**ORIGINAL ARTICLE** 



# Effective bioremoval of Fe(III) ions using paprika (*Capsicum annuum* L.) pomace generated in the food industry

Tomasz Kalak<sup>1</sup> · Joanna Dudczak-Hałabuda<sup>1</sup> · Yu Tachibana<sup>2</sup> · Ryszard Cierpiszewski<sup>1</sup>

Received: 30 April 2020 / Accepted: 30 September 2020 / Published online: 6 November 2020  $\ensuremath{\mathbb{C}}$  The Author(s) 2020

## Abstract

In these studies, removal of Fe(III) ions by biosorption processes from aqueous solutions was carried out using paprika (*Capsicum annuum* L.) pomace generated during processing in the food industry. The biosorbent material was characterized using several analytical methods, including particle size distribution, XRD, SEM–EDS, electrokinetic zeta potential, surface area analysis (BET, BJH), thermogravimetry, morphology (SEM), spectrophotometry FT-IR. Several factors, such as biosorbent dosage, initial concentration, contact time and initial pH were analyzed to show an effect on the bioremoval process, efficiency and adsorption capacity. As a result, the maximum adsorption efficiency and capacity were determined to be 99.1% and 7.92 mg/g, respectively. Based on the kinetics analysis, the bioremoval process is better described by the Langmuir isotherm model and the pseudo-second order equation model. In conclusion, the achieved research results suggest that paprika biomass can be an effective material for efficiently removing iron(III) from wastewater and improving water quality. These studies on the recovery of iron metal from the environment fit in the latest trends in the concept of the global circular economy.

Keywords Water quality · Biosorption process · Paprika pomace · Fe(III) ions · Cleaner environment

# Introduction

Heavy metals are considered to be one of the most dangerous pollutants occurring in the marine environment, inland waters, as well as in the terrestrial environment. Their increasing amounts are emitted into the natural environment due to globalization, rapid development of industry and technology. Properties, such as non-biodegradability, ability to bioaccumulation and toxic effects on living organisms and human make them become a serious problem to be solved

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10163-020-01133-z) contains supplementary material, which is available to authorized users.

Tomasz Kalak tomasz.kalak@ue.poznan.pl

<sup>1</sup> Institute of Quality Science, Department of Industrial Products and Packaging Quality, Poznań University of Economics and Business, Niepodległości 10, 61-875 Poznań, Poland

<sup>2</sup> Department of Nuclear System Safety Engineering, Graduate School of Engineering, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka, Niigata 940-2188, Japan worldwide [1]. One of the metals whose excessive concentration in water is undesirable and even harmful is iron. It is not considered highly toxic, but it affects the quality and chemical properties of water, such as water turbidity, ability to react with other materials in the aquatic environment or to regulate bacterial growth. The reactions of iron cations and compounds with oxygen can be especially important when they produce oxygen radicals and peroxides that can damage DNA [2, 3]. Iron in soluble or insoluble form exists mainly in groundwater. Water containing the metal completely dissolved in ionic form is transparent and colorless. Instead, it becomes turbid and a reddish-brown precipitate insoluble in water (oxidized iron hydroxide) begins to form when in contact with oxygen-rich air [4]. This occurrence is a source of many aesthetic, health and economic troubles. In the aquatic environment, insoluble iron deposits are consumed by fish and other organisms. However, the degree of toxicity can be reduced by binding iron ions to other anionic water components, including biosorbents [5].

The use of several biosorbents were reported in the literature, including oil-palm fibers, leaves, yeast biomass, seaweed, olivestones, sawdust, chitin, rice hulls, bacteria, fungi, fruit and vegetable waste after industrial processing and others. These types of biomass are rich in chemical components that are capable of binding metal ions effectively, including polysaccharides (e.g., alginic acid, pectic acid, chitosan), polyphenols (e.g., tannin, catechin) and proteins. In addition, biosorbents with low adsorption efficiency can be subjected to a chemical or physical modification to increase efficiency (e.g. modification with concentrated sodium hydroxide solution). The other biomass component is lignin, found in all plants (along with cellulose). According to the literature, lignin itself poorly adsorbs metal ions, while its interaction with phenol or polyphenol compounds causes much better adsorption capacity [6].

The example of biomass capable of binding heavy metal ions may be paprika waste obtained in the food industry. In 2017, the global value of chillies and paprika production was about 36,092,631 tons and the larger manufacturer was China (17,821,238 tons). Other largest productions were located in the following countries: Mexico (3,296,875 tons), Turkey (2,608,172 tons), Indonesia (2,359,441 tons), Spain (1,277,908 tons) and United States (962,679 tons) [7]. Nowadays, Poland is the largest producer of paprika in Central and Eastern Europe. About 80% of the production is transferred to consumers through shops, supermarkets or wholesalers. On the other hand, the value of 20% is production for processing purposes, i.e. for all kinds of food products, frozen foods, for pizza and others. The production is mainly located in the Radom area and on average is estimated at about 100,000 tons per year. The area harvested oscillates around 600 ha on over 2000 farms (over 50 thousand tunnels) [8]. Dried paprika pomace is rich in cellulose, protein, pungent principles, phenols, flavonoids, capsaicinoids, carotenoids and vitamins, resins, pentosans, coloring pigments, mineral elements and small amounts of volatile oil. The seeds contain non-volatile oil containing triglycerides (60%), mainly linoleic acid and other unsaturated fatty acids [9]. All of these substances contain various functional groups, such as hydroxyl, phenol, carboxyl, sulfone and amino, which are capable of binding metal ions. The processes of chemisorption of metal ions with functional groups can take place as a result of ion exchange, complexation and chelation reactions. In addition, physical adsorption, redox reactions or microprecipitation may also occur on the surface of biomass [10, 11].

The purpose of the research was to investigate the possibility of bioremoval of Fe(III) ions from water by paprika (*Capsicum annuum* L.) pomace obtained from the processing in the food industry in Poland under different conditions of initial concentration, biosorbent dosage, contact time and initial pH. Moreover, the goal was to characterize this biomass by determining selected physical and chemical properties. Over and above that, the adsorption kinetics, equilibrium and isotherms were studied.

# **Experimental procedure**

# **Materials and methods**

#### Paprika pomace preparation and characterization

In the studies, paprika (*Capsicum annuum* L.) residues were generated during processing in one of the factories of the food industry in Poland. Before the experiments, the biomass was comminuted, sifted and separated into individual portions. Particles with the smallest diameters ranging from 0 to 0.300 mm were used in the research. Afterwards, drying at 60 °C and then storage in a desiccator was carried out.

At the start of the study, the biomass material was characterized using several methods, including particle size distribution, SEM–EDS, thermogravimetry, surface area (BET, BJH), electrokinetic zeta potential, morphology (SEM) and spectrophotometry (FT-IR ATR). A description of the methods and apparatus used has been attached as a supplementary file (SM Methods).

#### The Fe(III) biosorption process

Batch experiments at room temperature  $(23 \pm 1 \, ^{\circ}\text{C})$  were carried out to examine bioremoval efficiency of Fe(III) ions on paprika residues. The metal ions with analytical purity (standard for atomic absorption spectroscopy (AAS) 1 g/L, Sigma-Aldrich (Germany)) and distilled water were used. The dried particles of paprika (2.5-100 g/L) and solution (10 mL) ranging from 2.5 to 20 mg/L of Fe(III) ions at a certain pH (2-5) were agitated during 1 h at 150 rpm. The pH of Fe(III) stock solutions was regulated using 0.1 M NaOH and HCl. After adsorption processes, the solutions were centrifuged at 4000 rpm to separate the phases. The particle size distribution analysis by the laser diffraction method showed one peak at 295.3 nm, therefore the paprika adsorbent particle size was less than 300 nm, but the dried solid phase material was nevertheless removed properly by centrifugation without next filtration. In the end, the Fe(III) ions concentration [mg/L] was determined by the flame atomic absorption spectrometry (F-AAS,  $\lambda = 248.3$  nm for iron, SpectrAA 800 apparatus). The measurements were repeated three times and average results were reported.

Calculations of the adsorption efficiency A [%] and capacity  $q_e$  [mg/g] were carried out according to Eqs. 1 and 2, respectively:

$$A = \left[\frac{C_0 - C_e}{C_0}\right] \times 100\tag{1}$$

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{m} \tag{2}$$

where:  $C_0$  and  $C_e$  [mg/L] are initial and equilibrium Fe(III) ion concentrations, respectively; V [L]—volume of solution and m [g]—mass of paprika sorbent.

The analysis of kinetics, equilibrium and isotherm parameters was conducted using pseudo-first-order (3), pseudo-second-order (4), Langmuir (5) and Freundlich (6) models based on the equations, respectively:

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

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

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{5}$$

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

where:  $q_t$  [mg/g] is the amount of Fe(III) ions adsorbed at any time t [min.];  $q_e$  [mg/g]—the equilibrium amount of adsorbed Fe(III) ions;  $k_1$  [1/min.]—the rate constant of pseudo-first-order adsorption;  $k_2$  [g/(mg·min.)]—the rate constant of pseudo-second-order adsorption;  $q_{max}$  (mg/g) the maximum adsorption capacity;  $K_L$ —the Langmuir constant;  $C_e$  [mg/L]—the equilibrium concentration after the adsorption process;  $K_F$ —the Freundlich constant and 1/n the heterogeneity factor.

# **Results and discussion**

# Characterization of the paprika biomass

In the present work, the particle size distribution of dried paprika pomace was determined by laser diffraction and four peaks were observed at 1.5, 32.7, 122.4 and 295.3 nm (Fig. SM1). The particle size distribution has an influence on the properties of materials, such as the strength and rate of hydration. Furthermore, it is an important indicator of the quality and performance of particles in various processes. Smaller particles have the ability to dissolve faster and get better suspension than larger ones, as well as smaller adsorbent particle sizes lead to higher adsorption performance [12]. Therefore, on the basis of the literature review, particles of dried paprika pomace smaller than 0.300 mm in diameter were taken for experiments in this research. Figure 1 shows unground and unscreened dried paprika waste generated in the food processing.

The SEM–EDS analysis was performed in next studies. The following peaks are present in the spectrum (Fig. SM2) corresponding to the elements from the largest amount to the smallest (by weight [%]): C (44.51%), O (41.03%), P (3.27%), S (3.23%), Al (2.3%), Mg (2.07%), Si (1.84%), K (0.92%) and Ca (0.83%). Paprika pomace is an organic material, which is why the largest number of carbon and oxygen atoms was demonstrated. The number of counts in the EDS microanalysis was the basis for the calculation of the content of elements, and it was not estimated based on analytical measurements. This biomass material is not homogeneous, so there may be slight differences in composition depending on the location of the measuring point on the paprika



**Fig. 1** Industrial dried paprika waste (not ground and sifted, scale bar: 15 mm)

sample by the method. Furthermore, the distribution of various elements on the material was determined by SEM-EDS mapping using a backscattered detector. As a result of the analysis, almost homogeneous distribution of the elements (C, O, Al, Si, K, P, S, Ca, Mg) was observed, however, the intensity depends on the type of the element and the material characteristics (Fig. SM3).

At a temperature range of 29-600 °C thermogravimetric measurements were carried out (Fig. SM4). The analysis showed that a gradual increase in temperature resulted in a weight loss of the biomass. TGA and DTG curves showed the first phase of paprika biomass decomposition in the range between about 30 and 118 °C, and the second in the range from 150 to 500 °C. In the first stage, slight weight loss (3.7%) probably appeared as a result of evaporation of water molecules associated with the biomass surface. In the next stage, the greater weight loss (about 39.6%) was the result of a pyrolysis process in which most of the volatile substances evaporated. For this intense peak (DTG) at 329 °C, degradation of organic chemicals (carbohydrates, proteins and lipids) was likely to occur [13].

The BET analysis was performed and the low-temperature BET adsorption and desorption isotherm, linear form of BET adsorption isotherm, pore volume distribution (the BJH method) for adsorption and desorption were determined (Figs. SM5, SM6, SM7, SM8). The BJH method, which is related to capillary condensation in mesopores, was used to analyze the pore volume distribution for adsorption and desorption. The obtained summarizing parameters are as follows: specific surface area ( $S_{BET}$ ) 3.446 m<sup>2</sup>/g, volume of the pores (V\_p) 0.0055 cm<sup>3</sup>/g and average pore diameter (A<sub>pd</sub>) 6.415 nm. The adsorption and desorption isotherms match

iron(III) ions

the type II adsorption behavior. The paprika contains pores with a diameter ranging from 2.0 to 50 nm, which classifies them as mesopores according to the IUPAC nomenclature [14].

Zeta potential values of the analyzed paprika samples were determined using a combination of electrophoresis and speed measurement of particles in liquid by red laser  $(\lambda = 633 \text{ nm})$  based on the Doppler effect (LDV). Suspensions are more stable at higher zeta potential values because charged particles repel each other and overcome the natural tendency to form aggregates and agglomerates. In these studies, it has been revealed that pH values affect the surface charge, which shows a decrease from 2.03 mV (pH 2.1) to -30 mV (pH 6.46). The isoelectric point (IEP) is reached at pH 2.3, which can be explained by the fact of achieving a balance between positive and negative ions, which is very important from a practical point of view (the system is the least stable). At this point, paprika particles have the lowest viscosity, solubility and osmotic pressure (Fig. SM9).

#### Analysis of Fe(III) bioremoval process

#### Effect of paprika dosage

The impact of paprika dosage on the bioremoval efficiency of Fe(III) in the pH range 2-5 was studied and the results are shown in Fig. 2. The following conditions were applied during the experiments: the initial concentration of iron(III) ions 9.25 mg/L,  $T = 23 \pm 1$  °C, contact time 60 min. Based on the results, the bioremoval efficiency became higher with the increase in the dosage up to 30-50 g/L. The doses of 50, 70 and 100 g/L can be considered optimal, because



the maximum biosorption efficiency is estimated at 98.1%, 99.02% and 99.13% at pH 3, respectively. In addition, high efficiency is also reported at pH 4 (91.5-95.5%, 40-100 g/L). There was no need to increase the paprika dosage because no essential changes were visible. Furthermore, the removal capacity decreased from 1.8 mg/g (2.5 g/L) to 0.08 mg/g (100 g/L) (Fig. SM10). With high probability active centers were fully utilized during the interaction between Fe(III) ions and the biosorbent at smaller dosages, and were not fully utilized at larger dosages [15]. The growth of process efficiency may result from an increase in biomass mass and thus a greater number of available metal ion binding sites. Thus, the decline in sorption capacity occurred [16].

#### Effect of initial concentration of Fe(III) ions

The impact of Fe(III) initial concentration on the biosorption process is shown in Fig. 3. Based on the results obtained previously, the following conditions were used during the experiments: initial pH 4, contact time 60 min.,  $T = 23 \pm 1$  °C, optimal paprika dosage 50 g/L. The equilibrium pH after the process ranged from 3.6 to 3.9. An increase in initial concentration up to 2.5 mg/L caused a sharp increase in bioremoval efficiency (96.4%). In the concentration range from 2.5 to 20 mg/L, a little increase was observed from 94.7 to 98.5%. In addition, a gradual increase in biosorption capacity from 0.02 to 0.4 mg/g was achieved. Analysis of the adsorption process showed that the initial concentration of iron ions significantly affects the saturation of the surface of paprika biomass. It seems that iron ions are able to diffuse onto the surface of paprika at higher concentrations due to intramolecular diffusion. However, hydrolyzed ions can diffuse much more slowly. In the first adsorption phase, the lower iron ion concentration was sufficient to initiate an ion exchange between the biomass solid phase and the aqueous phase. Nouri et al. reported that a higher metal ion removal efficiency would be when there was a greater driving force of mass transfer and less metal uptake resistance [17]. According to the literature, the  $Fe^{3+}$  ion radius is estimated at 65 pm. The smaller the ionic radius of metals, the higher tendency for hydrolysis reactions to occur, resulting in a decline in the process efficiency [18, 19].

#### Effect of initial pH on the process

The impact of initial pH on the process is demonstrated in Fig. 4 and Fig. SM11. The following experimental conditions were used: the initial concentration of iron(III) ions 9.25 mg/L,  $T = 23 \pm 1$  °C, contact time 60 min., paprika dosage 2.5 - 100 g/L. The process efficiency, pH and paprika dosage are interdependent. In addition, interfacial tension and contact angle parameters at the solid-liquid interface has an influence on the process [20]. There is revealed that the best biosorption results are obtained at pH 3 for dosages of 50 g/L (98%), 70 g/L (99%) and 100 g/L (99.1%). An increase between pH 2 and 3, and a slight decrease in efficiency between pH 4 and 5 was observed. Furthermore, the lowest adsorption occurred at an adsorbent dosage of 2.5 g/L (11.9-45.8%). In all likelihood, the cation exchange mechanism was responsible for binding iron ions. Functional groups present on the surface of paprika biomass were protonated by a larger amount of hydrogen ions, which was the reason for the decrease in the number of negatively charged sites and an increase in the number of positively charged ones. When the pH increased, ion exchange and electrostatic interaction occurred during the adsorption process of Fe(III) ions. The acid groups of the biomass were deprotonated and Fe(III) cations were given the opportunity to be bound. The paprika surface became more negatively electrostatically charged at higher pH values. According to the literature, iron exists in ionic form in the pH 2-5 range. Thus, the maximum sorption capacity was obtained at pH 3 and 4. At pH 5 a decrease in the process capacity was noticed probably due to the competition of hydroxyl ions in sorption centers. Moreover, slowing down the ion exchange process can be caused by the other forms of the metal, such as  $Fe(OH)_3$ ,  $Fe(OH)_2^+$  and  $Fe(OH)^{2+}$ . Additionally, Negatively charged Fe(III) compounds might be repelled by negatively charged surface functional groups of the paprika biomass, which can also reduce the Fe(III)

12

14 16 18 20 22





– 100 g/L



removal efficiency. However, according to the literature, the solubility of negatively charged Fe(III) compounds in water is lower than those of positively charged at pH range of 4–5 [32]. Thus, the presence of negatively charged Fe(III) may be of minor importance for this process. Due to the fact that a downward trend in adsorption efficiency was observed and precipitation of Fe(III) ions could take place at higher pH values, it was not necessary to conduct experiments at pH > 5 [16, 21–24].

#### Adsorption kinetics analysis

Effect of contact time and kinetic models The influence of contact time on the process is shown in Fig. 5 and Fig. SM12. Previous studies allowed the setting of the following experimental conditions: initial concentration of iron(III) ions 9.25 mg/L, initial pH 4.0, adsorbent dosage 40 g/L,  $T=23\pm1$  °C. After just 5 min, the maximum sorption capacity (94.2% ±0.014, 0.22 mg/g) was reached and no



significant changes were observed up to 5 h (92.8%  $\pm$  0.021 to 94.0%  $\pm$  0.014, 0.21–0.23 mg/g). The equilibrium pH after adsorption was equal to 4.6. The probable reason for the rapid initial increase in adsorption may be the high concentration of iron cations at the biomass-water interface and the availability of more free active sites on the surface of paprika. The process equilibrium was reached gradually when active centers were occupied by iron ions [25].

Moreno-Piraján et al. reported in conclusions of their paper that 'the selected pH for an optimal rate of adsorption was 5.8 for all the ions investigated' (including iron ions) [24]. Therefore, the effect of contact time was additionally tested at pH 5 and 6 for adsorbent doses from 2.5 to 40 g / L. The results were similar to those for pH 4, i.e. equilibrium concentrations were reached after about 5 min.



 $\log C_{e}$ 

Kinetics of Fe(III) adsorption on paprika pomace was studied. The calculated parameters for the pseudo-first-order kinetic model are following:  $k_{ad} = 0.179$  1/min,  $q_e = 0.063$  mg/g,  $R^2 = 0.698$ . The calculated correlation coefficient  $R^2$  is not significantly close to the value of 1.0, therefore the research results were next analysed using the pseudo-second-order model. As a result of calculations (k = 127.49 g/mg min,  $q_e = 0.194$  mg/g,  $R^2 = 0.999$ ) a much higher correlation coefficient was achieved, suggesting that the pseudo-second-order kinetic model better describes the kinetics of the biosorption process. It is likely that chemical bonds were formed with Fe(III) ions during the biosorption process on the surface of paprika biomass (chemisorption) [26].

#### **Biosorption isotherm models**

In the next studies, the bioremoval process was analysed by the use of isotherm models. Based on the calculated parameters for the Langmuir model (Fig. 6,  $q_m = 7.923$  mg/g,  $K_L = 8.956$  L/mg,  $R^2 = 0.866$ ) and the Freundlich model (Fig. 7,  $K_f = 31.129 \text{ [mg/g] } [\text{L/mg}]^{(1/n)}$ , n = 1.085,  $R^2 = 0.494$ ), it was found that the adsorption process data is better suited to the Langmuir model. According to the equation, the adsorbent and solute-binding energy are closely related to the  $K_L$  constant, which describes the spontaneity of the biosorption process. As the  $K_L$  constant value increases, the spontaneity of the biosorption reaction also increases. This relationship is reflected in greater process efficiency and the presence of a more stable adsorbent. However, the Freundlich isotherm equation describes the relationship between the concentration of solute ions on the surface of an adsorbent  $(q_e)$  and the concentration of the solute in the liquid  $(C_e)$  it is in contact with. The calculated parameter values suggest that iron ions are able to easily transfer from the solution to the biomass surface. Table 1 compares the maximum Fe(III) adsorption capacity on paprika with other results available in the literature.

Table 1 Literature summary of sorption capacity of iron ions

Type of adsorbent/reference	q <sub>m</sub> [mg/g]
Paprika ( <i>Capsicum annuum</i> L.) pomace (these studies)	7.923
Hazelnut hull [27]	13.59
Pretreated orange peel [3]	18.19
Padina sanctae crucis algae [28]	34.65
Microbial biomass Rhizopus arrhizus [29]	34.73
Olive Cake [30]	58.479
Brown algae Sargassum Vulgare [23]	63.67
The husk of <i>Cicer arientinum</i> [31]	72.16

#### SEM morphology

Figure 8 a, b shows SEM images of paprika before and after Fe(III) adsorption that were analyzed. Many irregular shapes of biomass particles can be seen. Looking at the details, there can be seen different shapes of particles, such as oval, short and longer, angular, polygonal solids, as well as mild rather than sharp edges. Developed flat surfaces are visible and generally the structure is not homogeneous. Shape irregularities occur with both larger and smaller particles. After Fe(III) ions adsorption, generally speaking the biomass surface looks similar, however, it is a bit rough, small gaps were filled and particle agglomeration occurred. The texture changes may probably be the result of a reaction of iron ions binding on the surface of the paprika biosorbent or reaction with the components of the initial solution, e.g. NaOH.



Fig.8 a, b The SEM of paprika (magn.:  $\times$  10,000, scale bar: 2  $\mu m)$  before (a) and after (b) iron(III) sorption



Fig. 9 FT-IR bands of paprika before and after iron(III) ions sorption

FT-IR wavelengths [cm <sup>-1</sup> ]	Band vibration characteristics
3289	Stretching O–H (water or other hydroxylated molecules, e.g. alcohols)
2924	Asymmetric stretching C–H, –CH <sub>2</sub> - and –CH <sub>3</sub> (carboxylic acids)
2855	Stretching –CH <sub>3</sub> , C–H
1736	Stretching $C = O$ (e.g. esters)
1628	Stretching C–O bonds
1516	Stretching C=C, bending N-H bonds (aromatic ring)
1369	Deformation vibration C-H bonds
1234	Stretching C–O–C bonds
1033	Bending C-O bonds (polysaccharides)

## **FT-IR spectroscopy studies**

**Table 2**FT-IR peaks of paprikapomace and their description

The FT-IR measurements of paprika pomace before and after the biosorption process were carried out and the spectra are visible in Fig. 9. For this study, samples from the experiments in the following conditions were used: paprika dose 50 g/L, initial concentration of Fe(III) ions 9.25 mg/L, initial pH 3,  $T = 23 \pm 1$  °C, contact time 60 min. The most important FT-IR peaks are listed and explained in Table 2. Differences in frequency, shape and intensity of bands or possible interactions with Fe(III) ions were taken in the

comparative analysis of the paprika spectrum before and after the adsorption process. There is presented in Fig. 9 that after the bioremoval process, the peaks' intensity shifted significantly towards higher transmittance values and their positions remained at the same wavelengths or very slightly shifted. The changes are listed as follows: 3289.32 (shift to  $3289.07 \text{ cm}^{-1}$ ), 2924.65 (shift to  $2924.03 \text{ cm}^{-1}$ ), 2855.09 (shift to  $2854.57 \text{ cm}^{-1}$ ), 1735.66 (shift to  $1742.95 \text{ cm}^{-1}$ ), 1627.87 (shift to  $1628.11 \text{ cm}^{-1}$ ), 1516.34 (shift to  $1515.49 \text{ cm}^{-1}$ ), 1234.17 (shift to  $1232.80 \text{ cm}^{-1}$ ), 1032.92 (shift to  $1027.08 \text{ cm}^{-1}$ ). The observed phenomena of shifts

can be the result of interaction and bond formation of Fe(III) ions with functional groups of compounds present in paprika pomace as a part of the chemisorption process.

# Conclusions

Paprika waste (Capsicum annuum L.) obtained during processing in the food industry in Poland was used for examining the possibility of removing Fe(III) ions from aqueous solutions. The physicochemical properties of the biosorbent were determined using selected analytical methods. In the next stage, the effect of initial concentration, adsorbent dose, contact time and initial pH on the efficiency of the metal ion bioremoval process was analyzed in batch experiments. Based on the obtained research results, it was found out that the maximum adsorption efficiency was 99.1% (paprika dose 100 g/L, initial concentration of Fe(III) ions 9.25 mg/L, initial pH 3,  $T = 23 \pm 1$  °C, contact time 60 min.) and the calculated maximum adsorption capacity was 7.92 mg/g. In addition, biosorption was confirmed by changes visible on the FT-IR spectrum and SEM images. Finally, isotherms were determined, and characteristic process kinetics parameters were calculated and analyzed. The analysis showed that the pseudo second-order kinetic model and Langmuir model are best suited for the biosorption process.

In summary, these experiments have shown that paprika waste is capable of removing Fe(III) ions due to its favorable physicochemical properties and the content of relevant functional groups in the biomass composition. The promising research results are a premise for continuing experiments on the biosorption of other metal ions, but above all they create the possibility of industrial use of paprika waste to improve water quality.

**Acknowledgements** This research did not receive a specific grant from any a funding agency in the public, commercial or not-for-profit sectors.

## **Compliance with ethical standards**

Conflict of interest The authors declare no conflict of interest.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

## References

- Olawale SA, Emmanuel A, Aishat A, Ushie UJ (2017) biosorption of heavy metals from aqueous solution using termite feathers. Res J Chem Environ Sci 5:95–100
- Papanikolaou G, Pantopoulos K (2005) Iron metabolism and toxicity. Toxicol Appl Pharmacol 202(2):199–211
- Lugo-Lugo V, Barrera-Díaz C, Ureña-Núñez F, Bilyeu B, Linares-Hernández I (2012) Biosorption of Cr(III) and Fe(III) in single and binary systems onto pretreated orange peel. J Environ Manag 112:120–127
- Das B, Hazarika PI, Saikia GI, Kalita H, Goswami DC, Das HB (2007) Removal of iron from groundwater by ash: A systematic study of a traditional method. J Hazard Mater 141:834–841
- Dixit R, Malaviya D, Pandiyan K, Singh UB, Sahu A, Shukla R, Singh BP, Rai JP, Sharma PK, Lade H (2015) Bioremediation of heavy metals from soil and aquatic environment: An overview of principles and criteria of fundamental processes. Sustainability 7:2189–2212
- Inoue K, Parajuli D, Ghimire KN, Biswas BK, Kawakita H, Oshima T, Ohto K (2017) Biosorbents for removing hazardous metals and metalloids. Mater 10(8):857–889
- Factfish (2019) https://www.factfish.com/statistic/chill ies+and+peppers,+green,+production+quantity. Accessed 15 Nov 2019
- Agropolska, 2019, Polska przoduje w produkcji papryki. Przybywa nowych odmian, https://www.agropolska.pl/agrobiznes/ polska-przoduje-w-produkcji-papryki-przybywa-nowych-odmia n,1154.html. Accessed 15 Nov 2019
- Tepić A, Dimić GR, Vujičić B, Kevrešan ŽS, Varga M, Šumić ZM (2008) Quality of commercial ground paprika and its oleoresins. Acta periodica technologica: Acta per tech 39:1–212
- Kalak T, Dudczak J, Cierpiszewski R (2015) Adsorption behaviour of copper ions on elderberry, gooseberry and paprika waste from aqueous solutions. Proceedings of 12th International Interdisciplinary Meeting on Bioanalysis (CECE), Brno, Czech Republic, 123–127
- Kalak T, Kłopotek A, Cierpiszewski R (2019) Effective adsorption of lead ions using fly ash obtained in the novel circulating fluidized bed combustion technology. Microchem J 145:1011–1025
- Sulyman M, Namiesnik J, Gierak A (2017) Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: a review. Pol J Environ Stud 26(2):479–510
- Protić M, Miltojević A, Raos M, Đorđević A, Golubović T, Vukadinović A (2018) Thermogravimetric analysis of biomass and sub-bituminous coal. VIII International Conference Industrial Engineering and Environmental Protection 2018 (IIZS 2018) Oct 11–12th, 368-373, Zrenjanin, Serbia
- Sing KSW (1982) Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl Chem 54:2201–2218
- Alimin La Agusu, Ahmad LO, Kadidae LO, Ramadhan L, Nurdin M, Isdayanti N, Asria Aprilia MP, Hasrudin, (2018) Kinetics and Equilibrium of Fe<sup>3+</sup> Ions Adsorption on Carbon Nanofibers. IOP Conf. Series: Mater Sci Eng 367:1–6
- Benaisa S, El Mail R, Jbari N (2016) Biosorption of Fe(III) from aqueous solution using brown algae Sargassum Vulgare. J Mater Environ Sci 7:1461–1468
- Nouri L, Ghodbane I, Hamdaoui O, Chiha M (2007) Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. J Hazard Mater 149(1):115–125
- Mathivanan K, Rajaram R, Balasubramanian V (2015) Biosorption of Cd(II) and Cu(II) ions using Lysinibacillus fusiformis

KMNTT-10: equilibrium and kinetic studies. Desalind Water Treatment 1–12

- Kalak T, Dudczak-Hałabuda J, Tachibana Y, Cierpiszewski R (2020) Effective use of elderberry (*Sambucus nigra*) pomace in biosorption processes of Fe(III) ions. Chemosphere 246:125744
- Kalak T, Cierpiszewski R (2015) Correlation analysis between particulate soil removal and surface properties of laundry detergent solutions. Text Res J 85:1884–1906
- Janos P, Fedorovic J, Stankova P, Gröteschelová S, Rejnek J, Stopka P (2006) Iron humate as low-cost sorbent for metal ions. Environ Technol 27(2):169–181
- 22. Lu D, Cao Q, Li X, Cao X, Luo F, Shao W (2009) Kinetics and equilibrium of Cu(II) adsorption onto chemically modified orange peel cellulose biosorbents. Hydrometall 95(1-2):145-152
- 23. Vaghetti JCP, Lima EC, Royer B, Cardoso NF, Martins B, Calvete T (2009) Pecan nutshell as biosorbents to remove toxic metals from aqueous solution. Sep Sci Technol 44(3):615–644
- Moreno-Piraján JC, Garcia-Cuello VS, Giraldo L (2011a) The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells. Adsorption 17:505–514
- Wang SB, Ariyanto E (2007) Competitive adsorption of malachite green and Pb ions on natural zeolite. J Colloid Interface Sci 314:25–31
- 26. Kundu S, Gupta AA (2005) Sorption kinetics of As(V) with ironoxide-coated cement-a new adsorbent and its application in the removal of arsenic from real-life groundwater samples. J Environ Sci Health A Tox Hazard Subst Environ Eng 40:2227–2246

- 27. Sheibani A, Shishehbor MR, Alaei H (2012) Removal of Fe(III) ions from aqueous solution by hazelnut hull as an adsorbent. Int J Ind Chem 3:1–4
- Keshtkar M, Dobaradaran S, Akbarzadeh S, Bahreini M, Abadi DR, Nasab SG, Soleimani F, Khajeahmadi N, Baghmolaei MM (2016) Iron biosorption from aqueous solution by Padina sanctae crucis algae: isotherm, kinetic and modelling. Int J Pharm Technol 8:10459–10471
- Sag Y, Kutsal T (1996) Fully competitive biosorption of chromium(VI) and iron(III) Ions from binary metal mixtures by R. arrhizus: use of the competitive langmuir model. Process Biochem 31:573–585
- Al-Anber ZA, Al-Anber MAS (2008) Thermodynamics and kinetic studies of iron(III) adsorption by olive cake in a batch system. J Mex Chem Soc 52:108–115
- Ahalya N, Kanamadi RD, Ramachandra TV (2006) Biosorption of iron(III) from aqueous solutions using the husk of Cicer arientinum. Indian J Chem Technol 13:122–127
- Stumm W, Morgan JJ (1995) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Edition. John Wiley & Sons, Inc., ISBN: 978–0–471–51185–4

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.