

Biodepuration of domestic sewage, textile effluents and acid mine drainage using starch-based xerogel from recycled potato peels

Francisco Roque, Karla Diaz, Midwar Ancco, Daniela Delgado and Kevin Tejada

ABSTRACT

Water is a finite resource. Its safety and cleanliness are highly important to meet current and future human needs. Compared to other resources, water represents a main factor to achieve development in several areas and leads to economic progress of a nation. However, in recent years, the excessive demographic and industrial growth has exacerbated water contamination. In this study, the biodepuration process of domestic sewage (DS), textile effluents (TE) and acid mine drainage (AMD) is conducted using starch-based xerogel from potato (*Solanum tuberosum*) peels. Results showed that the treatment is effective to achieve the reduction of 5-day biochemical oxygen demand. The most important result was the achievement of heavy metals removal for the three components. Firstly, there was a reduction of barium, zinc, and cadmium (91, 60 and 46%, respectively) for raw AMD. Secondly, there was a reduction in the levels of zinc, aluminum, and barium (89, 86 and 64%, respectively) for TE biodepuration. Finally, results showed a reduction in zinc, iron and cadmium levels (81, 78 and 57%, respectively) for DS biodepuration.

Key words | biodepuration, potato peels, starch, wastewater and xerogel

Francisco Roque (corresponding author)

Karla Diaz

Midwar Ancco

Daniela Delgado

Kevin Tejada

Faculty of Pharmaceutical, Biochemical and Biotechnological Sciences,

Universidad Católica de Santa María,

Arequipa 0401,

Peru

E-mail: froque@ucsm.edu.pe

INTRODUCTION

One of the natural resources of great importance for the development of all economic activities and the survival of living beings is water. However, anthropogenic activities are generating serious impacts on the environment. For this reason, international development policies include environmental issues, social goals and promotion of the maintenance and care of this resource (Whittington *et al.* 2005).

Nowadays, water is being contaminated by the increase of domestic and industrial activities in our environment, generating detrimental changes in ecosystems and public health (Akar & Uysal 2010). The mining industry generates refractory compounds as water pollutants because of its extractive and refining operations. For instance, acid mine drainage (AMD) contains a high concentration of heavy metals, making it a potential contaminant of receptor

bodies (Carrero *et al.* 2015). In addition, textile factories generate effluents, containing different kinds of synthetic dyes that even in minimum concentrations might cause environmental impacts in water bodies (Panic & Velickovic 2014; Sahinkaya *et al.* 2016). Finally, world demographic growth is causing an excessive increase in domestic sewage (DS) discharges in municipal and sanitary sewers. These discharges contaminate rivers and riverbeds when they are not properly treated (Ghorbel *et al.* 2017).

Different conventional electrocoagulation (Mamelkina *et al.* 2017) and non-conventional technologies (bioremediation and nanotechnology (Anjum *et al.* 2016; Ma *et al.* 2016)) for wastewater treatment are used with different levels of efficiency in many countries around the world. Nevertheless, it is important to develop new wastewater treatment technologies that can reduce energy and utilize agroindustry waste materials, such as the use of multiple types of modified starches from different origin, as it is reported in literature (Dahri *et al.* 2014; Rangabhashiyam & Selvaraju 2015).

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

doi: 10.2166/wst.2018.008

Potato tubers (*Solanum tuberosum*) are the third most consumed food in the world, according to reports issued by specialized Peruvian organizations such as the International Potato Center. The worldwide industrial and domestic processing of potatoes generates peels and culls as residues in large quantities. They contain a wide variety of organic compounds such as starch, whose granules are in different integrity states, according to peeling method (Schieber & Saldaña 2009). Starch is the most abundant vegetal biodegradable polymer composed by amylose and amylopectin. These components confer potential properties for their physical and chemical modification with sewage depuration applications (Carvalho *et al.* 2003; Alvani *et al.* 2011).

Starch can be considered as a precursor of different semi-synthetic materials such as hydrogels (HGs) that can remove and purify suspended and dissolved particles in water bodies, which are polluted by swelling and physical absorption (Güçlü *et al.* 2009). Water-free HG is defined like xerogel. In addition, it has the same HG properties, and new features that confer the loss of water molecules (Kenar *et al.* 2014; Buscio *et al.* 2015).

The main objective of this study was to biodepurate three different kinds of residual effluents generated by the most common local anthropogenic activities, while using eco-friendly starch-based xerogel (XG) obtained from recycled potato peels, which are by-products of their industrial processing. In addition, physicochemical parameters and heavy metals were analyzed and quantified to determine the XG efficiency and biodepuration capacity.

METHODOLOGY

Potato peels used in this study belong to the OJO-AZUL variety (Peruvian native potato). These peels were residues of a local processing factory that uses potatoes to produce commercial products (frozen French fries and chips), and they are generally used as recycled animal feed (pigs, cows, rabbits, and others). This raw material was subjected to an aqueous homogenization process for the extraction of peel starch (PS) by using an electro-mechanical blender. Resulting suspensions were transferred to modified mechanical separators of Imhoff type in accordance with Coe and Clevenger (CC) settling theory for improving the static batch sedimentation process (Bürger & Wendland 2001). This modification consisted of the incorporation of a mechanical agitator in a hindered settling zone that inhibited the formation of the sedimentation critical point, allowing a

greater amount of compacted starch to be produced. Finally, the starch was isolated from the rest of components by decantation, and it was subjected to two washing cycles using distilled water. Finally, it was stored and dried in a stove at 60 ± 5 °C for 48 hours to avoid physical and chemical damage.

The obtained PS sample was subjected to scanning electron microscopy (SEM) to determine its structural morphology. The device used was the scanning electron microscope VEGA II LSH. On the one hand, water absorption capacity (WAC_{80}) (g H₂O/g starch), solubility (SOL_{80}) (g soluble fraction/g starch) and swelling capacity (SC_{80}), (g gel/g soluble fraction) were determined at 80 °C (Crosbie 1991; Bryant & Hamaker 1997). On the other hand, dispersion clarity (DC_{72} , % T₆₅₀) was determined at 72 hours at 650 nm (Crosbie 1991) and retrogradation (R_7 , %) at 4 °C after 7 days (Singh & Kaur 2004) in order to ensure the quality of the subsequently elaborated HG and XG. HG samples were prepared using a modification of the casting method reported by Pal *et al.* (2008), where 1,000 mL of a 2% starch solution was combined with 20 g of polyvinyl alcohol (PVA), to act as a plasticizer, with constant stirring until a homogeneous mixture was formed at room temperature. Crosslinking was achieved with the addition of 110 mL of alcoholic solution of glutaraldehyde (GA) and hydrochloric acid in isothermal and batch operation for 3 hours. This generated a pseudo-fluid mass known as an HG mixed with untransformed reagents. Subsequently, this sample was vigorously washed with distilled water to remove unreacted GA, PVA, ethanol and hydrochloric acid. Then, XG was obtained by drying it at standard temperature and pressure (STP) until a constant weight was generated. Finally, it was stored in hermetic bags for ensuring its conservation. XGs were characterized using SEM analysis and Fourier transform infrared spectroscopy (FTIR) with the transmittance method to characterize the presence of specific chemical groups in XG and verify their degree of crosslinking (Pal *et al.* 2008; Yu & Xiao 2008). Three different kinds of liquid effluents from different local anthropogenic activities were studied to determine XG biodepuration capacity. Grab samples were taken from a municipal sewer, textile factories and a typical Peruvian gold mine site located in the district of Ananea (San Antonio de Putina, Puno; 14°37'57" S, 69°26'45" W). Each of these effluents was physico chemically characterized by turbidity (TUR) (NTU), which was measured by using a portable VELB turbidimeter; electrical conductivity (EC) (μS/cm), which was measured with a Hanna HI-9628 conductivity meter; and dissolved oxygen (DO) (mg/L), which was

measured with a portable Hanna meter HI-9146. These characteristics reveal changes occurring in biological parameters because of aerobic or anaerobic phenomena, providing data for the evaluation of the condition of streams of a river water (Chang 2005). Furthermore, chemical oxygen demand (COD) (mg/L), and 5-day biochemical oxygen demand (BOD₅) (mg/L) were determined.

Effluents discharged by domestic and industries into the surface and ground water contaminate the quality of the water, which can be assessed by BOD₅ determination (Sawyer *et al.* 1994). Heavy metals content was determined using inductively coupled plasma optical emission spectrometry (ICP-OES). For evaluating acid digestion, a pretreatment with a mixture of 4 mL concentrated nitric acid and 2 mL hydrogen peroxide was used for 5 minutes. After this time, digestion was performed, and the mixture was digested for 15 minutes. The first step was heating to 450 W for 5 min. The second step was holding at 650 W for 10 minutes. Lastly, cooling down was conducted at room temperature. The digested solution was diluted to 50 mL with ultrapure water and filtered using a cellulose membrane and stored at 5 °C until further analysis (Ahmed *et al.* 2017).

Each of the effluent samples obtained and characterized in the previous method was depurated with the contact of XG samples by using a jar test, which was constantly stirred at 650 rpm, where 500 mL of each effluent sample was contacted with 17 g of dry and powdered XG at room temperature for 48 hours. Finally, sedimentation of swollen XG was observed, which allowed recovery of the purified water that was later characterized and compared with original crude samples. All assays were repeated in triplicate.

Uptake of metal ions was calculated with the next equation:

$$q = \frac{V \times (C_i - C_f)}{m} \quad (1)$$

where q is micrograms of heavy metal ions per gram of dry biosorbent; V is the reaction volume (L), C_i and C_f are the initial and residual metal concentrations (µg/L), respectively, and m represents the amount of dry biosorbent (g) (Tsekova *et al.* 2010).

DISCUSSION AND RESULTS

OJO-AZUL variety potato peels were selected and used as described in the methodology. Starch was extracted and isolated using Imhoff-type mechanical separators by applying CC sedimentation theory in order to obtain a higher

efficiency of starch recovery. Therefore, these were called CC cones (Bürger & Wendland 2001). Starch samples were characterized by SEM analysis and high-resolution micrographs with an accelerating voltage of 20 KV (Figure 1). This revealed that starch granules were not contaminated with other compounds and preserved their own integrity. Size, shape and distribution of starch granules observed in the microscope at 136×, 272×, 545× and 1,089× magnifications indicate their potential use as precursors of HG. Moreover, it is also observed that granules showed a completely even and smooth surface. It proved they did not suffer any physical, mechanical or enzymatic damage or deterioration (Zhang & Oates 1999). The size, shape, and structure of extracted starch showed that it belonged to potato starch reported in literature. Size and shape of granules are directly related to the precursor biological source. The size of the granules generally varies from 1 to 100 µm (Lindeboom *et al.* 2004). It was observed that there was a larger number of granules smaller than 20 µm at 136×, while granule abundance was recorded between 30 and 40 µm at 1,089×. Potato starch granules showed a round shape for the smallest, and an elongated spheroidal shape for the larger ones (Medina & Salas 2015). In addition, the analysis of micrographs at different magnifications showed regular edges and sizes grouped on the surface of potato starch obtained in accordance with the information reported by different authors in literature (Gunaratne 2002; Singh & Kaur 2004; Lizarazo *et al.* 2015).

Physicochemical characterization and functional properties of PS are shown in Table 1. They determined its quality and performance as a precursor of HG because of its significant influence on the synthesis of new structure. Values shown confirmed a high degree of crosslinking and extensive PS functionality as an ultimate precursor of XG (Crosbie 1991; Bryant & Hamaker 1997; Lovedeep *et al.* 2002).

Starch samples called PS had a lower WAC₈₀ value than ranges reported in literature (0.45–0.65 g/g; Nadir *et al.* 2015), probably due to the novel extraction method used in this study. Likewise, it was waste from a local potato processor. SC₈₀ value showed a lower value in potato starch samples compared to 52.81 g/g values reported by Hoover in 2001 cited by Nadir *et al.* (2015). SOL₈₀ value indicated that the soluble fraction was greater than 90% (0.92 g/g) in contrast to the values reported by the same authors (12–14 g/g), according to DC₇₂ value obtained in laboratory assays. For R₇ value, it resulted in a key feature of functionality of the recovered starch because high values indicated the disintegration of amylose and amylopectin networks to

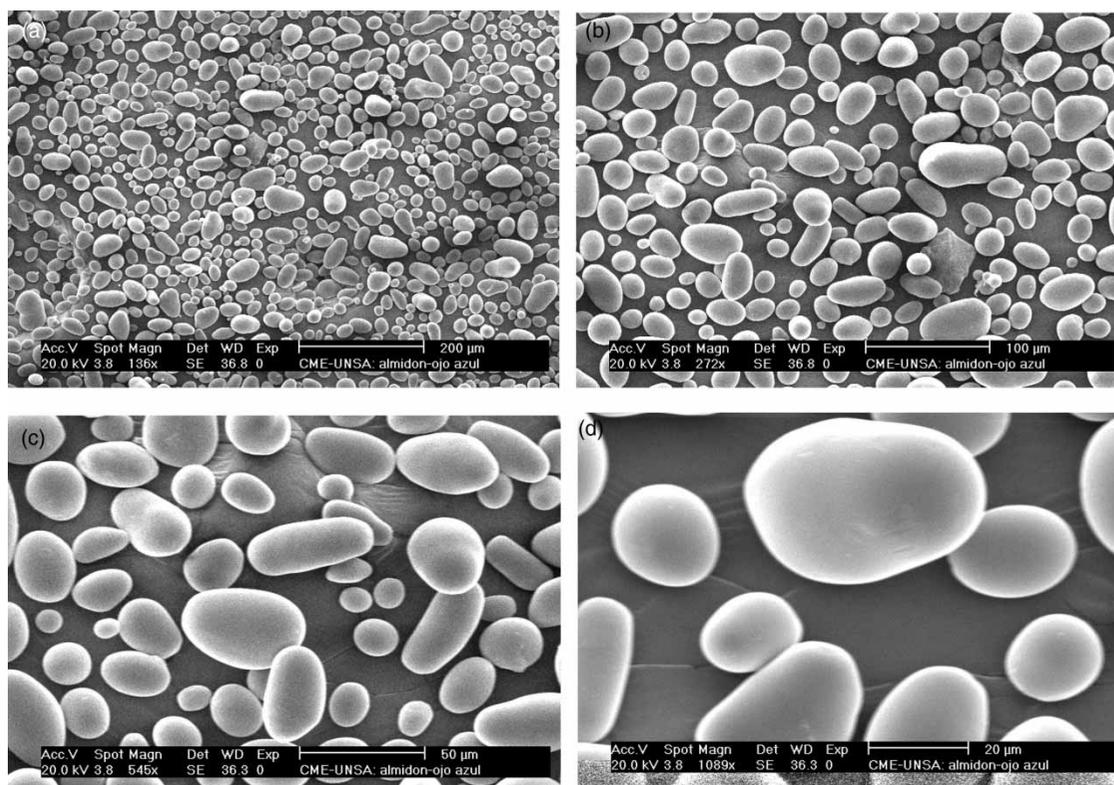


Figure 1 | Scanning electron micrographs of starch granules of OJO-AZUL potato peels at different magnifications: (a) 136 \times ; (b) 272 \times ; (c) 545 \times ; and (d) 1,089 \times .

form new modified structures confirmed by FTIR spectra, since OJO-AZUL PS had abundant hydroxyl groups, which could be used to easily prepare HG (Tako *et al.* 2014).

OJO-AZUL PS obtained and characterized was considered as an HG precursor because of the properties shown in Table 1 and previously discussed. Figure 2(a) shows a digital photograph of the macroscopic morphology of starch-based HG, which shows a high thickness, non-regular, corrugated, smooth consistency, high humidity, homogeneous white color, and tensile strength surface (Siddaramaiah *et al.* 2003). These properties were obtained by the addition of reagents such as PVA, GA, ethanol, and hydrochloric acid, as indicated in detail in the 'Methodology'

Table 1 | Functional properties of OJO-AZUL PS

Physicochemical property	Value	Unit
WAC ₈₀	0.1969 \pm 0.95	g H ₂ O/g starch
SOL ₈₀	0.92 \pm 0.72	g soluble fraction/g starch
SC ₈₀	14.51 \pm 1.48	g/g soluble fraction
DC ₇₂	3.82 \pm 0.23	% T ₆₅₀
R ₇	64.50 \pm 3.61	%

section. On the other hand, the reaction of PVA with GA was normally carried out as reported in international literature, forming acetal bridges among the pendant hydroxyl groups of PVA chains, which is known as crosslinking. This reaction was potentiated using hydrochloric acid as a catalyst (Mansur *et al.* 2008). The final XG was obtained from uniform drying of HG at STP (Kenar *et al.* 2014), showing new macroscopic characteristics like smaller thickness than its predecessor, flat and smooth surface, besides a remarkable gravimetric difference that resulted in the near total loss of free water. It also showed a semi-translucent whitish color, and a solid and resistant consistency, as shown in Figure 2(b). The main physical and even organoleptic difference between both modified structures of the precursor starch is focused on their water content.

Furthermore, Figure 3(a) shows a high-resolution electron micrograph of the XG surface in which remnants of apparently intact agglomerated starch granules with notable surface changes are observed. These are not smooth or uniform like the surface of PS shown in Figure 1. The irregular surface has well demarcated elevations and depressions, and a solid matrix, enveloping the highly porous starch granules, which give it desirable properties for swelling and water

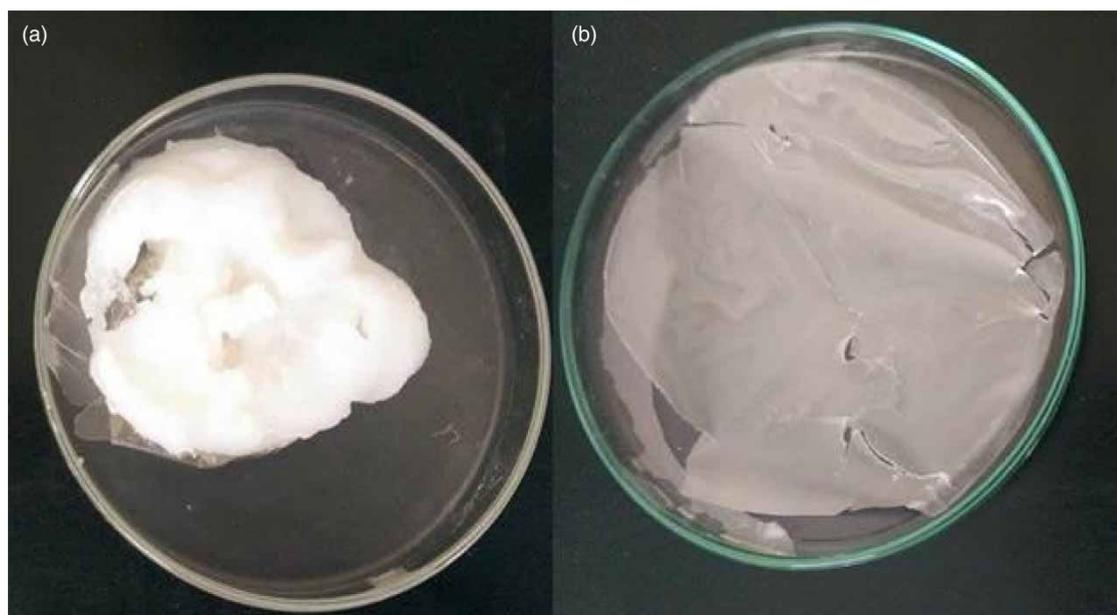


Figure 2 | Final physical organoleptic structures of (a) semi-solid HG of high water content, and fluid consistency, and (b) solid starch XG with low residual moisture.

absorption. These are observed in the dark fraction of [Figure 3\(b\)](#) and have porosity with an average size of approximately $2\ \mu\text{m}$ ([Glenn *et al.* 2011](#)).

FTIR characterization of the XG structure showed in its spectrogram the following 20 sequential transmittance peaks (% T) at 759.9, 844.86, 925.87, 1003.03, 1014.60, 1080.18, 1145.77, 1207.49, 1238.35, 1334.80, 1373.38, 1419.67, 1450.53, 1643.42, 1743.72, 1979.05, 2164.22, 2360.97, 2920.35 and $3317.71\ \text{cm}^{-1}$.

[Figure 4](#) shows up to seven sections of absorption bands for O-H, C-H, C-O-H, C-O-C, C-O, C-C and pyranose-glucose rings ([Kemas *et al.* 2012](#)).

The band between $3,200$ and $4,000\ \text{cm}^{-1}$ represented the O-H section. The absorption peak at $2,900\ \text{cm}^{-1}$ represented the C-H stretch. There was no absorption of aromatic rings in the typical region ($1,500$ – $1,600\ \text{cm}^{-1}$). However, the intense absorption at $1,643\ \text{cm}^{-1}$ would be a result of water molecules in amorphous regions of the

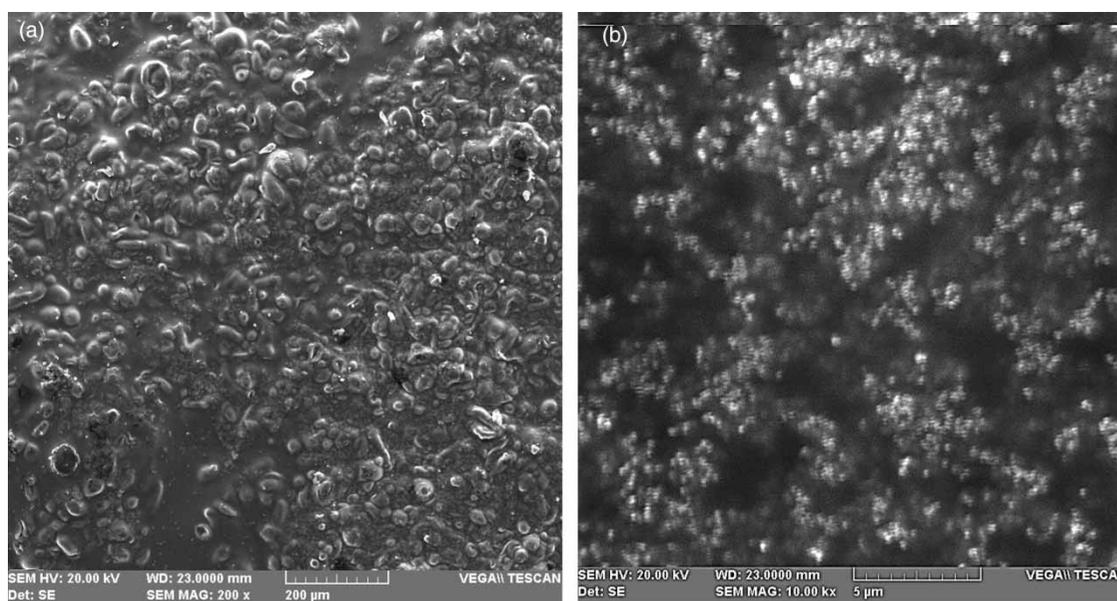


Figure 3 | Scanning electron micrograph showing surface and morphological properties of XG at different magnifications: (a) 200x and (b) 10,000x.

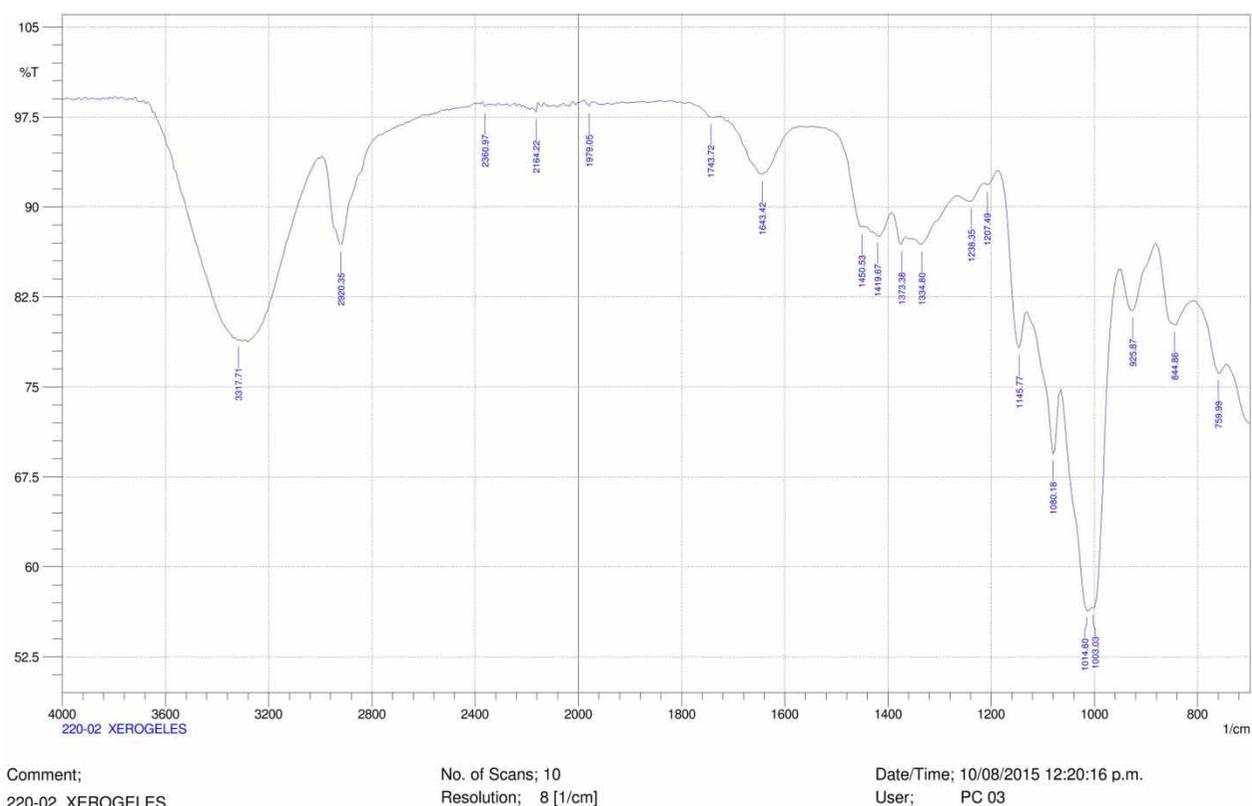


Figure 4 | FTIR spectrum for XG used in this study.

biomolecule of the starch analyzed. The absorption peak at $1,145\text{ cm}^{-1}$ represents C-C coupled mode and vibrations in the C-O stretch, while the absorption peak at $1,080\text{ cm}^{-1}$ represents the band with a possible flexural vibration in C-O-H bonds. The absorption at 925 cm^{-1} is typical for the C-O-C system in basic vibration mode of the α -1,4-glycosidic bond, whereas 589 and 461 cm^{-1} represent the basic mode of the pyranose ring, which was not obtained in this spectrum such as described in literature. In addition, the FTIR spectrum for XG is comparable with a high degree of significance with the FTIR spectrum for the potato starch shown in Figure 5 (Dupuy *et al.* 1997; Dolmatova *et al.* 1998; Cerna *et al.* 2003; Kemas *et al.* 2012).

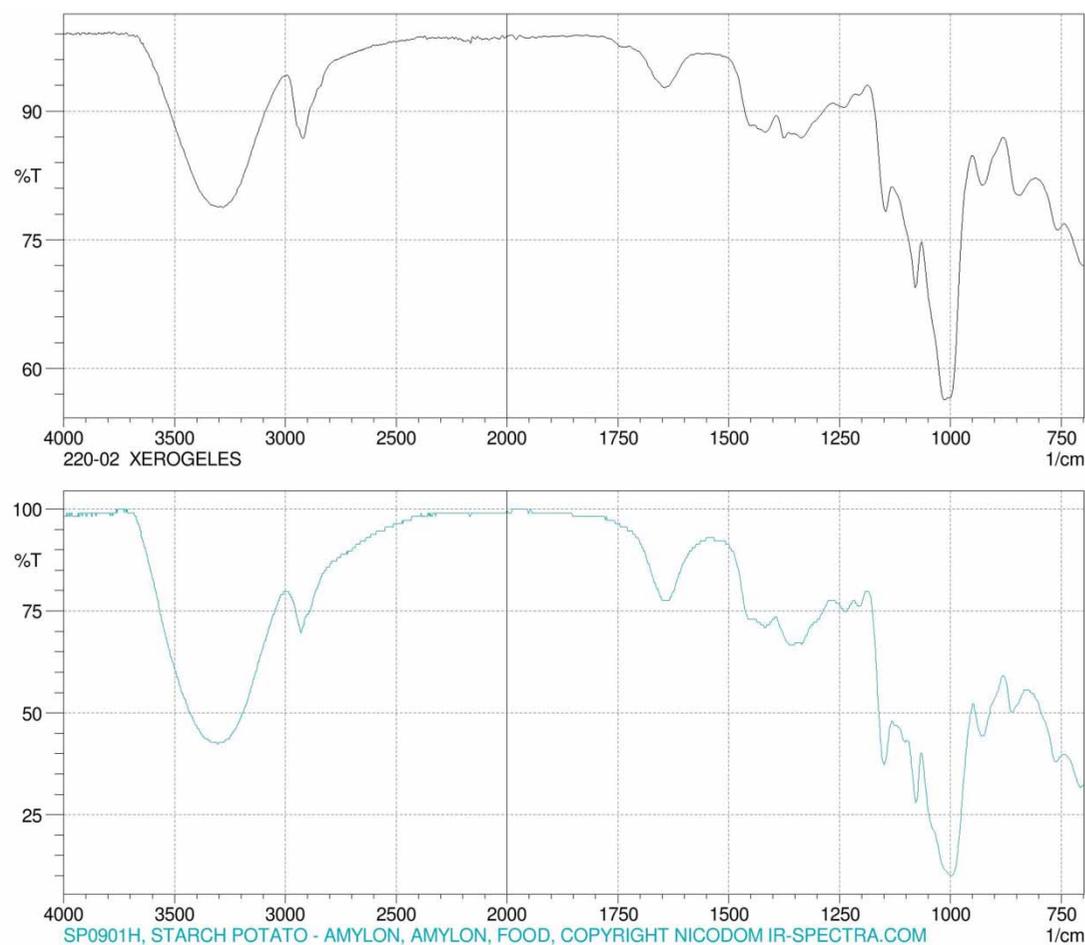
Figure 5 shows the comparison of FTIR spectra of PS and XG, with great similarity between the spectrograms even up to 91–93% probability. The starch spectrum was obtained from the 901 Nicodrom IR Suspect Powders Spec Library (Nicodrom Ltd).

HG has a crosslinked structure that is conducive to the development of biosorption. This mechanism involves a solid phase (sorbent) and a liquid phase (solvent) that species contain to be adsorbed. There are complexation and adsorption mechanisms in the superficial pores. There

is a process of ion exchange or adsorption by physical forces in the spaces of the structural network and in inter- and intrafibrillary capillaries. Characteristics mentioned above provide very interesting properties to the material to remediate contaminated water (Zheng *et al.* 2010; Muya *et al.* 2015).

DS treated with XG showed a significant TUR and EC reduction of 47.4% and 87.5%, respectively (Table 2). TUR and EC reduction are closely related to soluble and suspended solids removal, which increased oxygen solubilization capacity in depurated water bodies (Mitchell *et al.* 1999). In this study, it was verified that DO concentration increased in all cases with the reduction of the pollutant content of depurated water. Furthermore, pH values do not show a significant variation, which ensures the neutrality of XG used. Percentage removal was 80.4% in the case of BOD_5 , and 34.5% for COD. Results demonstrated the interesting properties of removing a higher fraction of organic matter compared to inorganic matter.

Textile effluents (TE) show a reduction in TUR and EC of 60.7% and 39.0%, respectively (Table 3). It can be observed that pH value does not have a significant variation.



	Score	Library	Note found / Title
1	910	901 - Nicodrom IR Suspect Powders.	SP0901H, STARCH POTATO - AM

Figure 5 | FTIR spectrum of XG (top) and potato starch (bottom) provided by a spectral library (Nicodrom Ltd).

Removal percentage was 88.2% in the case of BOD₅, and 20.2% for COD.

AMD shows a reduction in TUR and EC of 33.3% and 36.0%, respectively (Table 4). It can be seen that pH value

does not have a significant variation. Removal percentage was 63.7% in the case of BOD₅, and 28.4% for COD.

Tables 5–7 show removal percentage and adsorption capacity of Al, Ba, Cd, Fe, Ni, Pb and Zn in samples of

Table 2 | Physicochemical characterization of raw and depurated DS

Parameters	Raw	Depurated	Legislation ^a	Compliance ^b
TUR (NTU)	62.70 ± 0.51	29.73 ± 0.25	n.s. ^c	n.s.
EC (μS/cm)	1,120 ± 2.41	980 ± 2.56	n.s.	n.s.
DO (mg/L)	1.02 ± 0.09	3.57 ± 0.21	n.s.	n.s.
pH (-)	6.99 ± 0.14	7.14 ± 0.20	6.5–8.5	✓
BOD ₅ (mg/L)	2,700 ± 3.06	530 ± 1.53	100	✗
COD (mg/L)	3385.1 ± 2.67	2218.5 ± 2.54	500	✗

^aPeruvian Legislation 2017.

^bCompliance under Peruvian legislation.

^cNot specified.

Table 3 | Physicochemical characterization of raw and depurated TE

Parameters	Raw	Depurated	Legislation ^a	Compliance ^b
TUR (NTU)	40.2 ± 0.74	24.4 ± 0.55	n.s. ^c	n.s.
EC (μS/cm)	4,056 ± 3.51	1,583 ± 2.31	n.s.	n.s.
DO (mg/L)	2.54 ± 0.03	4.39 ± 0.03	n.s.	n.s.
pH (-)	8 ± 0.2	8 ± 0.12	6.0–9.0	✓
BOD ₅ (mg/L)	1162.9 ± 4.4	137 ± 1.37	500	✓
COD (mg/L)	2,210 ± 3.21	1762.7 ± 4.98	1,000	✗

^aPeruvian Legislation 2017.^bCompliance under Peruvian legislation.^cNot specified.**Table 4** | Physicochemical characterization of raw and depurated AMD

Parameters	Raw	Depurated	Legislation ^a	Compliance ^b
TUR (NTU)	911 ± 1.25	303.8 ± 1.06	n.s. ^c	n.s.
EC (μS/cm)	3,690 ± 2.08	1,327 ± 2.65	n.s.	n.s.
DO (mg/L)	1.28 ± 0.03	4.02 ± 0.05	n.s.	n.s.
pH (-)	5.84 ± 0.04	7.17 ± 0.04	6.0–9.0	✓
BOD ₅ (mg/L)	1,598 ± 2.08	580 ± 0.78	n.s.	n.s.
COD (mg/L)	1,620 ± 1.15	1160.2 ± 3.49	n.s.	n.s.

^aPeruvian Legislation 2017.^bCompliance under Peruvian legislation.^cNot specified.

DS, TE and AMD, analyzed in triplicate by ICP-OES equipment with sensitivity, precision and accuracy. Table 5 shows that the most outstanding removal percentages for DS were for Pb, Fe and Ni with values of 80.67, 78.35 and 56.67%, respectively. Additionally, adsorption capacity is considerable for Fe and Pb with 205 and 8.89 μg/g, respectively.

Table 5 | Removal percentage and adsorption capacity of heavy metals in DS

	Heavy metal concentration (μg/L)		Removal (%)	Adsorption capacity (μg/g)
	Raw	Depurated		
Pb	308 ± 0.35	5.88 ± 0.36	80.67	8.89
Fe	9,078 ± 0.26	2,108 ± 0.35	78.35	205
Ni	38 ± 0.29	1.38 ± 0.35	56.67	1.08
Zn	288 ± 0.50	21.98 ± 0.35	21.79	7.82
Cd	1.88 ± 0.35	1.58 ± 0.25	16.67	0.01
Al	308 ± 0.29	257.8 ± 0.40	16.56	1.48
Ba	268.78 ± 0.23	226.58 ± 0.29	15.71	1.24

HG and XG had properties such as having a lighter hydrophilic structure than water, the suitability of the monomeric functional groups for direct synthesis, and additional penetration into the contaminants due to their three-dimensional structures. In addition, the research reports the removal of heavy metals (Zn and Ni) from synthetic industrial effluents (Sezgin & Balkaya 2015). XGs are composed of starch in this study. Starch is a polymer that contains hydroxyl and carboxyl groups. These are interlinked with metal ions to form metal complexes (Ciesielski & Tomasik 2004; Ciesielski & Krystijan 2009; Al-Qahtani 2016).

Table 6 shows that, for TE, the most significant percentages are Pb, Cd, Zn and Fe with a removal percentage of 89.25, 85.71, 64.52 and 60.63%, respectively. Concentration of heavy metals is the lowest of the three effluents used in the study. Therefore, the adsorption capacity is very low.

Results obtained for the removal of Fe in DS and TE show an efficiency of 78.35 and 60.63%, respectively, in Tables 5 and 6. These results are similar to those obtained by other researchers (El-Hag Ali *et al.* 2003; Yetimoğlu *et al.* 2007; Abd El-Mohdy *et al.* 2013; Huang *et al.* 2016).

Table 6 | Removal percentage and adsorption capacity of heavy metals in TE

	Heavy metal concentration ($\mu\text{g/L}$)			Adsorption capacity ($\mu\text{g/g}$)
	Raw	Depurated	Removal (%)	
Pb	40 \pm 0.36	4.3 \pm 0.27	89.25	1.05
Cd	0.7 \pm 0.36	0.1 \pm 0.33	85.71	0.02
Zn	3.1 \pm 0.33	1.1 \pm 0.37	64.52	0.06
Fe	16 \pm 0.32	6.3 \pm 0.32	60.63	0.29
Al	70 \pm 0.27	51 \pm 0.37	27.14	0.56
Ni	2 \pm 0.29	1.5 \pm 0.24	25.00	0.01
Ba	50.32 \pm 0.24	45.5 \pm 0.27	9.58	0.14

Likewise, interesting results were also obtained for the removal of Pb in DS and TE. XG had the capacity to remove such metal with an efficiency of 80.67 and 89.25%, respectively. These results are similar to those reported in investigations that used different biosorbents (Barakat 2011; Kim *et al.* 2014; Phetphaisit *et al.* 2016). However, efficiency is not good for Pb removal in AMD. A removal efficiency of 85.71% Cd can be observed in TE in Table 6. These results are comparable with those reported in other studies, using different modified polymers (Yetimoglu *et al.* 2007; Barakat 2011; Abdel-Halim & Al-Deyab 2014; Souda & Sreejith 2015; Huang *et al.* 2016; Phetphaisit *et al.* 2016).

Table 7 shows that, for AMD, the most significant removal percentages are Ba, Zn and Cd with 91.02, 60.29 and 45.71%, respectively. Likewise, the table shows considerable adsorption capacity of Fe, Al and Ba with 118.82, 79.12 and 10.76 $\mu\text{g/g}$, respectively.

Results show Zn removal efficiency in TE and AMD of 64.52 and 60.29%, respectively, in Tables 6 and 7. These results are comparable to those published by Souda & Sreejith (2015).

Table 7 | Removal percentage and adsorption capacity of heavy metals in AMD

	Heavy metal concentration ($\mu\text{g/L}$)			Adsorption capacity ($\mu\text{g/g}$)
	Raw	Depurated	Removal (%)	
Ba	401.92 \pm 0.31	36.1 \pm 0.33	91.02	10.76
Zn	68 \pm 0.34	27 \pm 0.32	60.29	1.21
Cd	7 \pm 0.36	3.8 \pm 0.32	45.71	0.09
Fe	13,300 \pm 0.28	9,260 \pm 0.36	30.38	118.82
Al	9,200 \pm 0.25	6,510 \pm 0.23	29.24	79.12
Pb	70 \pm 0.36	51.6 \pm 0.25	26.29	0.54
Ni	12 \pm 0.25	11.1 \pm 0.31	7.50	0.03

Gupta *et al.* (2015) compiled adsorption capacities of different biomass types such as peels of vegetables, tubers, fruits, and several microbial species, which are of great importance to understand the behavior of other biosorbents that have undergone previous treatments, which are very different to those used to obtain XG in this study.

The removal of heavy metals depends on a large extent on the concentration. This means that, in fact, high concentration in solution implicates high metal ions fixed at the surface of the biosorbent (Barka *et al.* 2013). The three effluents treated have a low concentration of heavy metals. Therefore, the adsorption capacity is remarkably small. It was determined in all cases that XG had a removal capacity of heavy metals in different proportions and with different affinity for this type of ionic and soluble contaminants of water bodies. Finally, waste generated after the treatment of effluents (contaminated XG) had a quality that met current legal regulations in order to avoid the repercussions of these contaminants in any receiving body.

CONCLUSIONS

The XG obtained from husks and debris of local industries of potato processing demonstrated partial biodepuration capacity for three different types of wastewater from anthropogenic activities that are common in the local area (DS, TE, and AMD). Results showed a significant reduction in BOD₅, TUR, COD, and EC, according to an increase in DO concentration in all cases. In addition, the depuration of heavy metals (Al, Ba, Cd, Fe and Zn) determined a removal percentage in accordance with the following order: Ba > Zn > Al > Fe > Cd, considering the three types of wastewater treated with XG. The XG was able to improve water quality by removing these metals at certain concentrations that are detrimental to human health and ecosystems. In conclusion, it is proposed that XG can be an effective agent for the final treatment of DS, as it has high levels of BOD₅ reduction, and especially can be used for removal of heavy metals such as Ba, Zn, Al, Fe and Cd in wastewater produced by different anthropogenic activities.

ACKNOWLEDGEMENTS

Authors acknowledge the financial support from the Office of the Vice Chancellor for research of Universidad Católica de Santa María (Arequipa, Peru).

REFERENCES

- Abd El-Mohdy, H. L., Hegazy, E. A., El-Nesr, E. M. & El-Wahab, M. A. 2013 Metal sorption behavior of poly(N-vinyl-2-pyrrolidone)/(acrylic acid-co-styrene) hydrogels synthesized by gamma radiation. *Journal of Environmental Chemical Engineering* **1** (3), 328–338. <https://doi.org/10.1016/j.jece.2013.05.013>
- Abdel-Halim, E. S. & Al-Deyab, S. S. 2014 Preparation of poly (acrylic acid)/starch hydrogel and its application for cadmium ion removal from aqueous solutions. *Reactive and Functional Polymers* **75** (1), 1–8. <https://doi.org/10.1016/j.reactfunctpolym.2013.12.003>
- Ahmed, M., Chin, Y., Guo, X. & Zhao, X. 2017 Microwave assisted digestion followed by ICP-MS for determination of trace metals in atmospheric and lake ecosystem. *Journal Of Environmental Sciences* **55**, 1–10. <http://dx.doi.org/10.1016/j.jes.2016.06.014>
- Akar, S. T. & Uysal, R. 2010 Untreated clay with high adsorption capacity for effective removal of C.I. Acid Red 88 from aqueous solutions: batch and dynamic flow mode studies. *Chemical Engineering Journal* **162** (2), 591–598. <https://doi.org/10.1016/j.cej.2010.06.001>
- Al-Qahtani, K. M. 2016 Water purification using different waste fruit cortexes for the removal of heavy metals. *Journal of Taibah University for Science* **10** (5), 700–708. <https://doi.org/10.1016/j.jtusc.2015.09.001>
- Alvani, K., Qi, X., Tester, R. F. & Snape, C. E. 2011 Physico-chemical properties of potato starches. *Food Chemistry* **125** (3), 958–965. doi: <https://doi.org/10.1016/j.foodchem.2010.09.08>
- Anjum, M., Miandad, R., Waqas, M., Gehany, F. & Barakat, M. A. 2016 Remediation of wastewater using various nano-materials. *Arabian Journal of Chemistry*. doi: <https://doi.org/10.1016/j.arabjc.2016.10.004>
- Barakat, M. A. 2011 New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* **4**, 361–377. <https://doi.org/10.1016/j.arabjc.2010.07.019>
- Barka, N., Abdennouri, M., El Makhfouk, M. & Qourzal, S. 2013 Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (*Opuntia ficus indica*) cladodes. *Journal of Environmental Chemical Engineering* **1** (3), 144–149. <http://dx.doi.org/10.1016/j.jece.2013.04.008>
- Bryant, C. M. & Hamaker, B. R. 1997 Effect of lime on gelatinization of corn flour and starch. *Cereal Chemistry* **74** (2), 171–175.
- Bürger, R. & Wendland, W. 2001 Sedimentation and suspension flows: historical perspective and some recent developments. *Journal of Engineering Mathematics* **41** (3), 10–116.
- Buscio, V., Marín, M. J., Crespi, M. & Gutiérrez-Bouzán, C. 2015 Reuse of textile wastewater after homogenization–decantation treatment coupled to PVDF ultrafiltration membranes. *Chemical Engineering Journal* **265**, 122–128. doi: <https://doi.org/10.1016/j.cej.2014.12.057>
- Carrero, S., Pérez-López, R., Fernandez-Martinez, A., Cruz-Hernández, P., Ayora, C. & Poulain, A. 2015 The potential role of aluminium hydroxysulphates in the removal of contaminants in acid mine drainage. *Chemical Geology* **417**, 414–423. <https://doi.org/10.1016/j.chemgeo.2015.10.020>
- Carvalho, A., Job, A., Alves, N., Curvelo, A. & Gandini, A. 2003 Thermoplastic starch/natural rubber blends. *Carbohydrate Polymers* **53** (1), pp. 95–99.
- Cerna, M., Antonio, S. B., Alexandra, N., Silvia, M. R., Ivonne, D., Jana, C. & Manuel, A. C. 2003 Use of FTIR spectroscopy as a tool for the analysis of polysaccharide food additives. *Carbohydrate Polymers* **51**, 383–389.
- Chang, H. 2005 Spatial and temporal variations of water quality in the Han River and its tributaries, Seoul, Korea, 1993–2002. *Water, Air, & Soil Pollution* **161** (1–4), 267–284. <http://dx.doi.org/10.1007/s11270-005-4286-7>
- Ciesielski, W. & Krystynjan, M. 2009 Starch – metal complexes and their rheology. *E-Polymer* **9** (1), 1628–1640.
- Ciesielski, W. & Tomasik, P. 2004 Complexes of amylose and amylopectins with multivalent metal salts. *Journal of Inorganic Biochemistry* **98** (12), 2039–2051. <https://doi.org/10.1016/j.jinorgbio.2004.09.010>
- Crosbie, G. B. 1991 The relationship between starch swelling properties, paste viscosity and boiled noodle quality in wheat flours. *Journal of Cereal Science* **13**, 145–150.
- Dahri, M. K., Kooh, M. R. R. & Lim, L. B. L. 2014 Water remediation using low cost adsorbent walnut shell for removal of malachite green: equilibrium, kinetics, thermodynamic and regeneration studies. *Journal of Environmental Chemical Engineering* **2** (3), 1434–1444. doi: <https://doi.org/10.1016/j.jece.2014.07.008>
- Dolmatova, L., Ruckebusch, C., Dupuy, N., Huvenne, J. P. & Legrand, P. 1998 Identification of modified starches using infrared spectroscopy and artificial neural network processing. *Applied Spectroscopy* **52**, 329–338.
- Dupuy, N., Wojciechowski, C., Ta, C. D., Huvenne, J. P. & Legrand, P. 1997 Mid-infrared spectroscopy and chemometrics in corn starch classification. *Journal of Molecular Structure* **410**, 551–554.
- El-Hag Ali, A., Shawky, H. A., Abd El Rehim, H. A. & Hegazy, E. A. 2003 Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution. *European Polymer Journal* **39** (12), 2337–2344. [https://doi.org/10.1016/S0014-3057\(03\)00150-2](https://doi.org/10.1016/S0014-3057(03)00150-2)
- Ghorbel, L., Coudert, L., Gilbert, Y., Mercier, G. & Blais, J. F. 2017 Determination of critical operational conditions favoring sulfide production from domestic wastewater treated by a sulfur-utilizing denitrification process. *Journal of Environmental Management* **198** (1), 16–23. doi: <https://doi.org/10.1016/j.jenvman.2017.04.058>
- Glenn, G., Imam, S. & Orts, W. 2011 Starch-based foam composite materials: processing and bioproducts. *MRS Bulletin* **36** (9), 696–702. <http://dx.doi.org/10.1557/mrs.2011.205>
- Güçlü, G., Al, E., Emik, S., İyim, T., Özgümüş, S. & Özyürek, M. 2009 Removal of Cu²⁺ and Pb²⁺ ions from aqueous solutions by starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite hydrogels. *Polymer Bulletin* **65** (4), 333–346. <http://dx.doi.org/10.1007/s00289-009-0217-x>
- Gunaratne, A. 2002 Effect of heat–moisture treatment on the structure and physicochemical properties of tuber and root

- starches. *Carbohydrate Polymers* **49** (4), 425–437. [http://dx.doi.org/10.1016/s0144-8617\(01\)00354-x](http://dx.doi.org/10.1016/s0144-8617(01)00354-x)
- Gupta, V., Nayak, A. & Agarwal, S. 2015 Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environmental Engineering Research* **20** (1), 1–18. <http://dx.doi.org/10.4491/eer.2015.018>
- Huang, Y., Wu, D., Wang, X., Huang, W., Lawless, D. & Feng, X. 2016 Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation. *Separation and Purification Technology* **158**, 124–136. <https://doi.org/10.1016/j.seppur.2015.12.008>
- Kemas, U., Agbowuro, A. & Ocheke, N. 2012 Effect of chemical modification on the proximate composition of *Plectranthus esculentus* starch and characterization using FTIR spectroscopy. *World Journal of Pharmaceutical Research* **1** (5), 1234–1249.
- Kenar, J., Eller, F., Felker, F., Jackson, M. & Fanta, G. 2014 Starch aerogel beads obtained from inclusion complexes prepared from high amylose starch and sodium palmitate. *Green Chemistry* **16** (4), 1921–1930. <http://dx.doi.org/10.1039/c3gc41895b>
- Kim, I., Lee, M. & Wang, S. 2014 Heavy metal removal in groundwater originating from acid mine drainage using dead *Bacillus drentensis* sp. immobilized in polysulfone polymer. *Journal of Environmental Management* **146**, 568–574. <https://doi.org/10.1016/j.jenvman.2014.05.042>
- Lindeboom, N., Chang, P. & Tyler, R. 2004 Analytical, biochemical and physicochemical aspects of starch granule size, with emphasis on small granule starches: a review. *Starch – Stärke* **56** (34), 89–99. <http://dx.doi.org/10.1002/star.200300218>
- Lizarazo, S., Hurtado, G. & Rodriguez, L. 2015 Physicochemical and morphological characterization of potato starch (*Solanum tuberosum* L.) as raw material for the purpose of obtaining bioethanol. *Agronomía Colombiana* **33** (2), 244–252. <http://dx.doi.org/10.15446/agron.colomb.v33n2.47239>
- Lovedeep, K., Narpinder, S. & Navdeep, S. S. 2002 Some properties of potatoes and their starches. II Morphological, thermal and rheological properties of starches. *Food Chemistry* **79**, 183–192.
- Ma, C., Yang, G., Zhang, Q., Zhuang, L. & Zhou, S. 2016 Complete genome of *Thauera humireducens* SgZ-1, a potential bacterium for environmental remediation and wastewater treatment. *Journal of Biotechnology* **225**, 59–60. doi: <https://doi.org/10.1016/j.jbiotec.2016.03.029>
- Mamelkina, M. A., Cotillas, S., Lacasa, E., Sáez, C., Tuunila, R., Sillanpää, M. & Rodrigo, M. A. 2017 Removal of sulfate from mining waters by electrocoagulation. *Separation and Purification Technology* **182**, 87–93. doi: <https://doi.org/10.1016/j.seppur.2017.03.044>
- Mansur, H., Sadahira, C., Souza, A. & Mansur, A. 2008 FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Materials Science and Engineering: C* **28** (4), 539–548. <http://dx.doi.org/10.1016/j.msec.2007.10.088>
- Medina, J. & Salas, J. 2015 Caracterización morfológica del granulo de almidón nativo: Apariencia, forma, tamaño y su distribución. *Revista De Ingeniería* **27**, 56–62.
- Mitchell, S., West, J. & Guymer, I. 1999 Dissolved-oxygen/suspended-solids concentration relationships in the upper humber estuary. *Water and Environment Journal* **13** (5), 327–337. <http://dx.doi.org/10.1111/j.1747-6593.1999.tb01057.x>
- Muya, F., Ward, M., Sunday, C., Baker, P. & Iwuoha, E. 2015 Environmental remediation of heavy metal ions from aqueous solution through hydrogel adsorption: a critical review. *Water Science and Technology* **73** (5), 983–992. <http://dx.doi.org/10.2166/wst.2015.567>
- Nadir, A. S., Helmy, I. M. F., Nahed, M. A., Wafaa, M. M. A. & Ramadan, M. T. 2015 Modification of potato starch by some different physical methods and utilization in cookies production. *International Journal of Current Microbiology and Applied Sciences* **4** (10), 556–569.
- Pal, K., Banthia, A. K. & Majumdar, D. K. 2008 Effect of heat treatment of starch on the properties of the starch hydrogels. *Materials Letters* **62**, 215–218.
- Panic, V. V. & Velickovic, S. J. 2014 Removal of model cationic dye by adsorption onto poly(methacrylic acid)/zeolite hydrogel composites: kinetics, equilibrium study and image analysis. *Separation and Purification Technology* **122**, 384–394. <https://doi.org/10.1016/j.seppur.2013.11.025>
- Phetphaisit, C. W., Yuanyang, S. & Chaiyasith, W. C. 2016 Polyacrylamido-2-methyl-1-propane sulfonic acid-grafted-natural rubber as bio-adsorbent for heavy metal removal from aqueous standard solution and industrial wastewater. *Journal of Hazardous Materials* **301**, 163–171. <https://doi.org/10.1016/j.jhazmat.2015.08.056>
- Rangabhashiyam, S. & Selvaraju, N. 2015 Adsorptive remediation of hexavalent chromium from synthetic wastewater by a natural and ZnCl₂ activated *Sterculia guttata* shell. *Journal of Molecular Liquids* **207**, 39–49. doi: <https://doi.org/10.1016/j.molliq.2015.03.018>
- Sahinkaya, E., Yurtsever, A. & Çınar, Ö. 2016 Treatment of textile industry wastewater using dynamic membrane bioreactor: impact of intermittent aeration on process performance. *Separation and Purification Technology* **174**, 445–454. doi: <https://doi.org/10.1016/j.seppur.2016.10.049>
- Sawyer, C. N., McCarthy, P. L. & Parkin, G. F. 1994 *Chemistry for Environmental Engineering and Science*, 4th edn. McGraw-Hill, New York, pp. 365–577.
- Schieber, A. & Saldaña, M. D. A. 2009 Potato peels: a source of nutritionally and pharmacologically interesting compounds – a review. *Food* **3** (2), 23–29.
- Sezgin, N. & Balkaya, N. 2015 Adsorption of heavy metals from industrial wastewater by using polyacrylic acid hydrogel. *Desalination and Water Treatment* **57** (6), 2466–2480. <http://dx.doi.org/10.1080/19443994.2015.1030453>
- Siddaramaiah, Raj, B. & Somashekar, R. 2003 Structure-property relation in polyvinyl alcohol/starch composites. *Journal of Applied Polymer Science* **91** (1), 630–635. <http://dx.doi.org/10.1002/app.13194>
- Singh, N. & Kaur, L. 2004 Morphological, thermal, rheological and retrogradation properties of potato starch fractions varying in

- granule size. *Journal of the Science of Food and Agriculture* **84** (10), 1241–1252. <http://dx.doi.org/10.1002/jsfa.1746>
- Souda, P. & Sreejith, L. 2015 Magnetic hydrogel for better adsorption of heavy metals from aqueous solutions. *Journal of Environmental Chemical Engineering* **3** (3), 1882–1891. <https://doi.org/10.1016/j.jece.2015.03.007>
- Tako, M., Tamaki, Y., Teruya, T. & Takeda, Y. 2014 The principles of starch gelatinization and retrogradation. *Food and Nutrition Sciences* **05** (3), 280–291. <http://dx.doi.org/10.4236/fns.2014.53035>
- Tsekova, K., Todorova, D. & Ganeva, S. 2010 Removal of heavy metals from industrial wastewater by free and immobilized cells of *Aspergillus niger*. *International Biodeterioration & Biodegradation* **64** (6), 447–451. <http://dx.doi.org/10.1016/j.ibiod.2010.05.003>
- Whittington, D., Wu, X. & Sadoff, C. 2005 Water resources management in the Nile Basin: the economic value of cooperation. *Water Policy* **7**, 227–252.
- Yetimoglu, E. K., Kahraman, M. V., Ercan, Ö., Akdemir, Z. S. & Apohan, N. K. 2007 N-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid based hydrogels: synthesis, characterization and their application in the removal of heavy metals. *Reactive and Functional Polymers* **67** (5), 451–460. <https://doi.org/10.1016/j.reactfunctpolym.2007.02.007>
- Yu, H. & Xiao, C. 2008 Synthesis and properties of novel hydrogels from oxidized Konjac glucomannan cross linked gelatin for in-vitro drug delivery. *Carbohydrate Polymers* **72**, 479–489.
- Zhang, T. & Oates, C. 1999 Relationship between α -amylase degradation and physico-chemical properties of sweet potato starches. *Food Chemistry* **65** (2), 157–163. [http://dx.doi.org/10.1016/s0308-8146\(98\)00024-7](http://dx.doi.org/10.1016/s0308-8146(98)00024-7)
- Zheng, Y., Hua, S. & Wang, A. 2010 Adsorption behavior of Cu^{2+} from aqueous solutions onto starch-g-poly(acrylic acid)/sodium humate hydrogels. *Desalination* **263** (1–3), 170–175. <http://dx.doi.org/10.1016/j.desal.2010.06.054>

First received 8 May 2017; accepted in revised form 7 November 2017. Available online 4 January 2018