26. Huang, X.; Zhao, H.; Hu, X.; Liu, F.; Wang, L.; Zhao, X.; Ji, P. Optimization of preparation technology for modified coal fly ash and its adsorption properties for Cd^{2+}. *J. Hazard. Mater.* **2020**, *392*, 122461. [CrossRef]

27. Zhao, H.; Huang, X.; Zhang, G.; Li, J.; He, Z.; Ji, P.; Zhao, J. Possibility of removing cadmium pollution from the environment using a newly synthesized material coal fly ash. *Environ. Sci. Pollut. Res.* **2020**, *27*, 4997–5008. [CrossRef]

28. Park, J.H.; Eom, J.H.; Lee, S.L.; Hwang, S.W.; Kim, S.H.; Kang, S.W.; Yun, J.-J.; Cho, J.-S.; Lee, Y.-H.; Seo, D.C. Exploration of the potential capacity of fly ash and bottom ash derived from wood pellet-based thermal power plant for heavy metal removal. *Sci. Total Environ.* **2020**, *740*, 140205. [CrossRef]

29. Xu, W.; Wang, H.; Zhu, T. Mercury removal from coal combustion flue gas by modified fly ash. *J. Environ. Sci.* **2013**, *25*, 393–398. [CrossRef]

30. Chen, L.; Wang, L.; Cho, D.W.; Tsang, D.C.; Tong, L.; Zhou, Y.; Yang, J.; Hu, Q.; Poon, C.S. Sustainable stabilization/solidification of municipal solid waste incinerator fly ash by incorporation of green materials. *J. Clean. Prod.* **2019**, *222*, 335–343. [CrossRef]

31. Shin, W.S.; Kang, K.; Kim, Y.K. Adsorption characteristics of multi-metal ions by red mud, zeolite, limestone, and oyster shell. *Environ. Eng. Res.* **2014**, *19*, 15–22. [CrossRef]

32. Lan, T.; Li, P.; Rehman, F.U.; Li, X.; Yang, W.; Guo, S. Efficient adsorption of Cd2+ from aqueous solution using metakaolin geopolymers. *Environ. Sci. Pollut. Res.* **2019**, *26*, 33555–33567. [CrossRef]

33. Hafshejani, L.D.; Nasab, S.B.; Moradzadeh, M.; Divband, S.; Koupai, J.A. Cadmium removal from aqueous solution using nano/milli-sized particles of cedar leaf ash. *Desalin. Water Treat.* **2014**, *1–9*, 1–11. [CrossRef]

34. Xue, Z.; Liu, N.; Hu, H.; Huang, J.; Kalkhajeh, Y.K.; Wu, X.; Xu, N.; Fu, X.; Zhan, L. Adsorption of Cd (II) in water by mesoporous ceramic functional nanomaterials. *R. Soc. Open Sci.* **2019**, *6*, 182195. [CrossRef]

35. Cui, X.; Fang, S.; Yao, Y.; Li, T.; Ni, Q.; Yang, X.; He, Z. Potential mechanisms of cadmium removal from aqueous solution by Canna indica derived biochar. *Sci. Total Environ.* **2016**, *562*, 517–525. [CrossRef]

36. Bordoloi, N.; Goswami, R.; Kumar, M.; Kataki, R. Biosorption of Co (II) from aqueous solution using algal biochar: Kinetics and isotherm studies. *Bioresour. Technol.* **2017**, *244*, 1465–1469. [CrossRef]

37. Popoola, L.T.; Yusuff, A.S.; Adesina, O.A.; Lala, M.A. Brilliant green dye sorption onto snail shell-rice husk: Statistical and error function models as parametric isotherm predictors. *J. Environ. Sci. Technol.* **2019**, *12*, 65–80. [CrossRef]

38. Ismail, K.N.; Hussin, K.; Idris, M.S. Physical, chemical and mineralogical properties of fly ash. *J. Nucl. Relat. Technol.* **2007**, *4*, 47–51.

39. Pitawala, L.M.S.D.; Wijeyawardana, H.M.P.; Nanayakkara, K.G.N. Utilization of coal fly ash in the adsorptive removal of fluoride from contaminated groundwater. In *IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2020; Volume 849, p. 012025.

40. Fahimi, A.; Bilo, F.; Assi, A.; Dalipi, R.; Federici, S.; Guedes, A.; Fiameni, L. Poultry litter ash characterisation and recovery. *Waste Manag.* **2020**, *111*, 10–21. [CrossRef]

41. Valentim, B.; Flores, D.; Guedes, A.; Guimarães, R.; Shreya, N.; Paul, B.; Ward, C.R. Notes on the occurrence of phosphate mineral relics and spheres (phosphospheres) in coal and biomass fly ash. *Inter. J. Coal Geol.* **2016**, *154*, 43–56. [CrossRef]

42. Tan, W.F.; Wang, L.A.; Huang, C.; Liu, Y.Y.; Green, J.E.; Newport, D.; Green, T. Utilization of municipal solid waste incineration fly ash in lightweight aggregates. *J. Cent. South Univ.* **2012**, *19*, 835–841. [CrossRef]

43. Van der Merwe, E.M.; Prinsloo, L.C.; Mathebula, C.L.; Swart, H.C.; Coetsee, E.; Doucet, F.J. Surface and bulk characterization of an ultrafine South African coal fly ash with reference to polymer applications. *Appl. Surf. Sci.* **2014**, *317*, 73–83. [CrossRef]

44. Rajamma, R.; Ball, R.J.; Tarelho, L.A.; Allen, G.C.; Labrincha, J.A.; Ferreira, V.M. Characterisation and use of biomass fly ash in cement-based materials. *J. Hazard. Mater.* **2009**, *172*, 1049–1060. [CrossRef]

45. Staroń, P.; Kowalski, Z.; Staroń, A.; Seidlerová, J.; Banach, M. Residues from the thermal conversion of waste from the meat industry as a source of valuable macro-and micronutrients. *Waste Manag.* **2016**, *49*, 337–345. [CrossRef] [PubMed]

46. Agrela, F.; Cabrera, M.; Morales, M.M.; Zamorano, M.; Alshaaer, M. Biomass fly ash and biomass bottom ash. In *New Trends in Eco-Efficient and Recycled Concrete*; de Brito, J.A., Ed.; Woodhead Publishing: Duxford UK, 2019; pp. 23–58.

47. Leng, L.; Bogush, A.A.; Roy, A.; Stegemann, J.A. Characterisation of ashes from waste biomass power plants and phosphorus recovery. *Sci. Total Environ.* **2019**, *690*, 573–583. [CrossRef] [PubMed]

48.　Yilmaz, B.; Olgun, A. Studies on cement and mortar containing low-calcium fly ash, limestone, and dolomitic limestone. *Cem. Concr. Com.* **2008**, *30*, 194–201. [CrossRef]

49.　Mansur, A.A.P.; Santos, D.B.; Mansur, H.S. A microstructural approach to adherence mechanism of poly (vinyl alcohol) modified cement systems to ceramic tiles. *Cem. Concr. Res.* **2007**, *37*, 270–282. [CrossRef]

50.　Sukpreabprom, H.; Arquero, O.A.; Naksata, W.; Sooksamiti, P.; Janhom, S. Isotherm, kinetic and thermodynamic studies on the adsorption of Cd (II) and Zn (II) ions from aqueous solutions onto bottom ash. *Inter. J. Environ. Sci. Dev.* **2014**, *5*, 165–170. [CrossRef]

51.　Srivastava, P.; Singh, B.; Angove, M. Competitive adsorption behavior of heavy metals on kaolinite. *J. Colloid Interface Sci.* **2005**, *290*, 28–38. [CrossRef]

52.　Ayanda, O.S.; Fatoki, O.S.; Adekola, F.A.; Ximba, B.J. Activated carbon-fly ash-nanometal oxide composite materials: Preparation, characterization, and tributyltin removal efficiency. *J. Chem.* **2013**, *2013*, 1–16. [CrossRef]

53.　Ayala, J.; Fernández, B. Treatment from abandoned mine landfill leachates. Adsorption technology. *J. Mater. Res. Tech.* **2019**, *8*, 2732–2740. [CrossRef]

54.　Jiang, S.; Huang, L.; Nguyen, T.A.; Ok, Y.S.; Rudolph, V.; Yang, H.; Zhang, D. Copper and zinc adsorption by softwood and hardwood biochars under elevated sulphate-induced salinity and acidic pH conditions. *Chemosphere* **2016**, *142*, 64–71. [CrossRef]

55.　Li, W.C.; Law, F.Y.; Chan, Y.H.M. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. *Environ. Sci. Pollut. Res.* **2017**, *24*, 8903–8915. [CrossRef]

56.　Benaissa, H.; Benguella, B. Effect of anions and cations on cadmium sorption kinetics from aqueous solutions by chitin: Experimental studies and modeling. *Environ. Pollut.* **2004**, *130*, 157–163. [CrossRef] [PubMed]

57.　Weißpflog, J.; Gündel, A.; Vehlow, D.; Steinbach, C.; Müller, M.; Boldt, R.; Schwarz, S.; Schwarz, D. Solubility and Selectivity Effects of the Anion on the Adsorption of Different Heavy Metal Ions onto Chitosan. *Molecules* **2020**, *25*, 2482. [CrossRef] [PubMed]

58.　Huang, F.; Gao, L.Y.; Deng, J.H.; Chen, S.H.; Cai, K.Z. Quantitative contribution of Cd^{2+} adsorption mechanisms by chicken-manure-derived biochars. *Environ. Sci. Pollut. Res.* **2018**, *25*, 28322–28334. [CrossRef] [PubMed]

59.　Joseph, I.V.; Tosheva, L.; Doyle, A.M. Simultaneous removal of Cd (II), Co (II), Cu (II), Pb (II), and Zn (II) ions from aqueous solutions via adsorption on fau-type zeolites prepared from coal fly ash. *J. Environ. Chem. Eng.* **2020**, 103895. [CrossRef]

60.　Zhu, B.L.; Xiu, Z.M.; Liu, N.; Bi, H.T.; Lv, C.X. Adsorption of lead and cadmium ions from aqueous solutions by modified oil shale ash. *Oil Shale* **2012**, *29*, 268–278. [CrossRef]

61.　Zheng, W.; Li, X.M.; Yang, Q.; Zeng, G.M.; Shen, X.X.; Zhang, Y.; Liu, J.J. Adsorption of Cd (II) and Cu (II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste. *J. Hazard. Mater.* **2007**, *147*, 534–539. [CrossRef]

62.　Gupta, V.K.; Jain, C.K.; Ali, I.; Sharma, M.; Saini, V.K. Removal of cadmium and nickel from wastewater using bagasse fly ash—A sugar industry waste. *Water Res.* **2003**, *37*, 4038–4044. [CrossRef]

63.　Singanan, M. Removal of lead (II) and cadmium (II) ions from wastewater using activated biocarbon. *Sci. Asia* **2011**, *37*, 115–119. [CrossRef]

64.　Lim, S.F.; Lee, A.Y.W. Kinetic study on removal of heavy metal ions from aqueous solution by using soil. *Environ. Sci. Pollut. Res.* **2015**, *22*, 10144–10158. [CrossRef]

65.　Lundager Madsen, H.E.; Abbona, F.; Barrese, E. Effects of cadmium on crystallization of calcium phosphates. *Crystal Res. Tech. J. Exp. Industr. Crystal.* **2004**, *39*, 235–239. [CrossRef]

66.　Xu, Y.; Schwartz, F.W.; Traina, S.J. Sorption of Zn^{2+} and Cd^{2+} on hydroxyapatite surfaces. *Environ. Sci. Tech.* **1994**, *28*, 1472–1480. [CrossRef] [PubMed]