Full Paper

Cassava Root Husks as a Sorbent Material for the Uptake and Pre-concentration of Cadmium(II) from Aqueous Media

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Abstract: Cassava husks were undergone to simple processes to obtain a fine powder whose particle diameter varied from 63 μm to 75 μm. The characterization of the material indicated the presence of the groups alcohol, amine and thiocarbonyl. The material was tested through batch experiments and the effect of the contact time and pH over the adsorption of Cd(II) ions were evaluated. The material presented a rapid kinetic equilibrium, which was reached in less than 1 min, and the highest Cd(II) uptake occurred at pH 5. The optimum conditions obtained were applied to determine the material's maximum adsorption capacity with the aid of the linearized Langmuir equation (0.109 mmol g^{-1}). A pre-concentration experiment was also carried out, and provided a pre-concentration factor of 43-fold.

Keywords: cassava; cadmium; adsorption; pre-concentration; solid-phase extraction

1. INTRODUCTION

Environmental pollution has become one of the greatest concerns in our modern society. Throughout history, mankind has been developing a wide variety of materials and substances to attend its own needs and to facilitate people's daily lives; nevertheless, this led to the development of toxic substances, which became environmental contaminants [1]. Some common examples of contaminants of the environment comprehend pesticides, dyes, fertilizers and heavy metals [2]. Concerning the heavy metals, such a type of contaminant encompasses a variety of metal elements such as cadmium, lead, nickel, copper and zinc among others [1, 2], which does not present any biological function, or is just required at trace levels by organisms; so, once their concentrations exceed such a level, they may become toxic to several living beings [2].

The most common sources of heavy metal contamination include fossil fuels, mining activities, industries and incineration plants. Once released in the environment, such substances may be dispersed through the atmosphere, hydrosphere or the soil to reach the most remote places in the world, causing the contamination of a vast area [2].

Yet, several diseases are associated to heavy metal contamination, being among them polycythemia, Alzheimer's, kidney damage, over-production of red blood cells, abnormal thyroid artery, fatal cardiac arrest, right coronary artery problems, blood pressure, lung cancer, stomach cancer, gliomas and etc [3-14].

In view of that, it is evident the great importance of regulating the emissions of metal contents to the environment, in order to prevent the damages caused by human activities. To do so, nowadays, many techniques have been developed to reduce/eliminate the amount of heavy metal contaminants from effluents based on principles like precipitation, co-precipitation, membrane filtration, solvent extraction, cementation, coagulation, reverse osmosis, ion exchange, electrodialysis and adsorption of the metal ions [15-26]. Obviously, every technique possesses its merits and drawbacks to accomplish the removal of metal contaminants, though solid-phase extraction using sorbent materials has attracted great attention by its simplicity, high efficiency, and low

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cost (in general) [27-29]. This technique exploits the presence of chelating/complexing groups (*e.g.* carboxylic, amine, amide, thiol, phosphoryl *etc*.) on the surface of sorbents that are able to form coordinate covalent bonds with metal species, removing them from liquid media [30]. Nevertheless, solid-phase extraction is very dependent on parameters such as (but not only) contact time and pH. Since the sorption of pollutants has become a very important technique for the remediation of wastewaters, the study of such parameters has acquired great importance to evaluate the efficiency of sorbent materials. Whereas the elucidation of the kinetic process gives information over the mechanisms of sorption [31], the pH study allows us to uncover the optimum condition under which the sorption process is favored. One of the main effects of the medium's pH over the sorption process is related to presence of hydronium ions which may cause the protonation of the adsorption sites (obviously this process is more evident at low pHs). On the other hand, at higher pHs, another phenomenon takes place. In this case, the higher concentrations of hydroxyl ions may cause the precipitation of metal species due to hydrolysis reactions, not allowing them to coordinate to the material's adsorption sites [28].

Common materials that have being extensively applied for such a purpose include silicas, zeolites, clays, metal oxides, activated carbon and biosorbents [28]. Biosorbents, by their turn, present some advantages over other materials that include general large bioavailability, natural presence of chelating/complexing groups in their structure (without the need of previous functionalization, which could generate by-products and residues [27]) and simple preparation steps. Among the most studied biosorbents are fruit peels, vegetable husks, some agricultural wastes and etc [29].

In view of the promising properties provided by biomaterials for heavy metal solid-phase extraction, cassava (*Manihot esculenta*) root husks present a great potential for their application as a biosorbent in Brazil. Cassava is a plant of Brazilian origin, whose root is very appreciated in the native culinary. Its roots consist of a dark brown elongated root, which contains a white edible flesh in its interior. Some food industries in Brazil commonly extract the cassava root's inner flesh to trade it at supermarkets, but cassava root husks hardly ever have another destination rather than turning into vegetal manure. With that in mind, utilizing cassava husks as a heavy metal biosorbent would be a more interesting

application for this material. So, this work has as main aim, to produce a biosorbent made of cassava root husks, as well as to evaluate its adsorptive properties regarding the uptake and pre-concentration of cadmium(II) from aqueous media.

2. MATERIAL AND METHODS

Reagents and solutions

Cd(II) solutions were prepared using a high purity cadmium chloride (Merck) that was dissolved in ultrapure water (Elga system, Purelab). The standard solutions used in atomic absorption spectrometry were prepared by dilution of 1000 mg L^{-1} stock solutions (Tritisol Merck). For the adjustment of the pH, diluted HNO_3 (Carlos Erba) and NaOH (Synth) were used.

Equipments

The metal species were determined using an atomic absorption spectrometer (Shimadzu AA6800) equipped with a flame module, as appropriate. The monochromator of the equipment was adjusted to 228.8 nm, which are the most sensitive resonance line for cadmium. The infrared spectra were obtained using a Nicolet Nexus 670 spectrometer; samples were scanned 200 times at a resolution of 4 cm^{-1}, through reflectance mode. The pre-concentration experiments were carried out with the aid of dosing pumps Tecnopon DMC 100. Elemental analysis was performed on an EA 1110 CHNS-O analyzer from CE Instruments using 2.2 mg of material.

Preparation of the cassava husks biosorbent

Cassava roots were acquired from a conventional supermarket and washed with tap water to remove any earth particles that could be attached to them. Then, the clean roots had their husks manually extracted with the aid of a knife, and they were broken into pieces before being taken to a heated ventilated chamber at 100 °C. After 24 h in the chamber, the husks were grinded in a blade grinder to generate a gross powder of the material. Cassava root husks were later sieved in sieves of different particle sizes, and the powder fraction comprehended between 63 μm and 75 μm was chosen to perform the adsorption experiments. Prior to the adsorption experiments, it was accomplished a washing step, in order to remove any soluble organic substance that

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could be attached to the material. To do so, the husks were transferred to a becker containing 50 mL of 0.01 mol L^{-1} HCl solution, in which it was stirred for 2 h. After this step, the material was filtered in büchner funnel, and the material was rinsed several times with 100 mL of deionized water and, from time to time, 10 mL of the rinsing water was collected to perform pH analysis. When pH reached a value between 5 and 6, the material was removed from the funnel and taken to the heated ventilated chamber again at 55 °C, for drying. Since the material formed an agglomerate of the cassava husks powder, it was softly grinded manually so that powder particles could be released and used in the adsorption experiments.

Determination of the material's point of zero charge (PZC)

The procedure utilized to obtain the material's PZC was adapted from the one described by Regalbuto *et al.* [32]. The procedure applied to the cassava husks consisted of preparing solutions of different pHs (1, 2, 3, 4, 5, 6, 8, 9, 10 and 11), then, 25.0 mg of the cassava husks were transferred to flasks containing 20.0 mL of each solution and they were kept under agitation for 24 h. After the established time was completed, the solution of each flask had its pH measured, and a graph of final pH vs. initial pH was plotted. The PZC of the material consisted of the region in the graph in which it acted as a buffer.

Batch experiments

All the batch experiments were carried out using 1.8 mL of the metal solution and 20.0 mg of the biosorbent. Initially, it was performed a kinetic experiment, in which a 68.4 mg L^{-1} solution was shaken with the material for times varying from 1 min to 240 min. After the end of the established contact times, the material was filtered in a quantitative filter, and the supernatant was collected to have its concentration measured through Flame Atomic Absorption Spectrometry (FAAS). After the concentration analysis, it was possible to calculate the adsorption capacity of the material (N_f) for each contact time, what occurred by inserting the obtained data to Equation 1:

$$N_f = \frac{ni - ns}{m} \qquad (1)$$

in which n_i is the initial amount of Cd(II) (mmol) in the volume utilized for the experiment, n_s is the remaining amount of Cd(II) of the solution after the contact time (mmol), and m is the mass of the biosorbent (gram). This equation was also used to determine the adsorption capacity of all the subsequent batch experiments.

Later, it was studied the effect of the pH over the adsorption of Cd(II). For this parameter, 75 mg L^{-1} Cd(II) solutions, whose pH varied from 1 to 5, were prepared. The contact time established for this study was 10 min. The samples were subjected to the same procedure described for the kinetic study.

Finally, it was necessary to determine the maximum adsorption capacity of the material. To do so, the material was shaken with solutions of different concentrations (12.5 mg L^{-1} to 505.4 mg L^{-1}) for 10 min (the pHs of the solutions were adjusted to 5). As in the previous experiments, the concentrations before and after the contact time were analyzed and utilized to determine their N_f values for each condition.

Pre-concentration experiments

The pre-concentration experiments were carried out using a constant flow of 1.5 mL min^{-1}, and a mass of biosorbent of 5.00 mg. At first, the mass of the material was packed inside a 4 mm across cylindrical tube, which was connected to peristaltic pumps through Tygon tubes. At first, 50 mL of a 10 μg L^{-1} Cd(II) solution (pH ~ 5) was percolated through the material inside the column, and later, the retained metal species were eluted with 1 mL of a 2 mol L^{-1} HNO$_3$ solution. This procedure enabled to determine the pre-concentration factor of the cassava husks powder.

3. RESULTS AND DISCUSSION

Characterization of the biosorbent

The biosorbent was characterized through Fourier Transform Infrared Spectroscopy (FTIR) and elemental analysis.

According to the FTIR analysis, it indicated the presence of OH stretch band in the region of 3444 cm^{-1}, and CH stretch bands in 2929 cm^{-1} and 2846 cm^{-1}. These bands are expected since these groups are very common in materials constituted mainly by cellulose, which constitutes most of the vegetal structures on Earth. Moreover, C-N stretch band in

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1249 cm^{-1}, C=S stretch band in 1160 cm^{-1}, and NH wag bang in 928 cm^{-1} indicate the presence of amine and thiocarbonyl groups in the material. These are functional groups of interest for the occurrence of metal adsorption, since the presence of nitrogen and sulfur implies in the possibility of metal coordination to the non-bonding electron-pairs of such an elements. The presence of nitrogen-based groups was also verified through elemental analysis, which provided 1.01541758 wt % of nitrogen. The coordination phenomenon is attributed to the share of electron-pairs between Lewis bases and acids [33]. Since amine, hydroxyl and thiocarbonyl groups contain nitrogen, sulfur or oxygen atoms in their constitution (which possess non-bonding electron-pairs), such atoms may act as Lewis bases and form coordinated covalent bonds with metal ions (which, by their turn,

will behave as Lewis acids). So the presence of the as-mentioned groups plays a very important role in the adsorption process. Also, since pH exerts a great influence over the adsorption process, the PZC of the material was measured and found to be 5.33.

Batch Experiments

From the adsorption experiment in function of time, it was possible to know the minimum contact time in which the Cd(II) ions in solution reached the kinetic adsorption equilibrium onto the surface of the material. As it can be seen from Figure 1, the cassava husks powder presents a very rapid adsorption process, reaching kinetic equilibrium in less than 1 min.
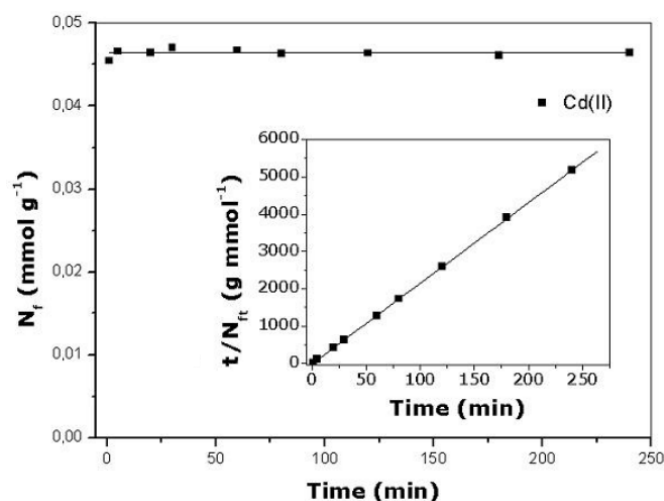

Figure 1. Isotherm of the kinetic experiment and its linearization according to the pseudo-second order kinetic model.

This short time to reach equilibrium indicates that the structure of the material provides high accessibility to its adsorption sites, so that Cd(II) ions could coordinate to them. This also implies that the material is adequate to perform pre-concentration experiments.

The data provided by the kinetic experiment were inserted to the pseudo-second-order kinetic model (Equation 2), which presented great accordance with this model, demonstrated by the high linear correlation coefficient ($r^2 = 1.0000$) (depicted in Figure 1 by the inserted graph), and by the great proximity of the experimental and theoretical N_f values at equilibrium (0.046 mmol g^{-1} and 0.0463 mmol g^{-1}, respectively). In Equation 2, t is the time (in min); N_{ft} is the adsorption capacity at time t (in mmol g^{-1}); N_f is the adsorption capacity at equilibrium (in

mmol g^{-1}); and K_2 is the pseudo-second order kinetic constant (g mmol^{-1} min^{-1}).

$$\frac{t}{N_{ft}} = \frac{1}{K_2 N_f^2} + \frac{1}{N_f} t \qquad (2)$$

Regarding the study about the influence of the pH over the material's adsorption capacity, it can be seen from Figure 2, that at pH 1, due to the high concentration of hydronium ions, the adsorption of Cd(II) is drastically reduced. This occurred because of the competition for the adsorption sites by the hydronium ions, which are in much higher concentration than the metal species, causing the protonation of the material's surface, as supported by the PZC of the material (5.33). Since the surface of the cassava husks is protonated under this pH value, it prevents the Cd(II) cations to bind to the material's

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coordinating groups not only because of the competition for the adsorption sites by the protons, but also because of the positively charged surface that repels Cd(II) cations.

Figure 2 also indicates that the material's adsorption capacity increases with the increase of the pH, till it attains the maximum Cd(II) uptake at pH 5, when the charge of the particles' surface is practically null, and the electron pairs of atoms such as nitrogen, sulfur, and oxygen are free to bind Cd(II) ions.
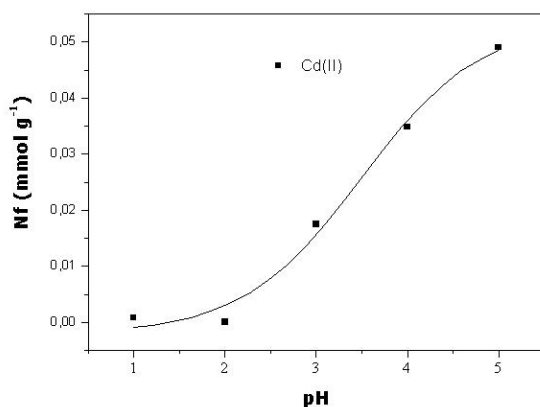

Figure 2. Effect of the pH over the adsorption of Cd(II).

At hand of the optimum contact time and pH obtained from the experiments, such conditions were applied to another experiment to uncover the material's maximum adsorption capacity. Hence, the moment in which cassava husks reached the saturation of its adsorption sites was evaluated as a function of Cd(II) concentration. Such a study is depicted in Figure 3 (a).

As it can be seen from Figure 3 (a), the isotherm as a function of the concentration approaches a maximum value of approximately 0.11 mmol g^{-1}, as the Cd(II) concentration increases. In Figure 3 (b), the obtained data were inserted to the linearized Langmuir equation (Equation 3), so that the maximum adsorption capacity could be estimated.

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \qquad (3)$$

The linearized Langmuir equation was a good model to fit the data, since it provided a high linear correlation coefficient (r^2) of 0.9905. Such a model tells that Cd(II) adsorption occurs through the formation of a monolayer over the material's surface. The angular coefficient ($1/N_s$) of the best-fit straight line enabled to calculate the material's theoretical maximum adsorption capacity (N_s), obtaining a value

of 0.109 mmol g^{-1}, which is approximate to the experimental value, observed in Figure 3 (a). This indicates that practically all the adsorption sites were able to sequester Cd(II) ions. Moreover, the calculated empirical constant (b) of Equation 3 was 763 L mmol^{-1}. As a comparison, Table 1 shows some materials with their respective maximum adsorption capacities for Cd(II):
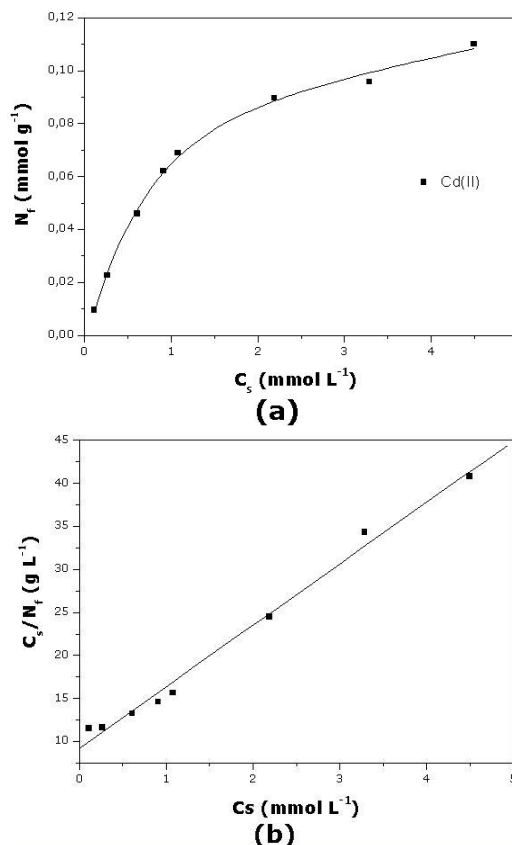

(a)

(b)

Figure 3. Isotherm for the adsorption of Cd(II) as a function of the concentration (a), and its linearization, according to the Langmuir equation (b).

Table 1 enables to compare the maximum adsorption capacity of cassava husks with other low-cost adsorbents. Among them, there are other crude biosorbents (coconut copra meal, raw rice husks, and broad bean peels), a chemically-treated biosorbent (NaOH-treated rice husks), functionalized adsorbents (dithiooxamide-modified cellulose and 2,2-bipyridine-modified silica gel), and a naturally occurring inorganic adsorbent (calcite). From such a table, it can be noted that there are materials much more efficient than cassava husks for the uptake of cadmium (*e.g.* broad been peels and 2,2-bipyridine-modified silica gel), however, less efficient materials also exist, like raw rice husks and coconut copra meal. Besides, functionalized cellulose also presented a

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lower cadmium maximum adsorption capacity than raw cassava husks. It is interesting to notice that a biosorbent material may have its efficiency improved by chemical treatment. In the table, this fact is illustrated by the increase in the adsorption capacity of rice husks, after a NaOH-treatment.

Table 1. Comparison of the maximum adsorption capacity of cassava husks powder and other adsorbents.

Material	*Maximum Adsorption Capacity (mmol g^{-1}) for Cd(II)*	*Reference*
Calcite	0.165	[34]
Dithiooxamide-modified cellulose	0.069	[35]
Coconut copra meal	0.044	[36]
2,2-bipyridine-modified silica gel	0.53	[37]
Raw rice husks	0.076	[38]
NaOH-treated rice husks	0.180	[38]
Broad bean peels	1.312	[39]
Cassava husks	0.109	This study

Pre-concentration experiments

Since pre-concentration experiments were carried out by percolating 50 mL of the metal solution and later eluting the retained metal with 1 mL of 2 mol L^{-1} HNO$_3$ solution, the pre-concentration factor is restricted to a maximum value of 50-fold. The experimental pre-concentration factor for Cd(II) obtained was 43-fold, what implies that the material recovered 86% of the metal content from the solutions. By uncovering the pre-concentration factor, this method allows to determine the amount of metal present in other samples through simple FAAS without resorting to more expensive and complex techniques (*e.g.* GFAAS, ICP-MS or ICP-OES).

4. CONCLUSION

Cassava husks infrared spectrum presented bands associated to the presence of alcohol, amine and thiocarbonyl groups. The material reached kinetic equilibrium in less than 1 minute, and its optimum pH to perform Cd(II) uptake was found to be 5, what is very approximate to the material's point of zero charge (5.33). The theoretical Cd(II) maximum adsorption capacity obtained was 0.140 mmol L^{-1}. The material's properties demonstrated to be adequate to perform pre-concentration experiments and it provided a pre-concentration factor of 43-fold.

5. ACKNOWLEDMENTS

6. REFERENCE AND NOTES

[1] Manahan, S. E.; Environmental Science and Technology, Boca Raton: Lewis 2000.

[2] REEVE, R. N.; Introduction to Environmental Analysis, Chichester: John Wiley & Sons LTD, 2002.

[3] Knight, C.; Kaiser, G. C.; Robothum, L. H.; Witter, J. V. *Environ. Geochem. Health.* **1997**, *19*, 63. [CrossRef]

[4] Loubieres, Y.; Lassence, A. D.; Bernier, M.; Baron, A. V.; Schmitt, J. M.; Page, B.; Jardin, F. *J. Toxicol. Clin. Toxicol.* **1999**, *37*, 333. [CrossRef]

[5] Strachan, S. *Curr. Anaesth. Crit. Care* **2010**, *21*, 44. [CrossRef]

[6] Robert, G.; Mari, G.; Human Health Effects of Metals, US Environmental Protection Agency Risk Assessment Forum, Washington, DC, 2003.

[7] Dieter, H. H.; Bayer, T. A.; Multhaup, G. *Acta Hydroch. Hydrob.* **2005**, *33*, 72.

[8] Nordberg, G.; Jin, T.; Bernard, A.; Fierens, S.; Buchet, J. P.; Ye, T.; Kong, Q.; Wang, H. *Ambio* **2002**, *31*, 478. [CrossRef]

[9] Steenland, K.; Boffetta, P. *Am. J. Ind. Med.* **2000**, *38*, 295. [CrossRef]

[10] Mortada, W. I.; Sobh, M. A.; El-Defrawy, M. M.; Farahat, S. E. *Am. J. Nephrol.* **2001**, *21*, 274. [CrossRef]

[11] Jarup, L. *Brit. Med. Bull.* **2003**, *68*, 167. [CrossRef]

[12] Barbee, J. Y. Jr.; Prince, T. S. *South. Med. J.* **1999**, *92*, 510. [CrossRef]

[13] Jarup, L.; Hellstrom, L.; Alfven, T.; Carlsson, M. D.; Grubb, A.; Persson, B.; Pettersson, C.; Spang, G., Schutz, A., Elinder, C. G. *Occup. Environ. Med.* **2000**, *57*, 668. [CrossRef]

[14] Muhammad, S.; Shah, M. T.; Khan, S. *Microchem. J.* **2011**, *98*, 334. [CrossRef]

[15] Gabaldon, C.; Marzal, P.; Ferrer, J.; Seco, A. *Water Res.* **1996**, *30*, 3050. [CrossRef]

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[16] Kadirvelu, K.; Faur-Brasquet, C.; Le Cloirec, P. *Langmuir* **2000**, *16*, 8404. [CrossRef]

[17] Mohan, D.; Pittman Jr., C. U. *J. Hazard. Mater. B* **2006**, *137*, 762. [CrossRef]

[18] Mohan, D.; Singh, K. P.; Singh, V. K. *J. Hazard. Mater.* **2006**, *135*, 280. [CrossRef]

[19] Mohan, D.; Singh, K. P. *Water Res*. **2002**, *36*, 2304. [CrossRef]

[20] Atkinson, B. W.; Bux, F.; Kasan, H. C. *Water SA* **1998**, *24*, 129.

[21] Babel, S. *J. Hazard. Mater.* **2003**, *97*, 219. [CrossRef]

[22] Mellah, A.; Chegrouche, S.; Barkat, M. *J. Colloids Interf. Sci.* **2006**, *296*, 434. [CrossRef]

[23] Prasad, M.; Saxena, S. *Ind. Eng. Chem. Res.* **2004**, *43*, 1512. [CrossRef]

[24] Liu, C. C.; Wang, M. K.; Li, Y. S. *Ind. Eng. Chem. Res.* **2005**, *44*, 1438. [CrossRef]

[25] Özcan, A.; Özcan, A. S.; Tunali, S.; Akar, T.; Kiran, I. *J. Hazard. Mater. B* **2005**, *124*, 200. [CrossRef]

[26] Kobya, M. *Adsorpt. Sci. Technol.* **2004**, *22*, 51. [CrossRef]

[27] Castro, R. S. D.; Caetano, L.; Ferreira, G.; Padilha, P. M.; Saeki, M. J.; Zara, L. F.; Martines, M. A. U.; Castro, G. R. *Ind. Eng. Chem. Res.* **2011**, *50*, 3446. [CrossRef]

[28] Walcarius, A.; Mercier, L. *J. Mater. Chem.* **2010**, *20*, 4478. [CrossRef]

[29] Rao, K. S.; Mohapatra, M.; Anand, S.; Venkateswarlu, P. *Int. J. Eng. Sci. Technol.* **2010**, *2*, 81.

[30] Jal, P. K.; Patel, S. B.; Mishra, K. *Talanta* **2004**, *62*, 1005. [CrossRef]

[31] Ho, Y. S.; McKay, G.; *Proc. Biochem.* **1999**, *34*, 451. [Crossref]

[32] Regalbuto, J. R.; Robles, J.; *The engineering of Pt/Carbon Catalyst Preparation,* University of Illinois: Chicago, 2004.

[33] Pearson, R. G. *J. Am. Chem. Soc.*, **84**, *16*, 1962.

[34] Yavuz, Ö.; Guzel, R.; Aydin, F.; Tegin, I.; Ziyadanogullari, R. *Pol. J. Environ. Stud.* **2007**, *16*, 467.

[35] Jorgetto, A. O.; Silva, R. I. V.; Longo, M. M., Saeki, M. J., Padilha, P. M.; Martines, M. A. U.; Rocha, B. P.; Castro, G. R. *Appl. Surf. Sci*. **2013**, *264*, 368. [CrossRef]

[36] Ho, Y. S.; Ofomaja, A. E. *Biochem. Eng. J.* **2006**, *30*, 117. [CrossRef]

[37] Souza, E. J.; Cristante, V. M.; Padilha, P. M.; Jorge, S. M. A.; Martines, M. A. U.; Silva, R. I. V.; Carmo, D. R.; Castro, G. R. *Pol. J. Chem. Tech.* **2011**, *13*, 28.

[38] Kumar, U.; Bandyopadhyay, M. *Bioresour. Technol.* **2006**, *97*, 104. [CrossRef]

[39] Benaissa, H. *J. Hazard. Mater.* **2006**, *132*, 189. [CrossRef]

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