

Evaluation with scanning electron microscopy of Cd, Cu, and Zn removal from aqueous solutions by ash from gasification of poultry feathers

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ABSTRACT

This study investigated the adsorption of heavy metals (Cd, Cu, Zn) as single or mixed pollutants from aqueous solutions. Ash from gasification of poultry feathers was used as the adsorbent. Batch experiments were performed at an adsorbent dosage of $1\text{g}\cdot\text{L}^{-1}$, an adsorption time of 2h and an agitation speed of 100 rpm. In each variant, the total concentration of individual metals or their mixture was assumed to be around $500\text{mg}\cdot\text{L}^{-1}$. The morphology and composition of ash before and after adsorption were characterized with X-ray diffraction, scanning

electron microscopy and energy-dispersive X-ray spectroscopy. The ash was rich in Ca, P and Si. Diffraction revealed the presence of calcium carbonate, calcium phosphate and calcium phosphate hydroxide. Microscopy confirmed the presence of Cd, Cu, and Zn on the ash surface after adsorption. Adsorption efficiency was higher for single metals than for their mixture. Spectroscopy revealed changes in ash composition that could be related to the mechanism of metal adsorption. Taking into account the high initial concentrations of metals, ash from poultry feathers is an attractive option for metal removal from wastewater.

INTRODUCTION

Increasing industrialization causes excessive release of toxic metals into the environment. Three such metals, cadmium (Cd), copper (Cu) and zinc (Zn), have been in industrial use for a long period of time. Cd is widely used in industrial processes, e.g. as an anticorrosive agent, as a stabilizer in PVC products, as a colour pigment, as a neutron absorber in nuclear power plants and in the production of nickel-cadmium batteries. Cu can be found in wastewater in concentrations from several thousand $\text{mg}\cdot\text{L}^{-1}$ (plating bath wastewater) to less than $1\text{mg}\cdot\text{L}^{-1}$ (Cu cleaning operations) (Baysal et al. 2013).

Cd, Cu, and Zn ions are particularly dangerous to health if they contaminate industrial wastewater. Cd is a non-essential and non-biodegradable element which slowly accumulates in the body, especially the kidney, where the

half-life of cadmium is approximately 10 years (Orlowski and Piotrowski 2003). A life-long intake can result in tubulus cell necrosis of the kidney, lung edema, and destruction of mucous membranes (Godt et al. 2006).

Trace levels of Cu are physiologically essential, but higher levels can be very toxic. Cu exerts adverse effects at concentrations just slightly higher than its physiological range. For example, cytopathological alterations were observed in the hepatocytes of fish treated with levels of Cu slightly above the concentrations at which no effects were observed (Khangarot 1992). In mammals, some studies report that chronic Cu poisoning, characterized by hepatic and renal cell degeneration, hemoglobinuria, jaundice and early death, may occur with a relatively low hepatic Cu level (Knobeloch et al. 1994; Sugawara et al. 1995; Todd and Thompson 1965). In humans, vomiting, nausea, abdominal

cramps, dizziness, and diarrhea appeared after a relatively short period of exposure to low levels of Cu^{2+} (Knobeloch et al. 1994).

Although Zn lacks redox activity and has traditionally been regarded as relatively non-toxic (Murphy 1970), there is increasing evidence that free ionic zinc is a potent killer of neurons and glia. Yokoyama et al. (1986) showed that 15min exposure to 300–600 μM Zn results in extensive neuronal death in cortical cell culture. Combined with the discovery that neurons store up to 300 μM of free Zn in their terminals (Frederickson et al. 1983) and release Zn when they are depolarized (Assaf and Chung 1984; Howell et al. 1984; Sloviter 1985), these findings indicate that Zn has an active role in neuronal injury.

For the above reasons, heavy metals have commonly been removed from water and/or wastewater by several processes, including chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption (Chandra Sekhar et al. 1998; Suzuki 1997). Adsorption with a suitable adsorbent is effective, and if the selected adsorbent is waste material, the process is economically attractive (Abas et al. 2013). To this end, fly ash from coal combustion has been tested (Bayat 2002). Chicken feathers could also be an interesting material for sorbents. In their composition, carbon, nitrogen and hydrogen

predominate (up to 70% of dry mass) (Kardaš et al. 2015). Thus, they have a high calorific value and can be combusted. However, ash from gasification of poultry feathers has not been tested as a sorbent of heavy metals. This kind of ash could potentially replace activated carbons and other common materials: the ash has high alkalinity and high contents of Ca, P, and Si, so it could remove metals from aqueous solution by precipitation, ion exchange or electrostatic attraction.

Thus, the aim of this study was to characterize waste ash from gasification of poultry feathers, and to test how effectively the ash removes heavy metals from aqueous solutions. Aqueous solutions were prepared with Cd, Cu, and Zn alone and in combination, and the adsorption process was investigated with X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

MATERIALS AND METHODS

Ash characteristics and preparation

Ash from gasification of poultry feathers was used as a metal adsorbent. The pH of a suspension ash in distilled water (1:10 ratio, w/v) was strongly alkaline (pH 13.2), and its major components were phosphorus oxide, calcium oxide and silica (Table 1). No other compounds or elements

Table 1. Major components and pH of ash from gasification of poultry feathers.

Characteristic	Unit	Value
pH	-	13.2
Ash content	fw $\text{t}\%$ *	98.58
H ₂ O content	fw $\text{t}\%$	0.14
Total Organic Carbon	wt $\%$ **	0.14
Chlorides	fw $\text{t}\%$	0.44
CaO	fw $\text{t}\%$	36.2
P ₂ O ₅	fw $\text{t}\%$	39.94
Al ₂ O ₃	wt $\%$	1.49
Fe ₂ O ₃	wt $\%$	0.72
SiO ₂	wt $\%$	10.90
Na ₂ O	wt $\%$	3.51
MgO	wt $\%$	2.20
K ₂ O	wt $\%$	2.24
SO ₃	wt $\%$	1.82
As	mg $\cdot\text{kg}^{-1}$	<0.19
Cd	mg $\cdot\text{kg}^{-1}$	<0.048
Cr	mg $\cdot\text{kg}^{-1}$	1.84
Cu	mg $\cdot\text{kg}^{-1}$	2.42
Hg	mg $\cdot\text{kg}^{-1}$	<0.19
Ni	mg $\cdot\text{kg}^{-1}$	<0.48
Pb	mg $\cdot\text{kg}^{-1}$	<0.48
Zn	mg $\cdot\text{kg}^{-1}$	0.29

- not applicable

* fresh weight percentage (fw $\text{t}\%$)

** weight percentage (wt $\%$)

exceeded 5 weight percent (wt%), and heavy metals were only present in trace amounts.

Before the adsorption experiments, the ash was milled in a cutting mill to obtain 0.5mm ash particles. To minimize its contact with moisture, the ash was kept in a tightly closed container.

Preparation of stock metal solutions

Stock metal solutions were prepared from nitrate salts of analytical grade: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. To obtain total metal concentrations of $10\text{g}\cdot\text{L}^{-1}$ in the stock standard solution (single metals or their mixtures), suitable weights of metal salts were dissolved in deionised water. For adsorption experiments, working metal solutions were prepared. Metal concentrations in the working solutions were assumed to be high ($\sim 500\text{mg}\cdot\text{L}^{-1}$).

Batch adsorption experiments

The experiments on metal removal using poultry ash were performed in 50mL falcon tubes with an adsorbent dosage of $1\text{g}\cdot\text{L}^{-1}$, an adsorption time of 2h and an agitation speed of 100 rpm. The suspensions were shaken horizontally on an orbital shaker, then filtered with Whatman 42 filters. Before metal analysis, the supernatants were acidified with HNO_3 . The filtered ash was then analyzed with SEM. The experiments were carried out in four variants:

1. Variant A investigated Cd removal from an aqueous solution,
2. Variant B investigated Cu removal from an aqueous solution,
3. Variant C investigated Zn removal from an aqueous solution,
4. Variant D investigated removal of a Cd, Cu, and Zn mixture from an aqueous solution.

Analytical methods

The BET (Brunauer–Emmet–Teller) specific surface area of the ash was determined by fitting the linear portion of a BET plot with the BET equation; the pore size distribution in the ash was calculated based upon the desorption plot of an N_2 adsorption–desorption isotherm and using the Barret-Joyner-Halenda method (BJH) (temperature, -196°C) (Micrometrics ASAP 2010, USA).

The XRD investigation was performed with an X`Pert Pro diffractometer (Panalytical) at an angular range of $5\text{--}90^\circ$ (2Theta). The diffraction pattern was then compared with a database of reference spectra.

Imaging Microscopy (SEM) was performed with a LEO 1430VP scanning electron microscope (Carl Zeiss) and a Quanta 3D FEG (FEI) equipped with a BSE detector. Analyses were performed at 100-fold magnification. Imaging mode for non-conductive testing was set at a pressure of 50Pa.

Qualitative and quantitative analysis of elemental composition (SEM-EDX) in ash before and after metal sorption was performed with a Quantax 200 energy dispersive X-ray spectrometer with an XFlash 4010 detector (Bruker

AXS), which was coupled with a LEO 1430VP scanning electron microscope equipped with a BSE detector (Carl Zeiss). Analyses of three areas were performed at 100-fold magnification. Imaging mode for non-conductive testing was set at a pressure of 50Pa. The results of the elemental composition were calculated in mass and atomic percentage.

Total metal concentrations were measured with a flame atomic absorption spectrometer (FAAS) (Varian, AA280FS).

RESULTS AND DISCUSSION

Characterization of the ash before adsorption experiments

The poultry ash had a BET specific surface area of $1.1966\text{m}^2\cdot\text{g}^{-1}$, and a total volume and total area in the pores of $0.0023\text{cm}^3\cdot\text{g}^{-1}$ and $0.618\text{m}^2\cdot\text{g}^{-1}$, respectively. In comparison to the literature, the obtained BET results are relatively low, but similar to those for fly ashes. Specific surface area, which is an important property for metal adsorption, strongly depends on adsorbent type. Srivastava et al. (2006) found that rice husk ash, used as an adsorbent for the removal of Cd, Ni, and Zn ions from aqueous solutions, had a BET surface area of $36.44\text{m}^2\cdot\text{g}^{-1}$. Sukpreabprom et al. (2015) showed that bottom ash from a power plant in Thailand had a specific surface area of $5.14\text{m}^2\cdot\text{g}^{-1}$. Bada and Potgieter-Vermaak (2008) reported that ash from coal-fired power thermal station in South Africa exhibited a BET surface area of $2.99\text{m}^2\cdot\text{g}^{-1}$. In contrast, Bayat (2002) used the laser beam method to show that the specific surface area of fly ash used for adsorption of Cd and Zn was $0.342\text{m}^2\cdot\text{g}^{-1}$.

XRD revealed the presence of calcium carbonate (CaCO_3), calcium phosphate ($\text{Ca}_4\text{P}_2\text{O}_9$) and calcium phosphate hydroxide, i.e. hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), in the ash, which indicates that the gasification process produces more complex mineral structures. Tugrul et al. (2012) found the presence of two minerals in fly ash from a thermal power plant, quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), using XRD.

SEM is used to examine surface morphology (particle associations, surface irregularities) and elemental composition in a given adsorbent (Singh and Pragma 2015). An SEM image of ash at 100 \times magnification is shown in Figure 1. In this image one can clearly see that the poultry ash contained mainly fine particles. Some bigger particles of irregular shape could have caused the particle aggregation that was observed.

During EDX analysis of ash samples, four micro-areas were chosen, which were numbered 24474, 24475, 24476 and 24478 (Figure 1). The areas were selected to highlight the differences in the elemental composition of different grain sizes (24475, 24478) or colours (24476). Sample 24474 is an area representative of the entire sample.

Figure 2 shows the EDX spectrum of elements occurring in poultry ash with a particle size of 0.5mm. The mass and atomic percentages of individual elements in four micro-areas (24474, 24475, 24476 and 24478) in the ash are depicted in Table 2. The results show that the ash contained mainly Ca, O, P, and Si, with

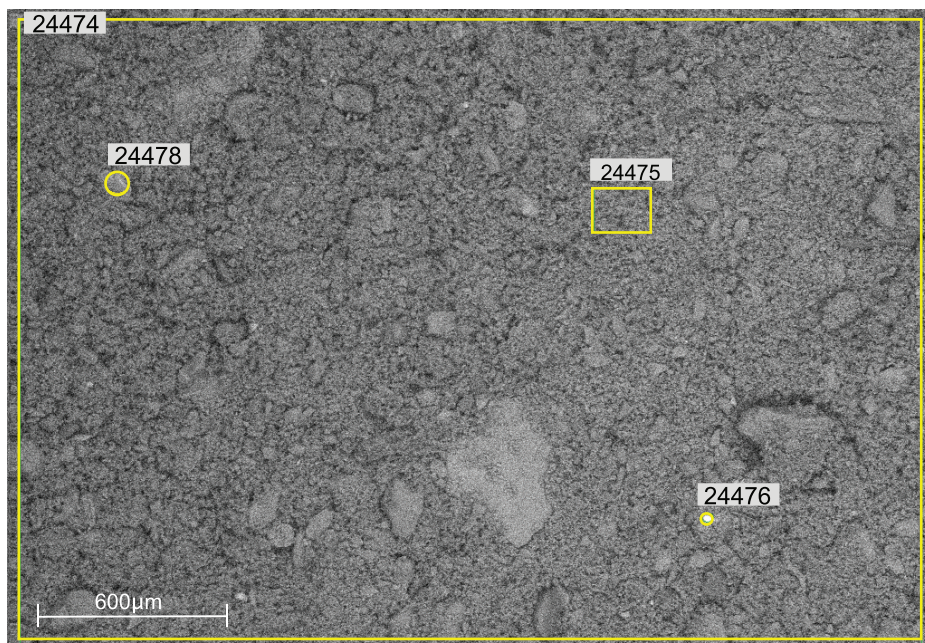


Figure 1. Scanning electron microscopy image showing particles of poultry feather ash before metal adsorption. Different numbers correspond to specific areas whose elemental composition was analyzed. Area 24474 is representative of the whole ash sample, 24475 and 24478 are areas of different grain size, and 24476 is an area of different color.

smaller quantities of Na, Mg, Al, K, and Fe. The high Ca content in the poultry feather ash may be related to the composition of the feedstock used for gasification. Although poultry feathers alone have a low Ca content (up to 0.2%) (Sosnowska et al. 2014), in the present study, they were mixed with meat processing remains (up to 10%), such as bones, beaks and claws, which are an additional source of Ca. In contrast, poultry feathers contain a large amount of sulfur (2.13%) (Sosnowska et al. 2014). Thus, the resulting ash is rich in this element. According to Vassilev et al. (2010) an extremely high S content

is characteristic of some waste, especially sewage sludge (2.33%), meat-bone meal (1.7%) and chicken litter (1.2%).

In the elemental composition of the area representative of the ash overall (24474), oxygen predominated, and the elemental composition of the other areas (24475, 24476 and 24478), was somewhat similar. Although area 24476 did have a 10%-higher share of sulfur, the elemental composition was homogeneous throughout the ash sample in general. The content of carbon was negligible, which confirms that the feathers and processing remains were completely decomposed

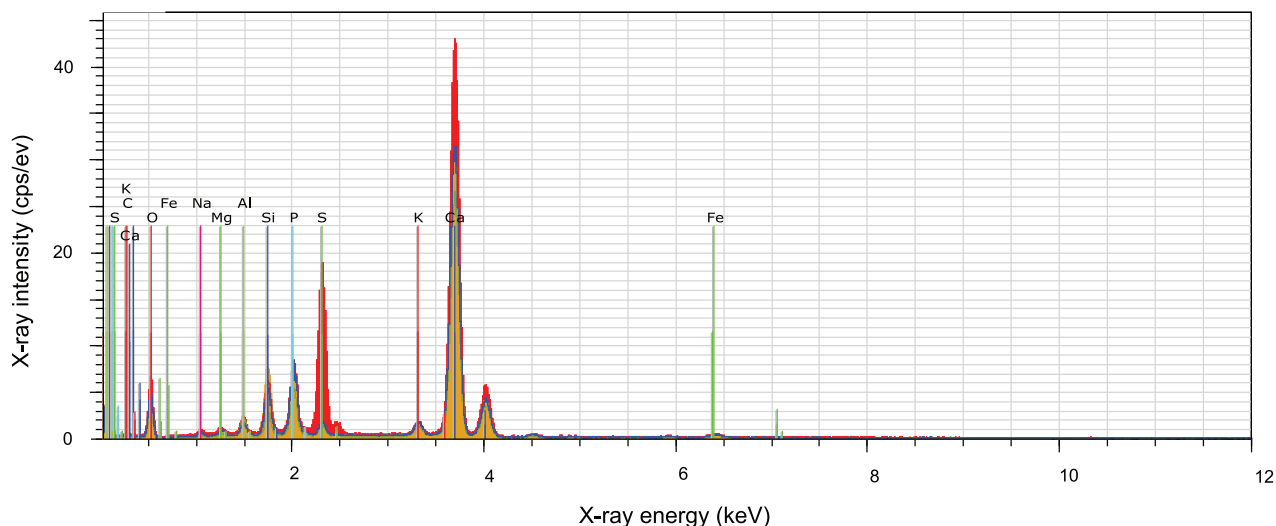


Figure 2. The collective energy-dispersive X-ray spectroscopy spectrum obtained from four areas of the poultry feather ash sample.

Table 2. Elemental composition of the poultry feather ash particles before metal adsorption, from calculations based on the results of energy-dispersive X-ray spectroscopy.

Examined area*	Element										
	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe
Mass percentage											
24474	0.01	31.45	1.76	1.22	1.62	5.08	8.18	1.41	1.86	46.35	1.06
24475	0.01	28.46	1.58	0.91	3.07	3.87	7.45	1.79	1.91	49.92	1.02
24476	0.03	22.92	1.75	1.08	1.54	4.08	5.71	13.11	1.31	47.65	0.81
24478	0.00	30.24	1.37	0.76	1.14	8.38	7.16	0.83	1.56	47.97	0.58
average	0.01	28.27	1.62	0.99	1.84	5.35	7.13	4.29	1.66	47.97	0.87
Atomic percentage											
24474	0.02	50.85	1.98	1.30	1.56	4.68	6.83	1.13	1.23	29.92	0.49
24475	0.02	47.48	1.83	1.00	3.04	3.67	6.42	1.49	1.31	33.25	0.49
24476	0.07	39.92	2.12	1.24	1.59	4.05	5.14	11.39	0.94	33.13	0.40
24478	0.01	49.40	1.56	0.82	1.10	7.80	6.04	0.68	1.05	31.28	0.27
average	0.03	46.91	1.87	1.09	1.82	5.05	6.11	3.67	1.13	31.89	0.41

* Numbers were assigned to the examined areas of ash (see Figure 1)

during gasification. The chemical composition of different adsorbents can vary greatly. For example, rice husk ash, consisting mainly of SiO₂ (>95 mass %), was found to be a suitable adsorbent for removal of Pb, and Hg (Feng et al. 2004), and Cd, Ni, and Zn (Srivastava 2006). In coal fly ash, in zeolite 4A, and in residues of treated coal fly-ash, the amount of CaO did not exceed 15 mass %, and that of SiO₂ ranged from 40 to 50 mass % (Hui et al. 2005).

Metal adsorption onto poultry feather ash

Under the conditions that were found to be optimal in our previous research (adsorbent dosage 1g·L⁻¹, adsorption time 2h, agitation speed 100 rpm), metals were removed more efficiently from solutions with single metals than from the solution with a mixture of metals (Figure 3). The initial concentrations of the metals in their aqueous solutions were as follows: Cd, 465mg·L⁻¹ (single) and 439mg·L⁻¹ (mixture); Cu, 429mg·L⁻¹ (single) and 445mg·L⁻¹ (mixture); Zn, 451mg·L⁻¹ (single) and 449mg·L⁻¹ (mixture). When metals were removed from solutions of single metals, more Cd (64.5%) was removed than Cu (47.7%) or Zn (50.8%). When the metals were present in a mixture, they were removed less efficiently. Cu was removed more efficiently from the mixed solution than Cd or Zn, which was probably related to the effect of competition between metal ions during adsorption.

In the present study, the use of waste ash from gasification of poultry feathers achieved high removal efficiency, especially for single metal ions (64.5% for Cd, 47.7% for Cu, and 50.8% for Zn) at high concentrations (~500mg·L⁻¹) in aqueous solutions. Thus, it is interesting to compare the adsorption properties of poultry ash with those of other commonly used adsorbents. For example, Srivastava et al. (2006) studied adsorption of Cd, Ni, and Zn on rice husk ash.

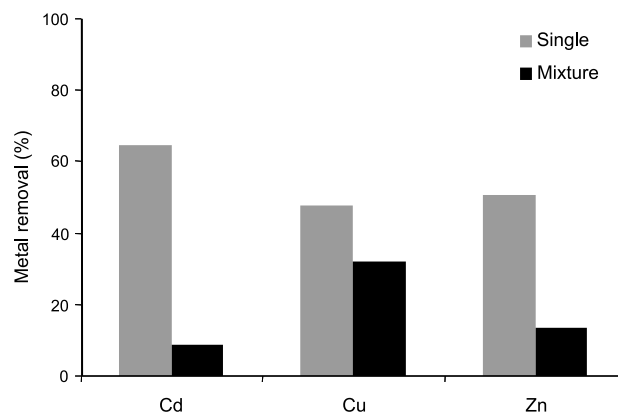


Figure 3. The efficiency of removal of individual metals from aqueous solutions of the metals alone or from an aqueous solution with a mixture of these metals during sorption onto poultry feather ash (adsorbent dosage 1g·L⁻¹, adsorption time 2h, agitation speed 100 rpm).

The largest amounts of metal (35.3% Zn, 27.8% Ni, and 23.3% Cd) were removed at initial metal concentrations of 500mg·L⁻¹ and an adsorbent dosage of 10g·L⁻¹. Gupta et al. (2003) used bagasse fly ash, an industrial solid waste from the sugar industry, for the removal of Cd and Ni from wastewater. The authors showed that as much as 90% removal of Cd and Ni is possible in about 60 and 80min, respectively, under batch test conditions. Mohan and Gandhimathi (2009) concluded that the optimum dose of coal fly ash for heavy metals removal was 2g·L⁻¹, with removal efficiencies of 39%, 28%, 74%, 42% and 71% for Cu, Mn, Pb, Zn, and Cd, respectively.

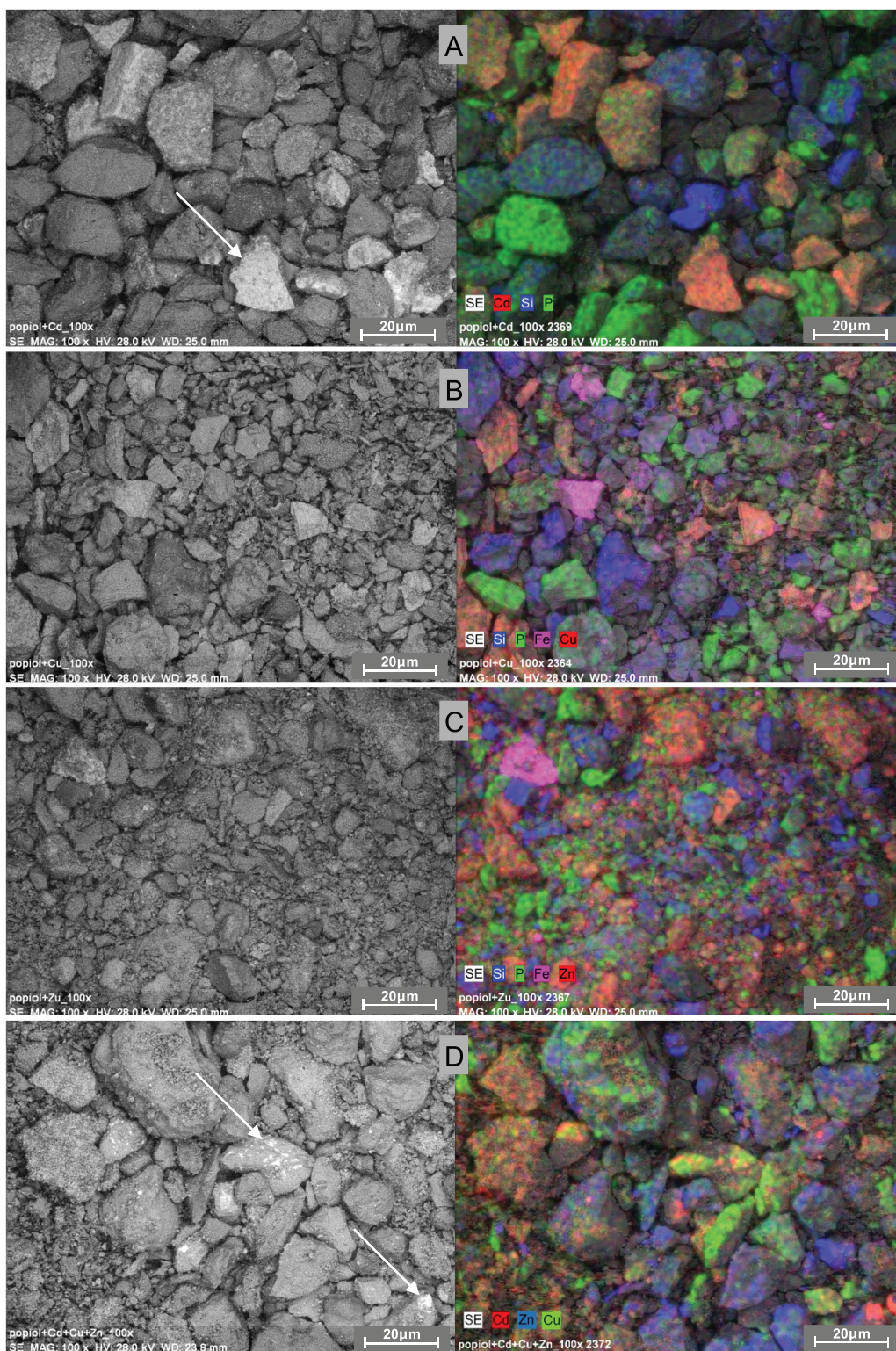


Figure 4. Scanning electron microscopy micrographs of poultry feather ash after metal adsorption. A, B, C – adsorption of Cd, Cu, and Zn alone, respectively; D – a mixture of Cd, Cu, and Zn. Figures on the left show the presence of deposits of solid substances. Arrows indicate some of the deposits of solid substances on the surface of ash particles after metal adsorption. Figures on the right show metals alone or in mixtures on the ash.

The SEM technique provides information on the association of metals in an adsorbent (Jo et al. 2010). In the present study, SEM coupled with EDX was used to investigate where the Cd, Cu, and Zn ions were bound to the ash particles. In the SEM micrographs (Figure 4), it is possible to observe the distribution of the individual metals

on the ash surface after adsorption. The brighter sites in the gray SEM micrographs (marked with white arrows) theoretically correspond to the location of elements with higher atomic weight. Graphic processing of the brighter sites in the EDX analysis confirmed that Cd was present in those sites.

Table 3. Elemental composition of the poultry feather ash after metal adsorption, from calculations based on the results of energy-dispersive X-ray spectroscopy.

Variant*	Element											
	C	O	Al	Si	P	S	K	Ca	Fe	Cd	Cu	Zn
Mass percentage												
fresh ash	0.01	28.27	1.84	5.35	7.13	4.29	1.66	47.97	0.87	-	-	-
Variant A	0.12	36.11	2.16	7.29	6.43	0.27	0.61	29.95	0.91	15.34	-	-
Variant B	0.18	47.93	2.18	7.24	4.93	0.61	1.65	19.81	0.92	-	10.01	-
Variant C	0.15	43.39	2.45	6.31	5.61	0.37	0.82	19.84	1.19	-	-	11.02
Variant D	0.08	40.10	2.57	7.64	5.94	0.56	1.75	24.11	1.11	3.21	6.61	5.19
Atomic percentage												
fresh ash	0.03	46.91	1.82	5.05	6.11	3.67	1.13	31.89	0.41	-	-	-
Variant A	0.28	51.2	1.73	5.81	4.67	0.23	0.39	17.16	0.39	3.39	-	-
Variant B	0.42	67.64	1.79	5.75	3.55	0.43	0.93	11.02	0.37	-	3.66	-
Variant C	0.29	65.22	2.18	5.35	4.40	0.28	0.50	11.93	0.48	-	-	4.21
Variant D	0.16	59.88	2.51	7.03	4.92	0.45	1.14	15.38	0.57	0.71	2.40	2.05

- not present

* Variants refer to removal from aqueous solution of A, Cd; B, Cu; C, Zn; D, a mixture of Cd, Cu, and Zn.

Table 3 shows the elemental composition of the ash after metal adsorption based on EDX analysis. This data on metal adsorption (expressed as mass or atomic %) confirmed that the ash efficiently adsorbed the metals (Figure 3).

The composition of the ash changed during adsorption, which could be connected with leaching and the mechanism of metal adsorption. In all samples, a decrease in Ca content was the most noticeable change; S content also decreased in all samples. In some samples, there was a decrease in K and P content.

The marked decrease in Ca and S content may be due to the solubility of these elements. Calcium is present in ash in multiple forms, primarily lime, anhydrite, calcite, and as part of the glassy matrix. With only water, the amount of Ca leached from fly ash could easily fall in the range of 100–15,000mg·kg⁻¹. The leachability of sulfur depends on the nature of the ash (i.e. pH), and is higher for acidic than for alkaline ashes (Izquierdo and Querol 2012). In the present study, the aqueous solutions of metals were slightly acidic, which favored leaching of Ca and S from the ash.

The sorption of metals by ash is likely due to two mechanisms: ion exchange and precipitation. Chirenje et al. (2006) attributed metal sorption by ash to ion exchange between metal ions in aqueous solution and Ca²⁺ on the

surfaces of calcite and gypsum in ash, which resulted in the formation of calcite-gypsum-like minerals. This mechanism of ion exchange could be the reason for the decrease in content of selected alkaline cations that was reported by other investigators. Vieira et al. (2014) found that the percentage of exchangeable potassium in rice husk ash drastically decreased after adsorption of Cu or Pb, from 1.40% to 0.53% after Cu adsorption, or to 0.45% after Pb adsorption. In the present study, the amount of K ions in the ash decreased only after Cd or Zn alone were adsorbed (Table 3). Precipitation with CaO or CaCO₃ could also cause metals to be retained (Xirokostas et al. 2003). Elemental analysis showed that the poultry ash used in this study was rich in Ca, in the form of CaO or CaCO₃. In addition, the ash was strongly alkaline. Mallampati et al. (2015) found that fly ash treated with nano-Fe/Ca/CaO and nano-Fe/Ca/CaO/PO₄ was very effective in immobilization of As, Cd, Cr, and Pb; all metals were precipitated in immobile Ca/PO₄ salts. The ash used in the present study was rich in Ca and P, which suggests that mainly these ions were responsible for metal adsorption. SEM showed deposits of solid substances on the surface of ash particles after adsorption (e.g. brighter sites marked with white arrows, Figure 4D), which could be metal precipitates.

CONCLUSIONS

Ash from gasification of poultry feathers is an effective sorbent for removing Cd, Cu, and Zn from aqueous solution, especially when they are present as single pollutants. X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy are useful techniques for evaluation of the adsorption process. X-ray spectroscopy showed changes in the chemical composition of ash, especially in the content of the predominant ions, Ca and P; these changes may indicate ion exchange during adsorption. In addition, scanning electron microscopy revealed the presence of precipitates on the ash surface that probably resulted from metal reaction with carbonates and phosphates. The ash from gasification of poultry feathers is a readily available by-product that could be an attractive sorbent for treatment at technical scale of industrial wastewater containing high concentrations of metal.

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