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ADSORPTION STUDIES OF SELECTED HEAVY METALS WITH AGRO WASTE BIOMASS FROM AQUEOUS MEDIA

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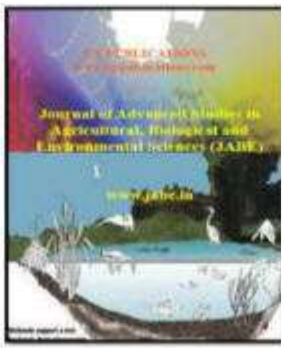

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ABSTRACT
Heavy metal pollution is becoming a serious environmental problem. The use of biomass as an adsorbent for the removal of toxic metals from industrial effluents appears as a promising alternative to existing technologies. Within this context comes the green coconut shell, which can be used as an adsorbent presenting the low cost of the material as an advantage. Green coconut shells were treated with acid, base and hydrogen peroxide solutions for 60, 90, 120 and 150minutes for removing toxic metals from synthetic wastewater. The removal of ions by the adsorbent treated with 0.1 mol /L KOH / 150min was 99.5% for Pb (II) and 97.9% for Cu (II) . The removal of Cd (II) , Ni (II) , Zn (II) , using adsorbent treated with 1.0 mol /L NaOH / 150min, was 98.5, 90.3 and 95.4%, respectively. Particle size, adsorbent concentration and adsorption kinetics were also studied. An adsorbent size of 60-99 mesh and a concentration of 30-40 g / L for 5 min exposure were satisfactory for maximum uptake of Pb (II) , Ni(II) , Cd (II) , Zn (II) and Cu (II) and can be considered as promising parameters for treatment the aqueous effluents contaminated with toxic metals.
Keywords: green coconut shells; toxic metals; wastewater.

INTRODUCTION

India is one of the world's largest producers of green coconut and the coastal region like East & West Godavari districts stands out for production and consumption, accounting for 75% of national production [1]. The agribusiness of the product in Andhra Pradesh stands out mainly for the consumption of the liquid of the fruit in nature. However, one of the main environmental problems of the green coconut fruit is the generation of solid residues. It is estimated that around 2 million tons of bark are generated annually as a result of the consumption of green coconut water in Andhra Pradesh. Efforts are currently being made to find new economically viable applications of green coconut shells. In this context, the use of green coconut shells as an adsorbent to treat contaminated effluents is a viable field of action, due to the abundance and low cost of this material. The literature reports the use of several agro-industrial materials as potential adsorbents in the removal of metal ions from wastewater [2]. However, most studies investigate the process of preparing carbonized bio adsorbent with a view to its use in the treatment of aqueous effluents contaminated by heavy metals. However, the carbonized material recycling process is quite expensive. On the other hand, few researchers have dedicated themselves to the study of non-carbonized adsorbents [3]. In this context, the use of green coconut shell as an adsorbent in the removal of toxic metals is a cheap and simple alternative to minimize the problems of urban and environmental pollution generated by the disposal of these residues, as

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well as reducing costs in the treatment of effluents from small industries.

The objective of this work was to investigate the efficiency of several chemical treatments given to the green coconut shell, aiming at its use in the treatment of aqueous effluents contaminated by toxic metals. After the treatment of the material, the parameters of concentration of the adsorbent, effect of granulometry and adsorption kinetics in a multielementary synthetic aqueous solution of metal ions were studied.

EXPERIMENTAL PART

Materials: Stock solutions 1000 mg / L of metal ions were prepared from their respective salts Cu $(NO_3)_2$ $.6H_2O$, Zn $(NO_3)_2$ $.6H_2O$, Cd $(NO_3)_2$ $.6H_2O$, Pb $(NO_3)_2$ and $(NO_3)_2$ $.6H_2O$ of Merck AR grade (India) using double distilled water. From the stock solution, a multielementary standard solution (100 mg/L at pH 5.0) was prepared for the batch adsorption study. Hydrochloric acid (HCl), nitric acid (HNO_3), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) (Merck, SP, India) were used to study the treatment of the adsorbent. Buffer solution of sodium acetate and glacial acetic acid at pH 5.0 was used to remove traces of 0.1 mol /L NaOH . The concentrations of metal ions were determined by atomic absorption spectrophotometry Model SL 168 – Elico (India).

Obtaining the green coconut shell: The green coconut shells were collected from the local area (Konaseema) Andhra Pradesh, India. Initially, the shells were lacerated (in a shredder with cutting knives and disintegrating hammers), then they were pressed in a "PRH" press (horizontal roller press) and classified in order to obtain two fractions: powder and fibre & JSM-7500F model Scanning electron microscopy (SEM) analyses were performed to observe the material's morphological characteristics.

Preparation of the adsorbent material: The material obtained was subjected to a granulometric separation process to obtain different fractions of the residue. The fractions were separated in granulometric ranges from 60 to 325 mesh (0.246 - 0.043 mm) using suitable sieves. These fractions were activated with acidic solutions (HCl 0.1 and 1.0 mol /L , HNO_3 0.1 and 1.0 mol /L and H_3PO_4 0.1 and 1.0 mol /L), basic solutions (NaOH 0.1 and 1.0 mol/L) and hydrogen peroxide (H_2O_2 0.1 and 1.0 mol /L) for 3, 6, 12 and 24 hours at room temperature. Subsequently, they were washed with distilled water, buffer solution (pH 5.0) and placed to dry at room temperature. Then, the fractions were left in the vacuum desiccator until the adsorption experiments were carried out.

Adsorbent adsorption capacity: The experiments to estimate the adsorption capacity of the material were performed in duplicate using Erlenmeyer's, containing an appropriate mass of the treated and untreated adsorbent and 10.0 mL of multielementary synthetic solution (Pb (II), Ni (II) , Cd (II) , Zn (II) and Cu (II)) at a concentration of 100.0 mg / L, at pH 5.0, kept under stirring at room temperature for 24 h. The adsorption capacity of the adsorbent, Q e (mg of the metal / g of the adsorbent) was determined based on the difference in concentration of the metal ions, using Equation 1 :

$$Qe = \frac{Co - Ce}{m} \times V \quad \text{Eq ..(1)}$$

where Co is the concentration of the solute in the initial solution (mg / L); Ce, solute concentration at equilibrium (mg / L); V , volume of solution (L); m mass of the adsorbent (g).

Study of the dosage effect: The effect of the adsorbent concentration on the removal of metal ions was verified for concentrations of adsorbent treated with 0.1 mol /L NaOH for 60min in 10, 20, 30, 40 and 50 g / L at room temperature, multi-elemental solution of 100 mg / L and pH 5.0. 10 ml of a 100 mg / L multi-elemental solution was added to each concentration and kept under stirring for 60min. Then, the adsorption capacities were analyzed and determined, according to Equation 1.

Study of the effect of Adsorbent particle size: Erlenmeyer's containing 2.0 g of each of the different fractions of the adsorbent (60-99; 100-149; 150-199 and 200-325 mesh) and 50 mL of 0.1 mol /L NaOH were placed under stirring at temperature 3 h to increase the material's adsorption capacity. After this procedure, each of the different fractions of the adsorbent was washed with deionized water and buffer solution (pH 5.0), to

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remove the excess and traces of remaining NaOH. Then, 0.3 g of each of the different fractions of the treated material was kept in contact with 10 mL of a multi-element synthetic solution (Pb (II) , Ni (II) , Cd (II) , Zn (II) and Cu (II)) at a concentration of 100 mg / L, at pH 5.0, under stirring at room temperature for 24 h and then analyzed. The experiments were carried out in duplicate.

Kinetics study: The kinetics study was conducted in a batch system. A series of flasks (125 ml conical flask) containing 0.4 g of the treated adsorbent (60-99 mesh) was placed in contact with 10 ml of multielementary ionic solution (Pb (II) , Ni (II) , Cd (II) , Zn (II)) and Cu (II)) at a concentration of 100 mg / L, at pH 5.0, under stirring. At pre-determined intervals, aliquots were removed, filtered and their residual concentrations were determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Material selection: The green coconut shell powder was subjected to different chemical treatments in order to increase its adsorption capacity and the results obtained are shown in Table 1. It can be seen that the values of adsorption capacity of the material submitted to treatments T5 (Treatment 5) and T10 were more expressive in relation to the other treatments. It was also observed that the treatment time of the investigated material (60/90/120/150 minutes) did not influence its adsorption performance.

Table 1. Absorption capacity of metal ions by green coconut powder with various chemical treatments

Treatment No	Pb(II)				Ni(II)				Cd(II)				Zn(II)				Cu(II)			
	60 min	90 min	120 min	150 min	60 min	90 min	120 min	150 min	60 min	90 min	120 min	150 min	60 min	90 min	120 min	150 min	60 min	90 min	120 min	150 min
1	4.59	4.61	4.59	4.61	3.12	3.13	3.12	3.13	3.18	3.19	3.18	3.19	2.16	2.17	2.16	2.17	1.47	1.48	1.47	1.48
2	4.41	4.40	4.01	4.59	3.00	2.99	2.72	3.12	3.15	3.14	2.86	3.28	2.14	2.13	1.94	2.23	1.46	1.45	1.32	1.52
3	4.46	4.50	4.50	4.52	3.79	3.83	3.83	3.84	3.41	3.44	3.44	3.45	2.90	2.93	2.93	2.94	2.46	2.49	2.49	2.50
4	4.49	4.37	4.49	4.52	4.04	3.93	4.04	4.06	4.20	4.09	4.20	4.23	3.78	3.68	3.78	3.80	3.40	3.31	3.40	3.42
5	4.37	4.47	4.49	4.49	4.41	4.51	4.53	4.53	4.41	4.56	4.08	4.08	4.45	4.61	4.12	4.12	4.50	4.65	4.16	4.16
6	4.44	4.50	4.55	3.44	3.02	3.06	3.09	2.34	2.72	2.75	2.47	2.22	2.45	2.48	1.98	2.11	2.20	2.23	1.58	2.00
7	4.44	4.47	4.50	4.52	3.02	3.04	3.06	3.07	2.84	2.86	2.88	2.89	1.93	1.94	1.96	1.96	1.31	1.32	1.33	1.33
8	4.38	4.38	4.47	4.25	3.72	3.72	3.80	3.61	3.69	3.69	3.76	3.57	3.13	3.13	3.20	3.04	2.66	2.66	2.72	2.58
9	4.44	4.41	4.53	4.47	4.00	3.97	4.08	4.02	3.20	3.18	3.26	3.22	2.88	2.86	2.94	2.90	2.59	2.57	2.64	2.61
10	4.52	4.41	4.44	4.31	4.56	4.45	4.48	4.35	3.83	3.74	3.77	3.65	3.87	3.78	3.80	3.69	3.91	3.82	3.84	3.73
11	4.37	4.38	3.92	4.41	3.93	3.94	3.52	3.97	2.59	2.60	2.33	2.62	2.33	2.34	2.09	2.36	2.10	2.11	1.88	2.12

T1: 0.1M NaOH; T2 1.0 M NaOH; 0.1 M T3 HCl; 1.0 M T4 HCl; T5 0.1M HNO_3; T6 HNO_3 1.0 M; 0.1 M T7 H_3PO_4; 1.0 M T8 H_3PO_4; 0.1 M T9 H_2O_2; 1.0 M T10 H_2O_2; T11 Gross; (-) negligible results. (Tn =Where T is treatment, n is Number)

The percentages of removal of metal ions by the treated and untreated adsorbent are shown in Figure 1. The Figure 1 showed that the dust of the coconut husk removed after treatment T5 of 89.6 and 90.87 % Pb (II) , 79 and 86 % Cu (II) , respectively. However, for Cd (II) , Ni (II) and Zn (II) ions , removals of 80 to 85% respectively, were obtained after treatment T5. Thus, it was found that the T5 and T10 treatments given to the green coconut shell powder showed better results than the raw material and the other corresponding treatments. However, T5 treatment was chosen for the development of the work, due to the ease of operation and due to cost. The time selected for the treatment of green coconut shell powder was 150min, since there was no significant variation in the adsorption of metal ions in relation to the other treatment times studied.

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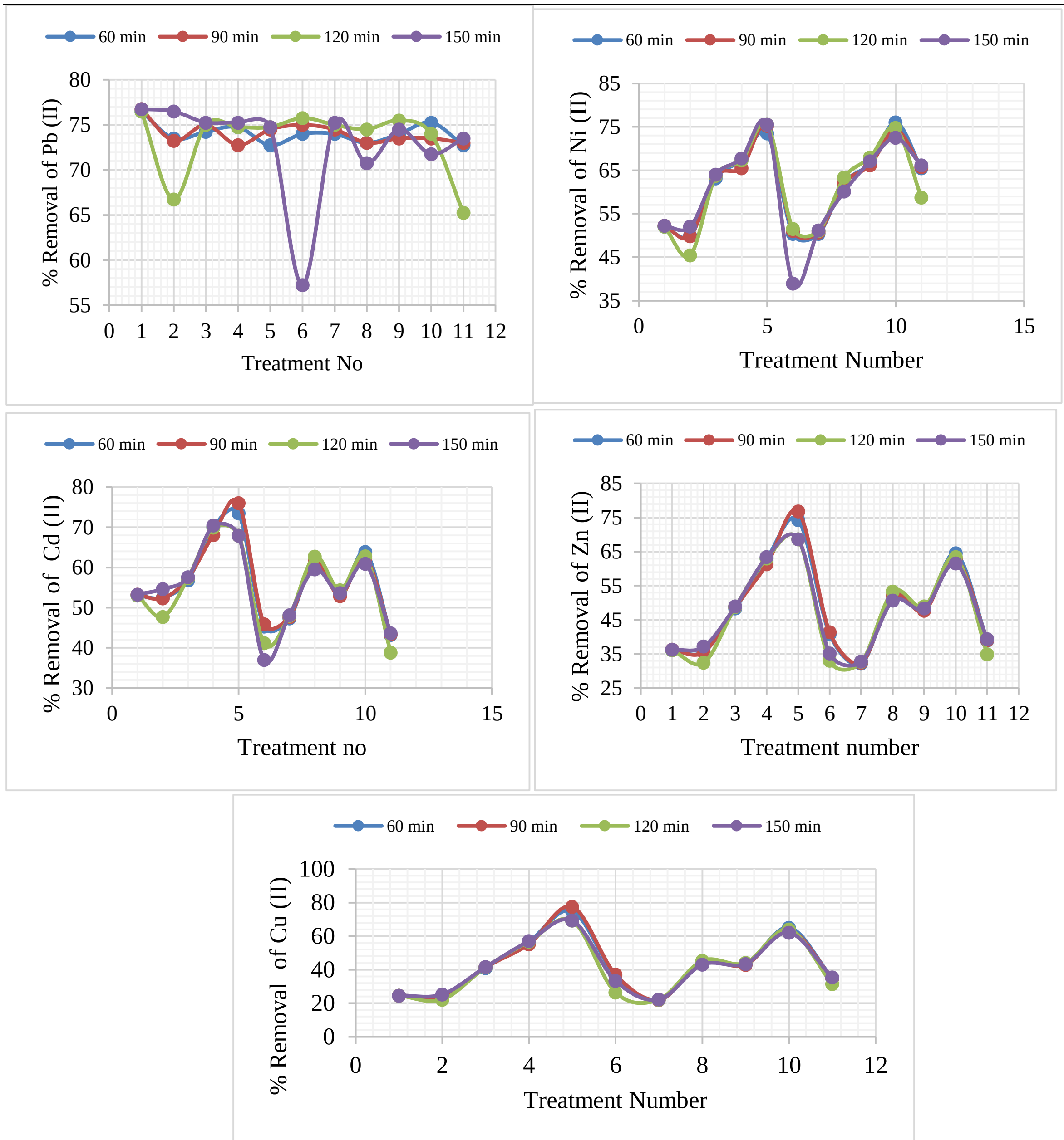

Figure 1: percent removal of selected metal ions from aqueous media (Graphs base don Table 1results)

Study of the effect of granulometry: The granulometry effect of the adsorbent was studied for the particle size range of 0.246-0.043 mm (60-325 mesh). The results (Figure 2), shown that a similar increase in the percentage of removal of metal ions for the 60-99, 100-149, 150-199 mesh ranges, while for the 200-325 mesh range there is a small decrease. Horsfall et al (2006) [4] , investigating the removal of Cd (II) ions in untreated green coconut shell, also observed a loss in removal efficiency with a particle size of 200-325 mesh. Since there was no significant effect of granulometry (60-199 mesh) on the removal efficiency of metal ions, the 60-99 mesh range was chosen for the development of the work, due to the ease of obtaining and operation.

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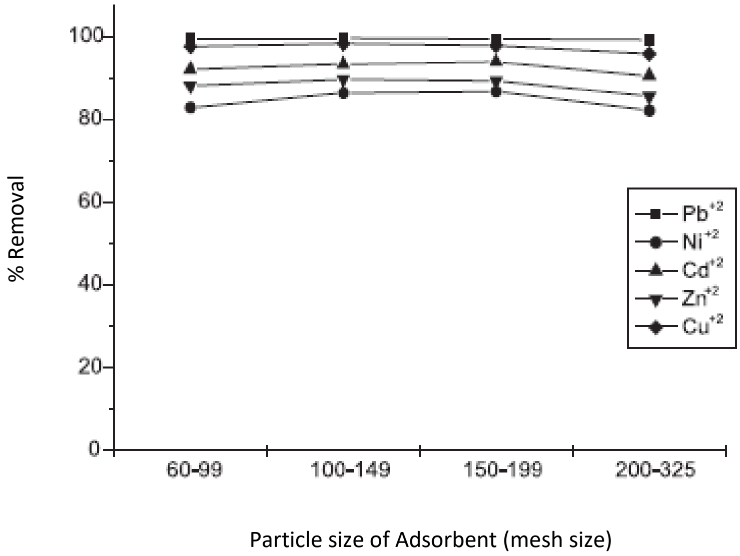

Figure 2. Percentage of metal ion removal for different particle size ranges, pH 5.0 and room temperature

Study of the surface of the adsorbent material

The material treated with 0.1 mol /L NaOH and the crude material, both with 60-99 mesh granulometry, were analyzed using the scanning electron microscopy (SEM) technique, in order to verify the morphological characteristics adsorbent (Figures 3).

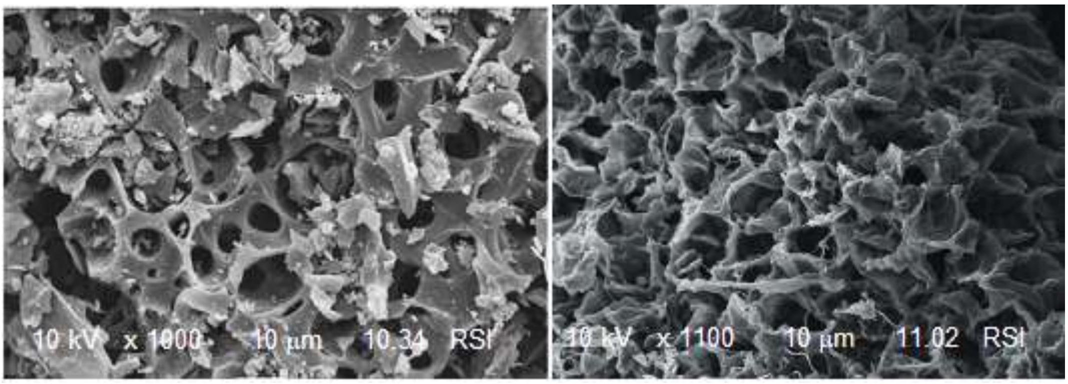

Figure 3. Surface of the 60-99 mesh crude material. Pore diameter equal to 40-60 µm (left) and Surface of the material treated with NaOH 0.1 mol L-1 of 60-99 mesh. Pore diameter equal to 40-42 µm (right)

In general, it is observed that the material is extremely porous and has a very irregular surface. In Figure 3 (left), it can be seen that the raw material consists of a porous surface with pore diameter ranging from 40-60 µm. In Figure 3 (right), it can be seen that the surface of the treated material is composed of pores with a smaller diameter range than the raw material, which favors better retention of metal ions [5].

Study of the dosage effect: To determine the minimum amount of adsorbent material necessary for the maximum removal of metal ions, a dosage study was carried out with concentrations ranging from 10, 20, 30, 40 and 50 g / L of adsorbent. In this study, it was found that a dose of 40 g / L of the material is sufficient for a maximum removal of the metal ions Zn (II) , Ni (II) , and Cd (II) under the mentioned conditions. For the metals Pb (II) and Cu (II) the maximum removal was verified with an adsorbent concentration of 30 g / L (Figure 4).

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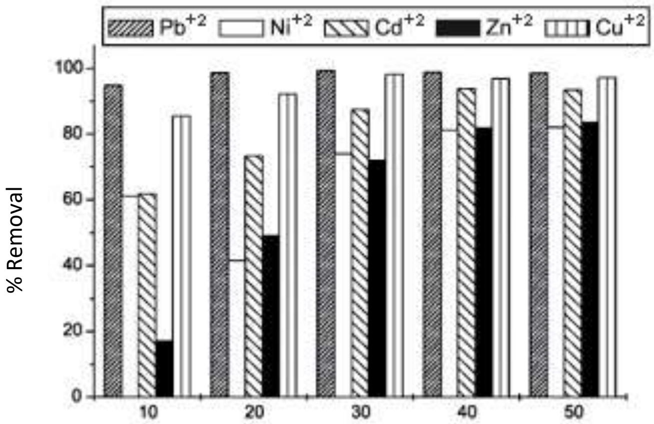

Figure 4. Percentage of removal of metal ions at different concentrations of adsorbents, pH 5.0 and room temperature

Adsorption kinetics of metal ions: The adsorption kinetics was studied with a multi-element solution (100 mg / L at pH 5.0) of the ions Pb (II) , Ni (II) , Cd (II) , Zn (II) and Cu (II) and the result can be seen in the Figure 5 . It was observed that the adsorption equilibrium time is quite fast, occurring within the first 5 min for all studied metal ions.

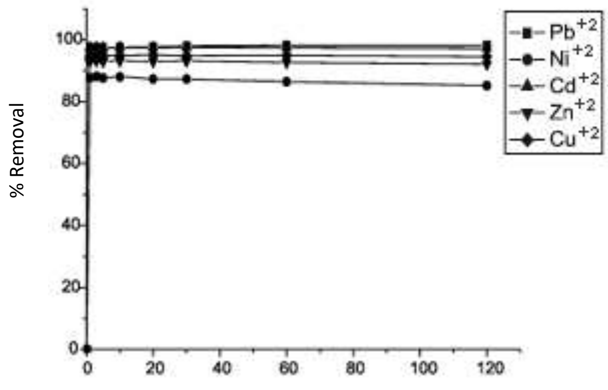

Figure 5. Percentage of removal of metal ions in multielementary solution (100 mg / L) of ions Pb(II), Ni(II), Cd (II), Zn (II) and Cu (II), at pH 5.0 and room temperature

The experimental data of adsorption kinetics were analyzed using the kinetics models of pseudo-first order and pseudo-second order intraparticle diffusion. For this, the first order (Equation 2) and second order (Equation 3) Lagergren equations and the intraparticle diffusion equation (Equation 4) were used [6].

$$\log(Qe - Qt) = \log Qe - \frac{K1}{2.303} \times t \quad \text{.....Eq 2}$$

$$\frac{1}{Qt} = \frac{1}{K_2 Qe^2} + \frac{1}{Qe} \times t \quad \text{.....Eq 3}$$

$$qt = Kf \times \sqrt{t} \quad \text{.....Eq 4}$$

where Qe and Qt are the adsorption capacity in balance and the individual capacity at a particular time (in mg / g) while $K1$, $K2$ *and* Kf are constants of the first order, second order and dissemination intraparticle

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and t the time in min.

The validation of the models was verified by the linear log graph (Qe - Qt) versus t for the pseudo-first order equation, t/Qt versus t for pseudo-second order and Qt versus $t^{0.5}$ for diffusion intraparticle [10]. The constants $K1$, $K2$ and Kf shown in Table 2 were calculated using the angular and linear coefficients of the lines of the graphs obtained (not shown). The results showed that the experimental value shows agreement with the calculated value, for the pseudo-first order and pseudo-second order models [7]. However, the linear correlation of both models (R) indicates that the results of pseudo-second order are better correlated than that of pseudo-first order. These results indicate that the adsorption kinetics of green coconut shell powder to a synthetic multi-element solution follows the pseudo-second-order model [8].

The intraparticle diffusion model was verified for the graph of Qt versus $t^{0.5}$, which recommends that if the graph is linear and passes through the origin, the predominant adsorption mechanism is the diffusion [9]. In this study, the behavior of the graph of Qt versus t $^{0.5}$ and the value of the correlation coefficient showed that there is neither a good linear correlation nor a straight line that passes through the origin (Table 2).

Table 2. Adsorption kinetics parameters in green coconut shell powder treated with 0.1 mol L-1 NaOH and 60-99 mesh granulometry

Ion	Ci	Qe (Exp)	Qe (Cal)	K1	r	Qe (Cal)	K2	r	Kf	r
Pb(II)	79.04	1.941	1.90218	0.04	0.89	1.94	23.01	0.999	0.0034	0.86
Ni(II)	80.05	1.924	1.88552	0.24	0.91	1.92	41.32	0.999	0.0034	0.23
Cd(II)	107	2.634	2.58132	0.04	0.98	2.63	263.31	0.999	0.0061	0.64
Zn(II)	97.68	2.345	2.2981	0.036	0.76	2.38	292	0.999	0.0051	0.422
Cu(II)	85.71	2.002	1.96196	0.11	0.95	2	54.61	0.999	0.0062	0.947

Conclusions

The basic treatment given to the green coconut shell powder with NaOH 0.1 mol /L 90min promoted an increase in the adsorption capacity of the toxic metals Pb (II) , Ni (II) , Cd (II) , Zn (II) and Cu (II) in multi-elementary synthetic aqueous solution. The study of the granulometry effect showed that the adsorption performance of the material is not influenced for particle sizes ranging from 60 to 99 mesh. An adsorbent concentration of 40 g / L is sufficient for a maximum adsorption of the metal ions Zn (II) , Ni (II) and Cd (II) , while for the metals Pb (II) and Cu (II)the maximum adsorption capacity of the adsorbent was verified with a material concentration of 30g/L. The adsorption process follows a pseudo-second order kinetics. The green coconut shell, a biodegradable agro industrial residue and from a renewable source, can be a viable low cost bio adsorbent alternative for the treatment of industrial effluents contaminated by toxic metals. Based on the respective results, batch adsorption and fixed bed studies are being finalized.

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