Influence of Particle Size on the Bioadsorbent Behavior of Orange Peel

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Abstract— *The physical treatment of citrus peels comprises five stages: collecting, washing, drying, grinding and sieving. It is very important to have a grinding system that allows to regulate the pre-established particle size for future applications of the shell. For this, it is necessary to complement the grinding with a good sieving.*

The optimal particle size for continuous applications through fluidized beds has been found to be between 500-1000 µm. Although the 200-500 µm range has applications in batch processes, particle sizes less than 200 µm are usually not used as they remain in suspension and only precipitate after a considerable period of time.

This work presents a modification of the chemical treatment of orange peel that aims to take advantage of the material that passes through a standard 200µm sieve and reuse it as a bioadsorbent. The results obtained with Cu (II), Mg (II) and Na (I) at different concentrations are consistent with the use of bioadsorbents in metal removal.

Keywords— bioadsorption; reuse; Orange peel; ultrasonic radiation, cation exchange.

I. INTRODUCTION

Currently, society is progressively committing itself to achieving a sustainable economy based on the exploitation of renewable resources by promoting waste recycling and the design of products obtained in ecologically efficient processes. From this point of view, biomass, mainly of plant origin, seems the best option to replace a high percentage of fossil fuels in their energy and chemical applications (Cherubini 2010).

However, according to the Food and Agriculture Organization of the United Nations (FAO), around 30% of global food production is lost during harvest, processing and final consumption, assuming this amount more than 1,300 million tons per year (Thi Phuong 2015).

Agri-food waste is potential raw material for various applications, which is why it is intended to develop high-value products such as cosmetics, fuels, medicines, essential oils, pectin, feed, activated carbon, pollutant adsorbents, fuels, energy, among others (Ortiz et al., 2020; Deba-Rementeria et al., 2021;). These wastes include fruit waste that is generally disposed of in landfills, composted, used as feed, incinerated or solidified; processes that may involve a high demand for energy or generate damage to the environment, which is why it is essential to reduce them and use them as an alternative source of renewable energy (Lin et al., 2021).

Of the wide variety of fruits and vegetables, whose processing generates waste suitable to be used as raw material, it is worth highlighting citrus fruits that generate large amounts of waste in the form of skin, pulp and seeds in the production process of juice and other derived foods (Mirabella et al. 2014).

Citrus fruits have various applications in the food, cosmetic and perfume industry thanks to their taste and aroma (Nateghpouret al., 2021). In the food industry approximately 26% of citrus fruits are used to make juice. During the processing of citrus fruits, the peels are the main by-product and a potential burden on the environment without additional treatment (Wang et al., 2015). Between 50-60% of the mass of the fruit remains after processing (peel, seeds and membrane residues), it is estimated that, annually, citrus waste created by food processing industries exceeds 54 million tons all over the world (Teigiserova et al., 2021).

Among the variety of edible citrus fruits, it should be noted that the most abundant in the world is the orange (Citrus sinensis L.), which represents about 60% of the world total (Erukainure et al, 2016). Part of the waste generated is used to feed livestock. However, it is in such a quantity that large amounts end up being deposited in landfills causing serious environmental and economic problems (Tripodo et al., 2004).

The waste from the manufacture of orange juice is made up of pulp, seeds and skin. The skin is made up of an orange outer layer (flavedo) and a fluffy white inner layer (albedo). The pulp is very moist and rich in monosaccharides (glucose and fructose) and disaccharides (sucrose). The inner layer of albedo is rich in pectin, while the outer layer of flavedo contains a large amount of essential oils, limonene being the main component, and flavonoids (Davies1994). Its composition varies depending on the crop, the time of year and the region and technology used in the production of juice. Despite these possible variations, the orange residue is always very humid, with a variable water content between 80 and 84% (Rezzadori et al,. 2012).

Depending on the particle size, the orange peel has different water adsorption capacity. Table 1 shows the results obtained with 5g samples of orange peel of different particle size and in Figure 1 the appearance of the orange peel after being in contact with water.

TABLE 1
WATER ADSORPTION IN 5 GRAM ORANGE PEEL SAMPLES OF DIFFERENT PARTICLE SIZES AT ROOM TEMPERATURE

Orange	Particle size	mL H_20 Medium	mL / g
	1mm> X> 500 µm	37.8 ± 0.35	7.6
	500 µm> X> 250 µm	28.2 ± 0.5	5.6
	X <250 µm	23.1 ± 0.8	4.6

It can be seen that the adsorption decreased as the particle size decreased. This behavior was attributed to the fact that the possibility of caking increases when there is more contact between the particles (Pietsch 2002). The powdery particles become wet, sticky and compact, finally reaching the liquefaction phase (figure 1).

On the other hand, from the extraction of albedo, citric pectin, a thickener commonly used in the food industry, is obtained by acid hydrolyzing. However, in most processes, obtaining pectins is linked to obtaining essential oil (Cerón-Salazar 2011).

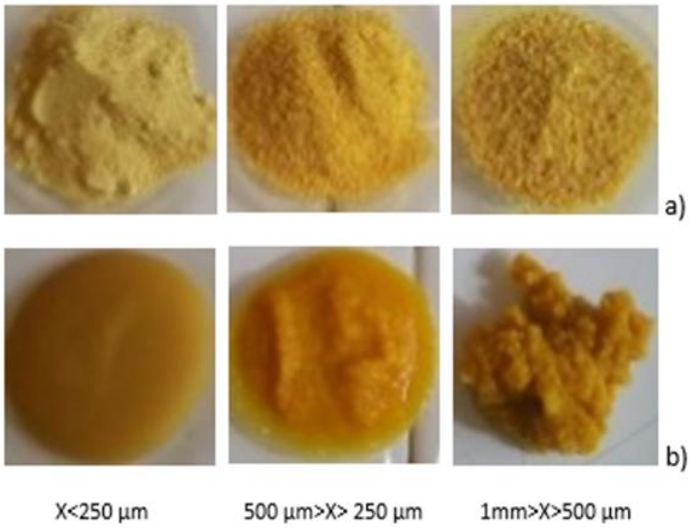

FIGURE 1: Appearance of the orange peel vs particle size a) dry b) saturated with water (Garcia Raurich et al, 2020a)

The industrial production of citrus pectin has the following stages: in the first stage, the peel must be washed to remove as much soluble solids and impurities as these components make the purification process difficult. Then, the shells are subjected

to a drying process, which inactivates the pectin esterase enzyme and lowers the moisture content, increasing the stabilization of the shell for storage and reducing the cost of transportation (Marti et al, 2014).

Subsequently, the dry matter is suspended in hot water with the necessary amount of a strong acid, starting the hydrolysis process. During this process, starting from the macromolecular structure formed by cellulose, hemicellulose and pectins, hemicellulose starts its degradation to glucose, galactose and fructose; cellulose to glucose and pectin to pectin monomer through a depolymerisation process (Chen et al, 2015). After a while, the resulting solution is removed from the insoluble solids by filtration. Next, it is mixed with alcohol, producing the recomposition of the pectin polymer and its corresponding precipitation. The precipitate is removed and purified by washing it with more alcohol. Finally, it is dried and ground (Claus, 2002). The material resulting from the pectin extraction is a poor food supplement for animals due to its low protein content and high sugar content (Siles et al, 2016).

On the other hand, the solid fraction presents the optimal conditions for its subsequent treatment as a bioadsorbent (Masmoudi et al, 2008). The resulting solid is treated in an alkaline medium. In this way, the saponification of the non-soluble pectin in an acid medium is achieved, as well as the solubilization of the soluble fraction of hemicellulose in an alkaline medium (Grace et al., 1996).

After chemical treatment, the resulting product has the characteristics of a cation exchanger. The optimal size for the removal of heavy metals in continuous processes has been established between 500-1000 µm (Garcia Raurich et al, 2020b).

The objective of this work has been to reuse the fraction less than 200 µm obtained in the grinding of the orange peel. For this, various modifications in the chemical treatment have been studied.

II. MATERIALS AND METHODS

The orange peel with a particle size <200 µm was subjected to different variants of the chemical treatment.

The reference treatment was carried out using HCl as the acid reagent. To do this, 50 g of the orange peel were mixed with 700 mL of deionized water in a sealed container and homogenized by stirring on a Movil-Rod rotary shaker. Once the mixture was homogenized, 5 mL of concentrated HCl were added and it was stirred again until further homogenization. Next, the mixture was subjected to an ultrasound treatment (US), using a US Elmasonic bath, model LC 30 H with a fixed frequency of 37.5 kHz and regulation of time and temperature, for a period of 60 minutes.

In order to extract the maximum amount of organic matter, three other modalities of acid attack were tested. In the first, in addition to the 5 mL of HCl, 5 mL of concentrated H_2O_2 (33%) were added. In the second, 5 mL of HCl and 50 mL of Dimethylsulfoxide (DMSO) were added to complete the total volume of 700 mL. Finally, in the third modality, 5 mL of HCl, 5 mL of concentrated H_2O_2 and 50mL of DMSO were added to complete the total volume of 700 mL.

On all occasions, at the end of the treatment, the solid phase was separated from the liquid phase by filtration. In the liquid phase, the presence of pectins was verified by precipitation in a hydroalcoholic medium, while the solid phase was subjected to a treatment with deionized water to eliminate excess HCl. To do this, solid obtained, 700 mL of deionized water were added to it and it was stirred for 30 minutes on a rotary shaker. Then it was filtered and the alkaline attack was carried out.

To carry out the alkaline attack, the resulting solid was introduced into an airtight container with 700 mL of deionized water and the amount of $Ca(OH)_2$ selected (1g vs 5g) previously weighed with a SCALTEC SBA 52 precision balance was added, the contents of the container were homogenized by stirring by means of the rotary shaker and, finally, the mixture was subjected to the influence of US radiation for a period of 60 '. The object of this saponification was to obtain the maximum number of anchor points in the form of carboxylate groups.

In order to obtain the final bioadsorbent, it was necessary to wash the solid phase with deionized water until the excess of calcium was eliminated and, finally, to place it in a Nahita 631/4 laboratory oven for 24 hours at 110ºC.

Experimentally, it was observed that at the end of the neutralization treatments there was a significant loss of solid phase from the initial acid treatment, since the initial size of the orange peel was very small (<200 µm). Table 2 shows the different experimental conditions and the results obtained.

As an alternative, it was decided to carry out the alkaline attack immediately after the acid attack without prior separation of the solid phase from the liquid phase. In Figure 2, it is observed how the solid phase protrudes, in a compact way, from the liquid phase as a consequence of the binding effect of the pectins extracted in the acid attack and that were not separated by filtration.

TABLE 2
FINAL BIOADSORBENT OBTAINED AND PERFORMANCE WITH RESPECT TO THE INITIAL WEIGHT (50g)

Acid treatment	Alkaline treatment	Obtained weight (g)	Performance (%)
5 mL HCl	1 g $Ca(OH)_2$	6.85 ± 1.2	13.70
5 mL HCl	5 g $Ca(OH)_2$	7.37 ± 0.9	14.75
5 mL HCl + 5 mL H_2O_2	1 g $Ca(OH)_2$	10.42 ± 1.8	20.83
5 mL HCl + 5 mL H_2O_2	5 g $Ca(OH)_2$	11.07 ± 1.5	22.14
5 mL HCl + 50 mL DMSO	1 g $Ca(OH)_2$	7.41 ± 1.2	14.82
5 mL HCl + 50 mL DMSO	5 g $Ca(OH)_2$	6.10 ± 1.4	12.20
5 mL HCl + 5 mL H_2O_2 + 50 mL DMSO	1 g $Ca(OH)_2$	10.08 ± 1.0	20.16
5 mL HCl + 5 mL H_2O_2 + 50 mL DMSO	5 g $Ca(OH)_2$	10.25 ± 1.3	20.51

FIGURE 2: Solid phase compacted by the binding effect of pectins

Before proceeding to eliminate the excess Ca(II), incorporated in the form of $Ca(OH)_2$ in the alkaline attack, the compacted solid phase was introduced inside the laboratory oven at 110ºC for a period of 24h. Table 3 shows the bioadsorbent weights obtained after removing the excess Ca(II) by repeated washing with deionized water and drying again at 110ºC for another 24h period. It can be seen that all were significantly higher than those obtained using the standard procedure.

TABLE 3
FINAL BIOADSORBENT OBTAINED AND YIELD WITH RESPECT TO THE INITIAL WEIGHT (50g) USING THE ALTERNATIVE TREATMENT.

Acid treatment + alkaline treatment	Obtained weight (g)	Performance (%)
5 mL HCl + 5 g $Ca(OH)_2$	26.91 ± 2.0	53.82
5 mL HCl + 10 g $Ca(OH)_2$	19.10 ± 1.9	38.20
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	23.82 ± 1.5	46.64
5 mL HCl + 5 mL H_2O_2 + 50 mL DMSO + 5 g $Ca(OH)_2$	17.40 ± 2.2	34.80

Figure 3 shows the IR spectra of the initial shell and of the bioadsorbents obtained by the conventional chemical treatment and the alternative chemical treatment between 1800-1000 cm^{-1}. The peaks that appear centered at 1747 cm^{-1} and at 1638 cm^{-1} that appear in the spectrum of orange peel, before their chemical treatment, are attributable to the carbonyl group (C=O) as indicators of esterified and free carboxylic groups. In fact, the disappearance of the peak at 1747 cm^{-1} in the orange peel spectrum once subjected to a chemical treatment indicates the disappearance of high methoxyl pectins in both the conventional chemical treatment and the alternative chemical treatment.

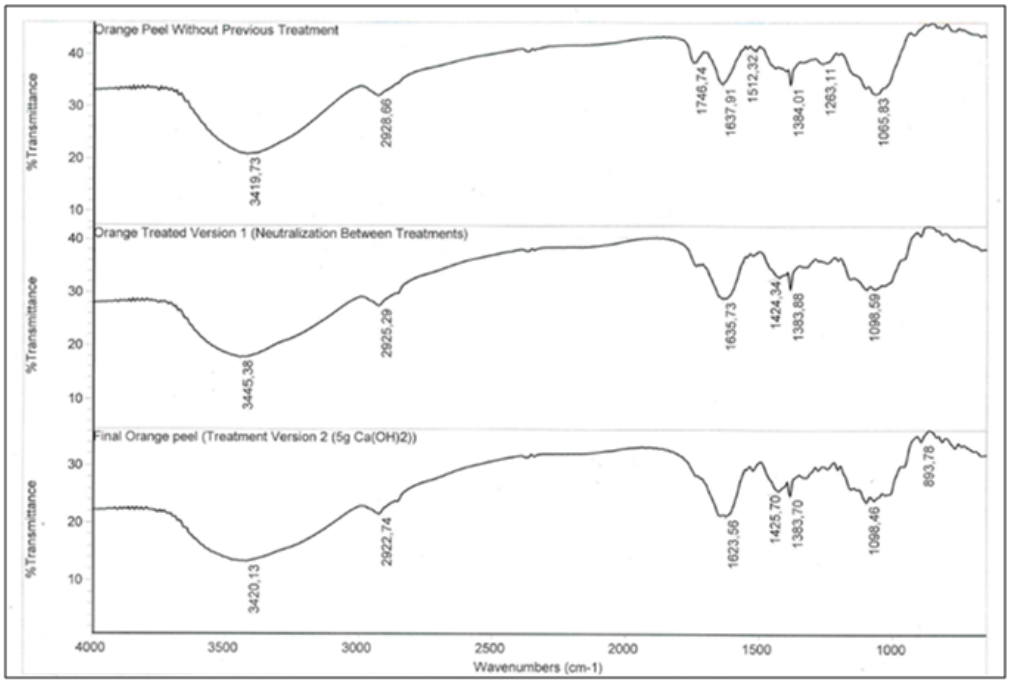

FIGURE 3: Comparison of the IR spectrum of the orange peel before being subjected to the chemical treatment with the IR spectra obtained with both the conventional chemical treatment and the modified chemical treatment.

2.1 Recovery of pectins

Although obtaining pectin from orange peels has been studied extensively (Msebahi et al., 2005), (Liu et al., 2006), (Yeoh et al., 2008), the extraction of pectins by conventional methods is carried out by heat treatment at 90°C for at least one hour in acidic aqueous solutions, so that the pectins that are not sensitive to calcium are extracted. After a while, the resulting solution is removed from the insoluble solid by filtration. Then, it is mixed with 90º alcohol and the pectin precipitates (Claus, 2002). For this, the same volume of alcohol is added as that of the liquid fraction obtained after the acid attack of the orange peel. Figure 4 shows the consistency of a pectin precipitate obtained by adding a volume of ethyl alcohol equal to the volume of the liquid fraction.

FIGURE 4: Appearance of the consistency due to the precipitation of the pectins after adding 100% vol. ethanol

The modification introduced (alkaline attack directly after the acid attack) achieved a higher yield of bioadsorbent, due to the binding effect of the pectins extracted in the acid attack.

The fraction soluble in aqueous medium (water-soluble pectins, excess of Ca(II) and organic matter) was jointly extracted from the bioadsorbent obtained from 50 g of orange peel. To do this, the solid obtained was brought into contact with 500 mL of deionized water and heated at 60°C for 30 minutes with gentle stirring. Next, the volume of the liquid phase was

reduced by means of an IR lamp to a volume of 20 mL. The addition of an equal volume of EtOH caused the pectins to precipitate.

The two experiences with the highest performance described in the table 3, performed with 5mL HCl + 5 g $Ca(OH)_2$ and with 5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$ and compared with one performed with NaOH, the alkali used in the conventional treatment (saponification with NaOH followed by crosslinking with $CaCl_2$).

Table 4 shows that the saponification and crosslinking process carried out in a single stage with the use of $Ca(OH)_2$ is superior to that carried out with NaOH, since the weight of the pectin is significantly lower. The oxidative influence of hydrogen peroxide, which caused a greater release of the pectin retained inside the bioadsorbent, was also detected.

TABLE 4
PERCENTAGE OF PECTIN RECOVERED FROM THE BIOADSORBENT OBTAINED FROM 50 g OF ORANGE PEEL

Acid treatment + alkaline treatment	Pectin weight (g)	Performance (%)
5 mL HCl + 5 g $Ca(OH)_2$	1.76 ± 0.4	3.52
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	3.78 ± 1.2	7.56
5 mL HCl + 5 g NaOH	3.48 ± 0.7	6.96

2.2 Bioadsorption of copper in discontinuous process

To determine the exchange capacity of the bioadsorbent obtained by the alternative procedure, it was ground, sieved and the solid fraction between 500-1000 µm was used.

In three containers of 50 mL capacity, 0.5; 1 and 2 g of bioadsorbent obtained through the simplest attack (5 mL of HCl + 5 g $Ca(OH)_2$) were introduced and hydrated for 24h with deionized water. After this period of time, by filtration, the solid phase was separated from the liquid phase. Then, inside each container, the hydrated solid was put in contact with 20 mL of a 250 ppm Cu(II) solution prepared from $CuSO_4 \cdot 5H_2O$ (supplied by PANREAC S.A.), equivalent to 5 mg of Cu(II).

Hermetically sealed, these containers were shaken for a period of 30' on the rotary shaker. Then, in three test tubes, a 5 mL sample from each container was introduced. Immediately, in each test tube, a spatula tip of KI and 5 mL of CH_2Cl_2 (both reagents supplied by PANREAC S.A.) were added and shaken for 5'. The presence of Cu(II) was only clearly evident in the 250 ppm Cu(II) reference sample, due to the formation of I_2 according to the reaction: $5I^- + 2Cu^{2+} \rightarrow Cu_2I_2 + I_3^-$

Figure 5 shows the different coloration of the organic phase in each of the test tubes. First, on the left of the image, the sample from the 250 ppm Cu(II) solution that was not put in contact with the bioadsorbent. Next, the samples from the containers in which the exchange took place between the Ca(II) contained in the bioadsorbent for the Cu(II) contained in the $CuSO_4 \cdot 5H_2O$ solution.

FIGURE 5: Colouring of the reference sample compared to those from the Ca (II) / Cu (II) cation exchange

This cation exchanger capacity was also shown in the rest of the bioadsorbents obtained in the different experimental conditions collected in the table 3.

To obtain quantitative results, the residual Cu(II) was determined by atomic absorption (AA). For this, a Varian SpectAA 110 spectrophotometer was used.

From the results of Table 5 it appears that, under the predetermined experimental conditions, a large excess of $Ca(OH)_2$ did not contribute to improving the exchange capacity of the bioadsorbent obtained. In addition, the rest of the values of the % of Cu(II) retained made the first treatment, the simplest of all, selected as the optimal treatment of the orange peel with a particle size <200 µm.

TABLE 5
Ca (II) / Cu (II) CATION EXCHANGE CAPACITY FROM 20 mL OF A 250 ppm Cu (II) SOLUTION

Acid treatment + alkaline treatment	BN (g)	ppm Cu (II) residual	ppm Cu (II) retained (*)	% Cu (II) Detained (*)	mg Cu (II) retained (*)	mg Cu (II) / g BN (*)
5 mL HCl + 5 g $Ca(OH)_2$	0.5	6.1 ± 0.9	243.9	97.6	4.88	9.76
	1.0	3.5 ± 0.3	246.5	98.6	4.93	4.93
	2.0	2.2 ± 0.5	247.8	99.1	4.96	2.48
5 mL HCl + 10 g $Ca(OH)_2$	0.5	4.1 ± 0.8	245.9	98.4	4.92	9.84
	1.0	7.0 ± 0.4	243.0	97.2	4.86	4.86
	2.0	10 ± 1.1	240.0	96.0	4.80	2.40
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	0.5	22 ± 3.2	228.0	91.6	4.56	9.16
	1.0	14 ± 1.3	236.0	94.4	4.72	4.72
	2.0	7.5 ± 0.8	242.5	97.0	4.85	2.43
5 mL HCl + 5 mL H_2O_2 + 50 mL DMSO + 5 g $Ca(OH)_2$	0.5	7.5 ± 0.4	242.5	97.0	4.85	9.7
	1.0	4.4 ± 0.6	245.6	98.2	4.91	4.91
	2.0	3.0 ± 0.5	247.0	98.8	4.94	2.47

Initial concentration Cu (II) = 250 ppm ⇔ 5mg of Cu (II) BN: bioadsorbent obtained from orange peel (*) mean value

2.3 Reuse of the bioadsorbent

Samples of 0.5; 1 and 2 g of bioadsorbent that had been subjected to the exchange process. For this, these samples were subjected to a treatment with HCl to achieve the solubilization of Cu(II), previously adsorbed, in the form of $CuCl_2$. In this way, Cu(II) was replaced by H^+. Subsequently, the alkaline attack was carried out with 5 g of $Ca(OH)_2$. Through the process of neutralization and crosslinking, the reintroduction of Ca(II) into the three-dimensional network of the bioadsorbent occurred.

Once the excess Ca(II) had been removed by successive washes with deionized water, the bioadsorbent was dried at 110ºC for 24 hours in a Nahita 631/4 laboratory oven. Once dry, it was ground and the particle size between 500-1000 µm was used. Table 6 shows the results obtained.

TABLE 6
Ca(II) / Cu(II) CATION EXCHANGE CAPACITY FROM 20 mL OF A 250 ppm Cu(II) SOLUTION OF REUSED BIOADSORBENT SAMPLES

Acid treatment + alkaline treatment	BNR (g)	ppm Cu (II) residual	ppm Cu (II) retained (*)	% Cu (II) Detained (*)	mg Cu (II) retained (*)	mg Cu (II) / g BNR (*)
5 mL HCl + 5 g Ca $(OH)_2$	0.47	14.47 ± 1.3	235.53	94.2%	4.71	10.02
	0.85	6.16 ± 0.4	243.84	97.5%	4.88	5.74
	1.70	5.82 ± 0.5	244.18	97.7%	4.88	2.87

Initial concentration Cu (II) = 250 ppm⇔ 5mg of Cu (II) BNR: Bioadsorbent obtained from regenerated orange peel (*) mean value

2.4 Bioadsorption of alkali and alkaline earth metals in batch process

To define the exchange characteristics of the bioadsorbent, the exchange with Mg(II) and Na(I) was determined. Experiences carried out with two types of bioadsorbents were compared, those obtained with the treatments (5 mL HCl + 5 g Ca $(OH)_2$) and (5 mL HCl + 5 mL H_2O_2 + 5 g Ca $(OH)_2$).

First, the samples of each bioadsorbent were hydrated in hermetically closed containers with deionized water for a period of 24 hours. The samples were 0.5; 1 and 4 g. Next, the deionized water was replaced by 80 mL of a 982 ppm Mg(II) solution made from $MgCl_2 \cdot 6H_2O$ (supplied by PANREAC SA), equivalent to 78.56 mg of Mg(II). All samples were kept shaking for 30 minutes.

The determination of the Mg(II) retained by the bioadsorbent was carried out volumetrically (Harris 2006). For this, by means of a double-level volumetric pipet, 10 mL of the $MgCl_2$ solution that had been in contact with the bioadsorbent was extracted and made up to the mark in a 100 mL volumetric flask. Samples of 25 mL were extracted from this solution and their evaluation was carried out. A 0.01M EDTA solution was used as titrating agent and EBT indicator. Both reagents were supplied by PANREAC SA.

In the first place, Mg(II) + Ca(II) was jointly titrated, at pH 10. Then, a second titration was carried out, after precipitation with oxalic acid of the Ca(II) displaced by Mg(II) in the exchange process carried out by the bioadsorbent. Precipitation took place in the form of CaC_2O_4.

The values in table 7 confirmed the greater effectiveness of the simplest treatment since the values of Mg(II) retained and those of Ca(II) displaced from inside the bioadsorbent were higher. These results confirmed that the oxidizing effect of hydrogen peroxide is counterproductive in the exchange process.

TABLE 7
Ca (II) / Mg (II) CATION EXCHANGE CAPACITY FROM 80 mL OF A 982 ppm Mg (II) SOLUTION.

Acid treatment + alkaline treatment	BN (g)	ppm Mg (II) residual	ppm Mg (II) retained (*)	% Mg (II) detained (*)	mg Mg (II) retained (*)	mg Mg (II) / g BN (*)	ppm Ca (II) displaced (*)
5 mL HCl + 5 g $Ca(OH)_2$	0.5	729.6± 10.0	252.4	25.70	20.18	40.35	420.7
	1.0	707.2± 5.0	274.8	27.98	21.97	21.97	458.0
	4.0	524.8± 7.0	457.2	46.56	36.55	9.14	762.0
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	0.5	870.4± 5.0	111.6	11.36	8.92	17.84	186.0
	1.0	857.6± 8.0	124.4	12.67	9.94	9.94	207.3
	4.0	624± 10.0	358	36.46	28.62	7.15	596.7

Initial concentration Mg (II) = 982 ppm ⇔ 78.56mg of Mg (II) BN: bioadsorbent obtained from orange peel (*) mean value

On the other hand, the values of the percentage retained, compared with those obtained in the solution of 250 ppm of Cu(II) show that the effectiveness of bioadsorption decreases when the concentration of the analyte is significantly above 250 ppm, According to (Sthiannopkao 2009).

To corroborate this trend, a solution of 11,000 ppm of NaCl was prepared. The determination of the displaced Ca(II) was carried out volumetrically by means of EDTA. On this occasion, the samples did not contain Mg(II), so the indirect determination of displaced Ca(II) was not necessary. The results obtained are collected in table 8 and show the same behavior as that observed in previous experiences: the introduction of hydrogen peroxide in the treatment of the orange peel does not contribute to obtaining a higher retention percentage of the analyzed analyte. In addition, the performance was much lower compared to the tests with Cu(II) and Mg(II).

TABLE 8
Ca(II) / Na(I) CATION EXCHANGE CAPACITY FROM 80 mL OF A 4329 ppm SOLUTION OF Na(I).

Acid treatment + alkaline treatment	BN (g)	mg Ca (II) displaced	ppm Na (I) retained (*)	ppm Na (I) residual (*)	% Na (I) Detained (*)	mg Na (I) retained (*)	mg Na (I) / g BN (*)
5 mL HCl + 5 g $Ca(OH)_2$	0.5	82.67 ± 2.0	95.07	4233.93	2.16%	7.50	14.99
	1.0	131.73 ± 7.0	151.49	4177.51	3.45%	11.95	11.95
	4.0	270.93 ± 12.0	311.57	4,017.43	7.09%	24.57	6.14
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	0.5	31.47 ± 4.0	36.19	4292.81	0.82%	2.85	5.71
	1.0	44.27 ± 6.0	50.91	4278.09	1.16%	4.01	4.01
	4.0	230.40 ± 15.0	264.96	4,064.04	6.03%	20.89	5.22

Initial concentration Na (I) = 4329 ppm ⇔ 346.32mg of bioadsorbent Na (I) BN: bioadsorbent obtained from orange peel (*) mean value

Finally, the behavior of the bioadsorbent was verified against a complex sample: seawater from the western Mediterranean basin.

Seawater is a solution made up of water and salts, in a proportion of 96.5% water and 3.5% salts. These salts are formed by a great variety of elements and chemical compounds, such as chlorine, sodium, magnesium, calcium, potassium, bromine, strontium, boron and fluorine mainly. Chlorine and sodium are the fundamental constituents of sea water and are found in the form of sodium chloride which is known as common salt and represents 80 percent of salts in solution. After chlorine and sodium, magnesium is the most abundant element in seawater (Anthoni 2000).

Unlike the trace components, the larger ions dissolved in seawater maintain remarkably constant relative concentrations with each other (Custodian1983). Table 9 shows the composition and typical characteristics of seawater (Grasshoff et al. 1999).

TABLE 9
COMPOSITION AND CHARACTERISTICS OF SEA WATER

Parameters	Reference ranges
Dissolved salts, mg / L	30,000 - 45,000
Sulfates, mg / L	2,425 - 3,000
Chlorides, mg / L	17,500 - 21,000
Sodium, mg / L	9,600 - 11,700
Potassium, mg / L	350 - 500
Calcium, mg / L	375 - 525
Magnesium, mg / L	1,025 - 1,400
Temperature ºC	15-35
pH	7.9-8.1

The procedure was analogous to when the exchange of the Ca(II) contained within the bioadsorbent for the Mg (II) of a solution prepared with $MgCl_2 \cdot 6H_2O$ was determined. In the first place, the joint content of Ca(II) + Mg(II) was determined, after the exchange process between the bioadsorbent and the seawater. Subsequently, the previous experience of precipitation of Ca(II) present in seawater in the form of calcium oxalate was repeated, before proceeding to the exchange between the bioadsorbent and seawater.

The Mg(II) content determined after Ca(II) precipitation was 1126.4 ± 25 ppm, while the Ca(II) content was 555 ± 13 ppm.

The experiences carried out with two types of bioadsorbents were compared, those obtained with the treatments (5 mL HCl + 5 g $Ca(OH)_2$) and (5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$) that, previously, had been hydrated in hermetically closed containers with deionized water for a period of 24 hours.

Table 10 shows the experimental values after different bioadsorbent samples of 0.5; 1 and 4 g were put in contact with 80 mL of seawater without previous precipitation of Ca(II).

TABLE 10
Ca(II) / Mg(II) CATION EXCHANGE CAPACITY FROM 80 mL OF SEAWATER WITHOUT PREVIOUS PRECIPITATION OF Ca(II).

Acid treatment + alkaline treatment	BN (g)	ppm Mg (II) residual	ppm Mg (II) retained (*)	% Mg (II) retained (*)	mg Mg (II) retained (*)	mg Mg (II) / g BN (*)	ppm Ca (II) displaced (*)
5 mL HCl + 5 g $Ca(OH)_2$	0.5	1030.4 ± 17.0	96.0	8.52%	7.68	15.36	160.0
	1.0	1020.8 ± 14.0	105.6	9.38	8.45	8.45	176.0
	4.0	627.2 ± 16.0	499.2	44.32%	39.94	9.98	832.0
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	0.5	1040.0 ± 30.0	86.4	7.67%	6.91	13.82	144.0
	1.0	1014.4 ± 23.0	112.0	9.94%	8.96	8.96	186.7
	4.0	812.8 ± 18.0	313.6	27.84%	25.09	6.27	522.7

Initial concentration Mg (II) 0 = 1126.4 ± 25 ppm; Initial concentration Ca (II) 0 = 555 ± 13 ppm (*) middle value

Table 11 contains the results of analogous experiments in which the bioadsorbent samples were put in contact with seawater that, previously, had been treated with excess oxalic acid to precipitate Ca(II) in the form of CaC_2O_4.

TABLE 11
Ca(II) / Mg(II) CATION EXCHANGE CAPACITY FROM 80 mL OF SEAWATER WITH PREVIOUS PRECIPITATION OF Ca(II).

Acid treatment + alkaline treatment	BN (g)	ppm Mg (II) residual	ppm Mg (II) retained (*)	% Mg (II) retained (*)	mg Mg (II) retained (*)	mg Mg (II) / g BN (*)	ppm Ca (II) displaced (*)
5 mL HCl + 5 g $Ca(OH)_2$	0.5	332.8± 12.0	793.6	70.45%	63.49	126.98	1,322.7
	1.0	291.2 ± 19.0	835.2	74.15%	66.82	66.82	1,392.0
	4.0	300.8 ± 10.0	825.6	73.30%	66.05	16.51	1,376.0
5 mL HCl + 5 mL H_2O_2 + 5 g $Ca(OH)_2$	0.5	323.2 ± 10.0	803.2	71.31%	64.26	128.51	1,338.7
	1.0	272.0 ± 15.0	854.4	75.85%	68.35	34.18	1,424.0
	4.0	265.6± 19.0	860.8	76.42%	68.86	17.22	1434.7

Initial concentration Mg (II) 0 = 1126.4 ± 25 ppm (*) middle value

The results obtained confirmed the displacement of Ca(II) inside the bioadsorbent by Mg(II) due to the interaction of excess oxalic acid introduced to precipitate the Ca(II) contained in seawater. In this way, Mg(II) was responsible for maintaining the three-dimensional structure of the bioadsorbent after microprecipitation of Ca(II) in the form of CaC_2O_4 .

III. DISCUSSION

Adsorption is a mass transfer process in which the substances present in a fluid are accumulated on a solid phase and therefore removed from it. The substance that is concentrated on the surface is called adsorbate and the phase that retains it is called adsorbent (Castellan 2000), differentiating between physical and chemical adsorption.

Physical adsorption (physisorption) occurs by both Van der Waals and electrostatic forces between the adsorbate molecules and the atoms that make up the adsorbent surface. Chemical adsorption (chemisorption) is the result of chemical interaction between the solid and the adsorbed substance. It takes place when chemical bonds are formed between adsorbate molecules and specific locations on the adsorbent's surface, also called active sites (Treybal, 1993).

An important consequence of chemisorption is that after the surface has been coated with a single layer of adsorbed molecules, it becomes saturated. Only additional adsorption can occur on the layer present and, in general, it is of a weak type. Because of this, chemisorption is related to the formation of a unimolecular layer, while physisorption can give rise to additional layers (Langmuir 1916).

On the other hand, adsorption falls squarely within ion exchange and is often called ion exchange adsorption, being grouped together as a single treatment in fixed bed processes (Kammerer et al. 2011).

The adsorption process using natural organic materials has been called biosorption (Volesky1990). Bioadsorption or biosorption is a physical-chemical process that includes the phenomena of adsorption of molecules and ions from different materials of natural origin, such as algae, fungi or fruits, which are found in great abundance in nature and the transformation of which biosorbents are not an expensive process (Romera et al, 2007).

The cell walls of bioadsorbent materials contain polysaccharides, proteins and lipids, and therefore numerous functional groups capable of binding heavy metals on their surface. Among the functional groups present, mention may be made of amino, carboxylic, hydroxyl, phosphate and thiol groups which differ in their affinity and specificity with respect to their susceptibility to bind to different metal ions. (Ghimire et al, 2003).

The complexity of the structures of bioadsorbents implies that there are different ways in which contaminants are captured. The mechanisms of bioadsorption are varied. In general, the bioadsorption process is affected by the concentration of surface functional groups (adsorption sites or anchor points); pH (influences the surface charge of the adsorbent and the way in which the species to be adsorbed are found); the surface and pore structure of the adsorbent; the nature of the adsorbate; equilibrium temperature and time (time to saturation of the bioadsorbent) (Ho et al, 2000).

It has been determined that the retention mechanism occurs initially with the migration of the adsorbate from the solution to the surface of the adsorbent, followed by a diffusion process to end in the fixation in the active site (Sivakumar 2010).

Unlike a much more complex phenomenon of bioaccumulation based on active metabolic transport, biosorption by dead biomass is passive and is based mainly on the affinity between the biosorbent and sorbate (Volesky 2007; Gadd 2008; Tejada et al, 2015).

On the other hand, heavy metals are understood to be those whose density is at least five times greater than that of water (> 5 g/cm^3) and with an atomic number value greater than 20 (excluding alkaline and alkaline earth metals). Toxic metals are those whose concentration in the environment can cause damage to the health of people even at low concentrations (Vardhanet al, 2019).

The terms "heavy metals" and "toxic metals" are often used synonymously. However, only a few specific cases belong to both groups. The USEPA (2007) takes into account five heavy metals as the most relevant in terms of their impact on health: Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb) and Mercury (Hg).

There are a large number of inexpensive biosorbents that are represented by lignocellulosic materials, algae, chitin / chitosan, activated sludge, bacterial biomass, fungal biomass, etc. (Castells 2005). Among these, lignocellulosic residues and chitin / chitosan can be applied on a large scale because they have a high availability (Tran et al, 2015).

Lignocellulosic materials (agave bagasse, coconut shell, rice straw, corn cob, rice husk, orange peel, barley straw, etc.) have been used mainly for the removal of metals and organic compounds (Azku 2005). The main components of lignocellulosic residues are: cellulose, hemicellulose and lignin and they have a reasonable adsorption capacity. The selection of a suitable adsorbent, and sometimes a correct chemical modification, can considerably improve the adsorption properties of the material (Abdolali et al, 2014).

Conventional methods for treating wastewater with low concentrations of heavy metals in the ionic state are extremely expensive. For this reason, bioadsorption techniques have gained acceptance due to their effectiveness in eliminating contaminants that are too stable for conventional methods, resulting in high-quality effluents (Basso et al, 2002).

The physical modifications entail a suitable dimensioning of the shell by cutting or grinding, complemented by heat treatments such as reflux, microwave or ultrasonic irradiation. Chemical modifications include treatment with different types of chemical agents, which are used to increase the binding groups in the final bioadsorbent, remove inhibitory groups, and increase its surface area (Patel, 2012).

IV. CONCLUSIONS

It has been proven that:

a) By modifying the chemical treatment, consisting of carrying out the alkaline attack without eliminating the soluble pectins in an acid medium, an easily filterable solid phase is obtained that allows the use of the orange peel of size <200 µm as a bioadsorbent. This modification represents important economic repercussions in an industrial process.

b) The percentage of cation exchange is higher at a lower analyte concentration, which makes bioadsorption a very suitable treatment for the removal of metals in ionic form in effluents with concentrations of around 150 ppm.

c) The exchange capacity is influenced by the presence of an agent that destabilizes the presence of Ca(II) in the bioadsorbent.

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