Bioremediation Potential of Bacteria and Rice Husk Biochar for Cadmium and Lead in Wastewater

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Abstract: Wastewater can be purified greatly when treated with biochar derived from natural rice husk. The present study provides the impact of bacteria (biofriend), commercial activated carbon, rice husk, and its biochar {pyrolysis at 300°C (RHB1), 400°C (RHB2) and 500°C (RHB3)} on synthesized and natural wastewater purification. The obtained results can be summarized as follow: RHB3 considered the best adsorbent ability for cadmium and lead in their single and mixed solutions. The presence of commercial activated carbon by the comparison it is found that it exceeds RHB3 in the case of lead. Rice husk resulted high adsorption values for cadmium and lead, but its adsorption of cadmium exceeds the lead. Addition of biofriend increase adsorption of cadmium and lead in most treatments but results still in the same trend as using rice husk or biochar only. RHB3 treatment observed its superiority and ability to purify lead and cadmium from synthesized and natural wastewater after 4 h contact time compared with other treatment under study.

Keywords: Rice husk, Biochar, lead, cadmum, wastewater.

1. INTRODUCTION

Water used in industry creates a wastewater that has a potential hazard for our environment because of introducing various contaminants such as heavy metals into soil through irrigation water resources. Heavy metal ions are now days among the most important pollutants in surface and ground water (Brinzo *et al*., 2009) [1].

The important toxic metals are Cd, Zn, Pb and Ni. Cadmium accumulates in the human body affecting negatively several organs: liver, kidney, lung, bones, placenta, brain and the central nervous system (Castro-Gonzlez and Méndez-Armenta, 2008) [2]. Other damages include reproductive, and development toxicity, hepatic, haematological and immunological effects (Apostoli and Catalani, 2011) [3]. The excess amount of Cd in soil causes disturbances in mineral nutrition and carbohydrate metabolism (Moya *et al.,* 1993) [4]. Cadmium accumulated in plants can interfere with several physiological processes resulting in low productivity (Obata and Umebayashi, 1997) [5]. Inhibition of germination and retardation of plant growth are commonly observed due to heavy metal toxicity (Singh *et al*., 2004) [6]. Egypt being in the semi-arid region of the world is exposed to water shortage, Rainfall is scarce and its amount in the Northern coastal area range from 100-200mm / year in which few winter crops could be grown (El-Mowlhi and Abd El-Hafez, 1999) [7].

Sewage wastewater, if properly treated, must be considered an important non-conventional water resource for irrigation, as it is sufficient to irrigate 208,000 ha (Abo Soliman, 1997) [8]. There are various methods to treat the metal contaminated effluent among these technologies adsorption is a user-friendly technique for the removal of heavy metal. The activated carbon is being used widely to treat wastewater to remove organic or inorganic pollutants (Park and Kim, 1999) [9]. Activated carbon remains an expensive material and not suitable for developing countries because of its high cost.

Scanning Electron Microscopy of the rice husks and rice husk biochar indicated that the surface was highly irregular and porous in nature. According to Tarley and Arruda (2004) [10]. Therefore, based on morphology and on the fact that a higher concentration of silica is present in the outer epidermis of the rice hulls, one can conclude that this material presents a morphological profile with the capability to retain metal ions. The results of specific surface area analysis demonstrated that the pyrolysis of RH increased surface and increased the total pore volume. They observed the decomposition of hemicellulose and cellulose between 250 and 360°C and the decomposition of lignin between 360 and 525ºC. The calcination temperature

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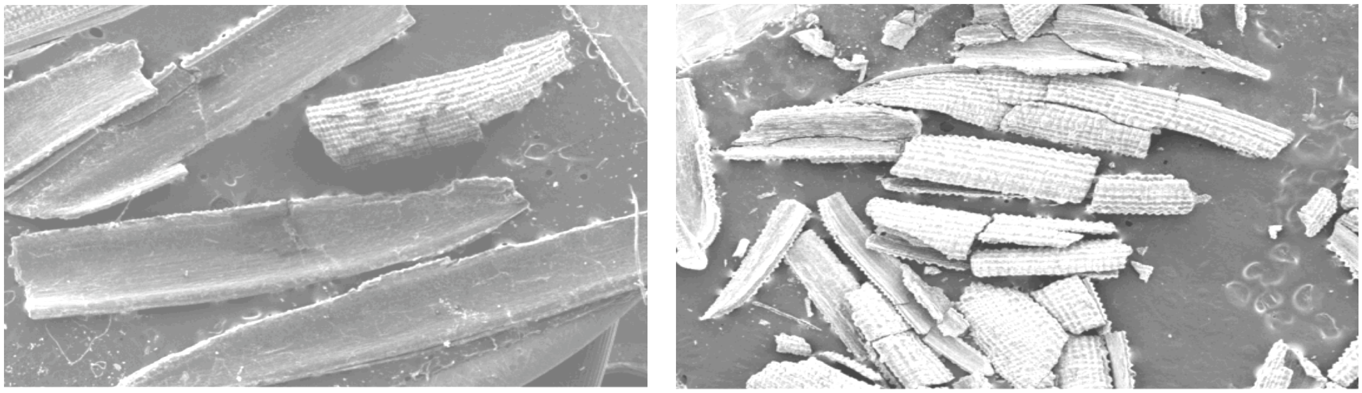


(**a**) (**b**)

Figure 1: Micrographs of Scanning Electron Microscopy: (**a**) Rice husk inner and outer epidermis with 50 x magnifications and (b) Rice husk biochar (at 500°C) inner and outer epidermis with 200X magnification (Vieira *et al*., 2014) [11].

was defined as 500°C, since the entire rice husk had been burnt (Figure **1**, Tables **1** and **2**). One of the characteristics of biochars is possessing large surface areas, which implies a high capacity for complex heavy metals on their surface. Surface sorption of heavy metals on biochar has been demonstrated on multiple occasions using scanning electron microscopy (Beesley and Marmiroli, 2011; Lu *et al*., 2012) [16, 17]. This sorption can be due to complexation of the heavy metals with different functional groups present in the biochar, due to the exchange of heavy metals with cations associated with biochar, such as Ca^{+2} and Mg^{+2} (Lu *et al*., 2012) [17], K^{+}, Na^{+} and S (Uchimiya *et al*., 2011a) [18], or due to physical adsorption (Lu *et al.,* 2012) [17]. Also oxygen functional groups are known to stabilise heavy metals in the biochar surface, particularly (Uchimiya *et al*., 2011b) [19] for softer acids like Pb^{+2} and Cu^{+2}.

Table 1: Some Chemical and Physical Characteristics of Rice Husk

Character	Range	References
Bulk density (kg/m^3)	96-160	Bronzeoak, 2003 [12]
Hardness (Mohr's scale)	5.0-6.0	[12]
Carbon (%)	≈ 35.0	[12]
Hydrogen (%)	4.0-5.0	[12]
Oxygen (%)	31.0-37.0	[12]
Nitrogen (%)	0.23-0.32	[12]
Sulphur (%)	0.04-0.08	[12]
Moisture (%)	8.0-9.0	[12]
Hemicelluloses (%)	25	Krishnani *et al*., 2008 [13]
Cellulose (%)	35	[13]
Silica (%)	17	[13]
Lignin (%)	20	[13]

Table 2: Some Chemical and Physical Characteristics of Biochar

Feature	Rice husk	Biochar 500°C	Biochar 400°C
Adsorption (mg g^{-1} DW)	30.724 Vieira *et al.* (2012) [14]	75.38 Jindo *et al*., 2014 [15]	44.07 Jindo *et al*., 2014 [15]
Surface area (m^2 g^{-1})	11.4 Vieira *et al.* (2012) [14]	262.00 Jindo *et al*., 2014 [15]	193.70 Jindo *et al*., 2014 [15]

Alkalinity of biochar can also be partially responsible for the lower concentrations of available heavy metals found in biochar-amended soils. Higher pH values after biochar addition can result in heavy metal precipitation in soils. Biochar pH value increases with pyrolysis temperature (Wu *et al*., 2012) [20], which has been associated with a higher proportion of ash content (Cantrell *et al*., 2012) [21]. Biochar can also reduce the mobility of heavy metals, altering their redox state of those (Choppala *et al.,* 2012) [22].

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants (Wong *et al.,* 2003) [23]. The rice husk showed good potential for the removal of cadmium from aqueous solutions. Rice husk was the most effective, for which the removal reached 98.15% of Pb at room temperature (Abdel-Ghani *et al.,* 2007) [24].

Many aquatic microorganisms, such as bacteria, yeast and algae can take up dissolved metals from their surroundings onto their bodies and can be used for removing heavy metal ions successfully (Asku *et al.,* 1991) [25]. Microbial biomass offers economical options for removing heavy metals by the phenomenon of biosorption (Gupta and Mohaptra, 2003) [26]. Lu *et al*. (2006) [27] investigated biosorption kinetics and equilibria of lead, copper and cadmium ions using the biomass of Enterobacter sp. J1.

Many microorganisms including bacteria (Cauerhff and castro, 2013) [28], fungi (Ahmad *et al*., 2003; Shahverdi *et al.,* 2007) [29, 30], actinomycetes (Prakasham *et al*., 2012; Silambarasan *et al.,* 2013) [31, 32], and algae (Zaki *et al*., 2012) [33] can aggregate inorganic materials and form nanoparticles (NPs) intracellularly or extracellularly. Natural compounds such as microbial biopolymers are also one of the resources which could be used for green synthesis of AgNPs. Recently, Sathiyanarayanan *et al*. (Sathiyanarasan and Abraham, 2013) [32, 34] reported that polysaccharides from microbial origin such as bioflocculants are a promising alternative for the synthesis and stabilization of nanoparticles. Indeed, this is an interesting area of research where both biosynthetic nanosilvers and bioflocculants are economically important. Bioflocculants are biodegradable, safe, and ecofriendly biopolymers secreted by microorganisms (Deng *et al*., 2003; Bhunia *et al.,* 2012) [35, 36]. They are used in the field of wastewater treatment for removing suspended solids and metal ions, at which colloids come out of suspension in the form of floc or flakes (Li *et al.,* 2003) [37]. In this regard, recently in our lab Bacillus mojavensisstrain 32A was isolated as an efficient bioflocculant producer (Elkady *et al*., 2011) [38]. In the present study, synthesis of nanosilver particles using bioflocculant-producing strain 32A and its extracted and purified bioflocculant was investigated. Produced nanoparticles were characterized using transmission electron microscope (TEM) and X-ray diffraction (XRD) techniques.

Also pH value affects the adsorption efficiency of heavy metals from their solutions. At low pH metal ions compete with the H^+ in the solution for active site and therefore the adsorption capacity decreases. At high pH (to some extent), the adsorbent surface has a higher negative charge which results higher attraction force, Huda and Kafia (2013) [39] and Boonamnuay (2004) [40]. Abdel-Ghani *et al*. (2008) [41] reported that, the uptake of Cu, Zn, Cd and Pb were dependent on pH, where optimal metal removal efficiency attained at pH range from 4.5 to 6.5 and then declining at higher pH.

The present study aims to investigation of the potential efficiency of rice husk and the biofriend (bacterial compound) to remove cadmium and lead elements from their separated and mixed synthetic solutions and natural wastewater.

2. MATERIALS AND METHODS

This study was conducted at Rice Research Section at Field Crops Research Institute, Agricultural Research Center, Sakha, Kafer El-Sheikh, Egypt (2014). Raw rice husk was taken from Rice Research Section at Field Crops Research Institute, Agricultural Research Center. Cadmium and lead nitrate were used for artificial contamination of water.

Rice husk is the outer most layer covering the rice grain. It is commonly detached during hulling process. The chemical and physical characteristics of the rice husk are listed in Table **1**. Biochar derived from rice

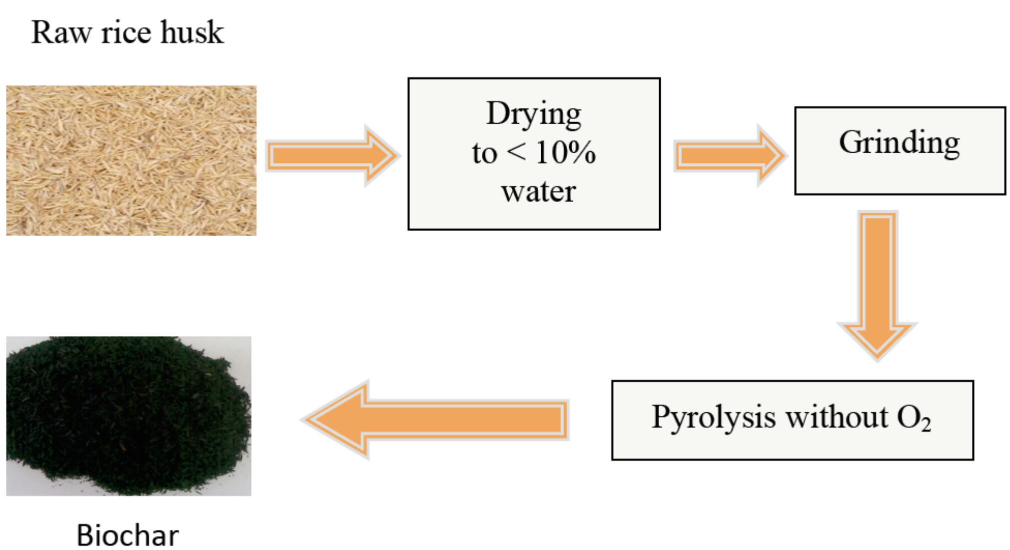


Figure 2: Schematic process diagram for fast pyrolysis for biochar production.

husk (as characterized by different researchers as listed in Table **2** and observed in Figure **1**) is prepared by thermal decomposition of rice husk under absence of oxygen by the process called pyrolysis as observed in Figure **2**. Three different degrees of carbonization temperatures had been used through the pyrolysis process (300, 400 and 500^{o}C) to produce three different types of biochar derived from rice husk. Biochar after grinding and sieving to 2-5mm diameter has been carbonized in electric oven under absent of oxygen in 30 minutes.

Biofriend (*Bacillus mojavensis strain* 32A) is a microbial compound containing a series of beneficial bacterial strains completely safe. It was produced by Environmental Biotechnology Department, Genetic Engineering and Biotechnology Research Institute, City of Scientific Research and Technology Applications. This product granted a patent No. 024011 from the Egyptian Patent Office, Academy of Scientific Research and Technology.

Bacillus mojavensis strain 32A used in this study was previously identified as an efficient bioflocculant producer by Elkady *et al.* (2011) [38]. Culturing, media, and production of bioflocculant and/or synthesis of silver nanoparticles were performed as described elsewhere (Elkady *et al.* 2011) [38]. The initial pH of all media was adjusted to 7.2 to 7.5 with NaOH (1M) and HCl (0.5M). All media were prepared with distilled water and sterilized at 121°C for 20min.

2.1. The Work was Divided into Two Experiments

2.1.1. Experiment 1

Removal of cadmium and lead from their separate synthetic solutions using raw rice husk, rice husk biochar under different temperatures (300, 400 and 500ºC) and the biofriend.

Cadmium and lead single synthetic solutions using aqueous cadmium nitrate, lead nitrate in distilled water were done, the cadmium conc. in the solution was 50 ppm while, lead conc. was 200 ppm, and the pH value of solutions was adjusted at 5. The three types of biochar {300ºC (RHB1), 400ºC (RHB2) and 500ºC (RHB3)} were prepared. Each type of biochar was incubated with 100ml of cadmium and lead synthetic solutions at various concentration and contact times, each biochar was used separately or combined with biofriend (with definite concentration 2%), also bacterial compound (2%) was used separately. Applied contact times were, at once, 2, 4 and 6 hours. Three concentrations of rice husk and biochar were used 1%, 2%, and 3%. Three replicates of each treatment were done. Cadmium and lead concentrations in the purified solutions were detected using atomic absorption spectrophotometer and the obtained data was statistically analyzed by using Genstat 0.5 software for Windows and analyzed with ANOVA and *F*-test for mean separation. The best treatments with the highest degree of purification were concluded.

2.1.2. Experiment 2

Removal of cadmium and lead in mixed synthetic solutions and natural wastewater using raw rice husk, biochar under different temperatures (300, 400 and 500ºC), commercial activated carbon and the biofriend.

Mixed synthetic solutions of cadmium and lead by using cadmium and lead nitrate ($Pb(NO_3)^2$) in distilled water with different initial concentration of cadmium and lead, respectively were done as absolved in Table **3**. The pH value of solutions was adjusted at 5. Two time intervals, 2 and 4 hours, one concentration of each adsorbent (3g/100ml of solution) were used and constant concentration of biofriend (2ml/100ml of solution) was used in mixed treatments (biochar + biofriend), as these treatments were the best in the first experiment. Cadmium and lead concentrations in the purified solutions were determined using an Atomic Absorption Spectrophotometer (AAS), and the obtained data was statistically analyzed by using Genstat 0.5 software for Windows and analyzed with ANOVA and *F*-test for mean separation.

Table 3: The Concentration of Cd and Pb for different Solutions

Solutions	Cd (mg L^{-1})	Pb (mg L^{-1})
(A)	50	200
(B)	25	100
(C)	25	50
(D)	12.5	100
(E)	12.5	50

3. RESULTS

3.1. Experiment 1

Adsorption percentage as observed in Figures **1** and **2** of cadmium and lead were differed with different types of adsorbents. The mean cadmium adsorption from the solution is following the order of RHB3 > Husk > RHB2 > RHB1, while adsorption of lead from the

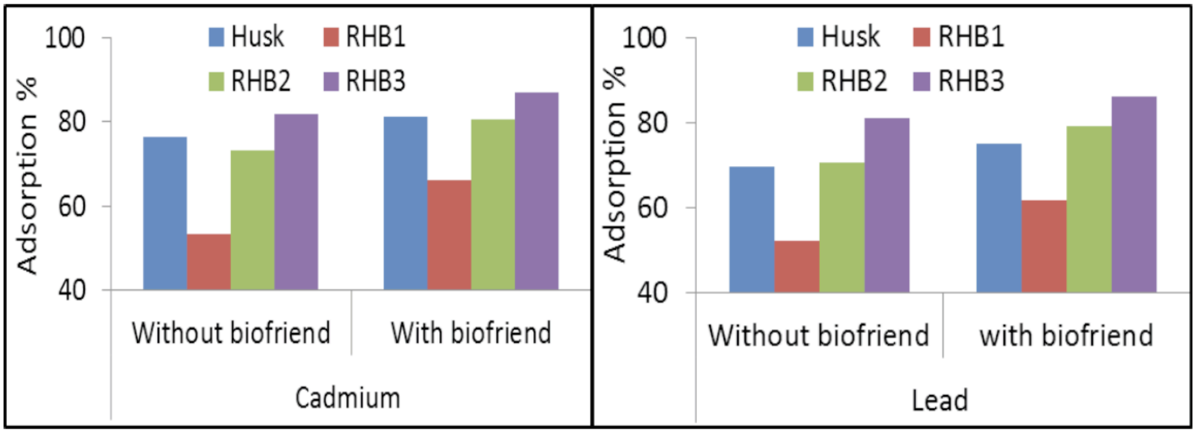


Figure 3: The mean cadmium and lead adsorptive values using the four adsorbents (husk, RHB1, RHB2 and RHB3) only or in the presence of biofriend.

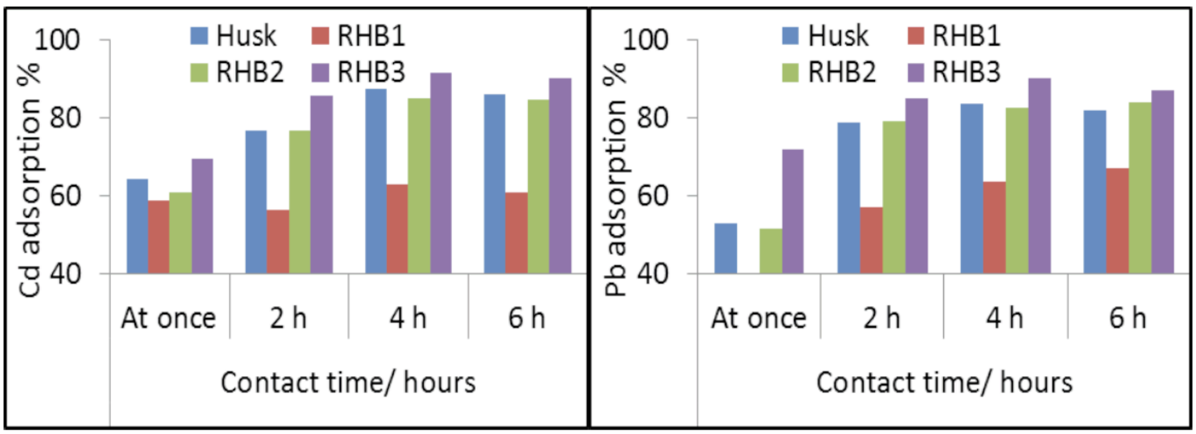


Figure 4: The mean cadmium and lead adsorptive values using different concentrations for all types of used adsorbents (husk, RHB1, RHB2 and RHB3), at different contact times.

solution following the order of RHB3 > RHB2 > husk > RHB1. Data also, showed that addition of biofriend to the biochar or husk increase the adsorption, but also follow the same pattern of adsorption as recorded with the biochar or husk only.

Four contact times were used, at once, 2, 4, and 6 hours, data showed that the adsorption of cadmium and lead from the solution increased with increasing contact time and reached its maximum value after 4 hours (Figures **3** and **4**). RHB3 recorded the highest adsorption value (91.62% and 90.41% for cadmium and lead, respectively) after 4 hours of mixing with cadmium and lead separate solutions, but after 6 hours there is no significant increase in adsorption.

Data of the effect of different three doses of the adsorbents on adsorption percentage showed that the cadmium and lead adsorption increase with increasing adsorbent dose and reached its maximum value with the highest concentration of the adsorbent, 3%, (Figure **5**). All types of adsorbents increased the cadmium adsorption at the high concentration and it follows the order of 3% > 2% > 1%. The highest value of cadmium and lead adsorption were recorded with RHB3. In the presence of befriend the mean value of the adsorption increased with the most of treatments.

The most appropriate contact between befriend only with lead and cadmium soiluations was 4 hours. The highest adsorptions values of cadmium and lead by using befriend only were 66.70 and 65.91% respectively. The results of using befriend only are less than that of mixing it with rice husk or biochar (Figure **6**).

Results showed also that the highest adsorption values of cadmium and lead as affected by the combination between befriend and Biochar is obtained after 4 hours of contact time, by using 3.0 g of each adsorbent. RHB3 only or mixed with befriend recorded the highest purification values followed by RHB2 and husk. RHB1 recorded the lowest adsorption values.

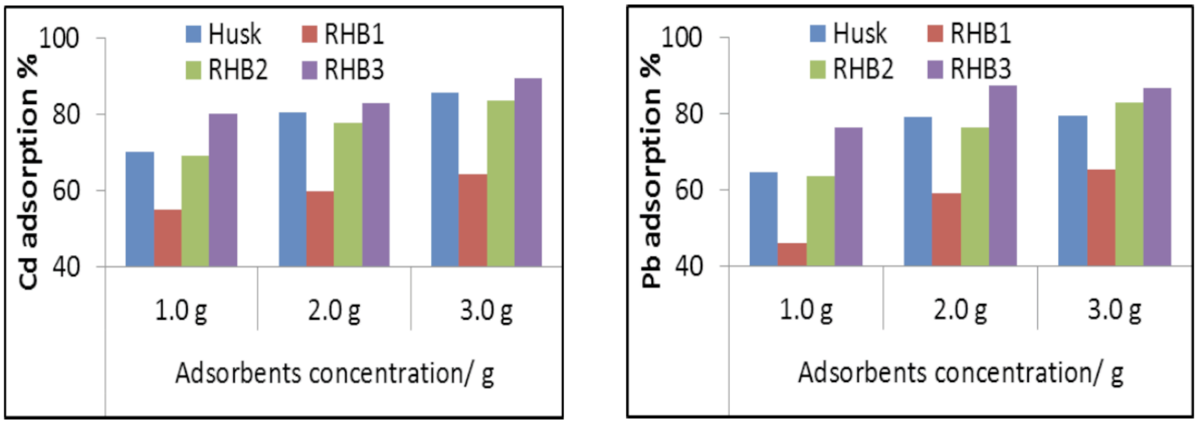


Figure 5: The mean cadmium adsorption percentages using different concentrations for all types of used adsorbents (husk, RHB1, RHB2 and RHB3).

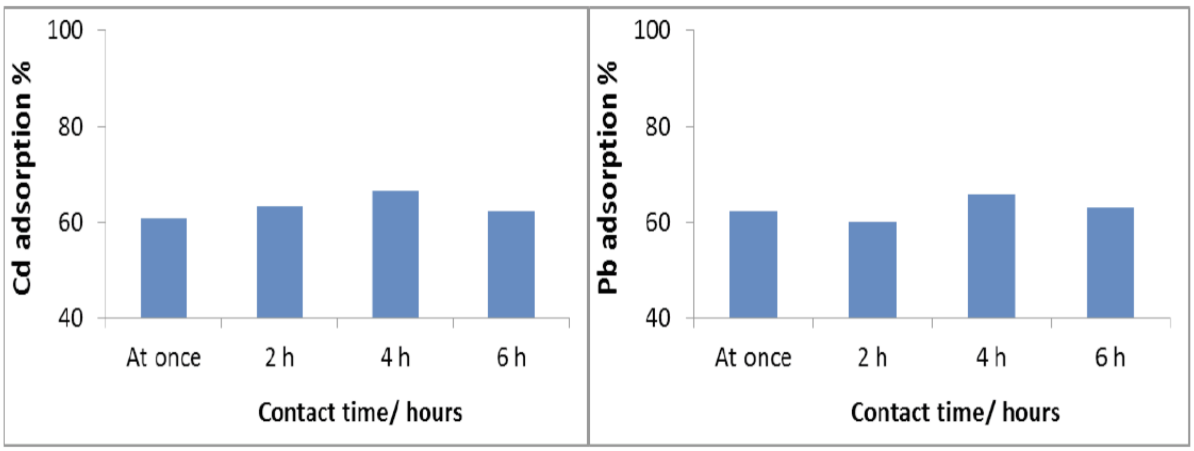
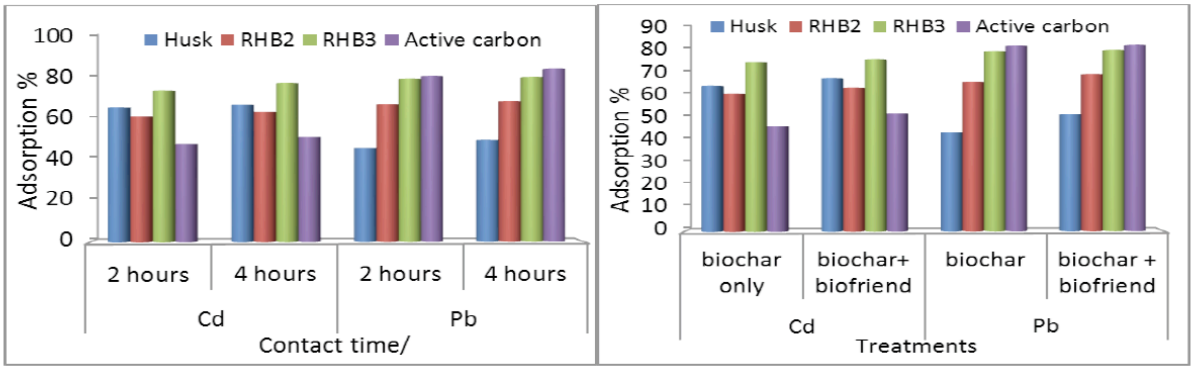


Figure 6: The mean cadmium adsorptive values using a definite concentration (2%) of biofriend only, at different contact times.

3.2. Experiment 2

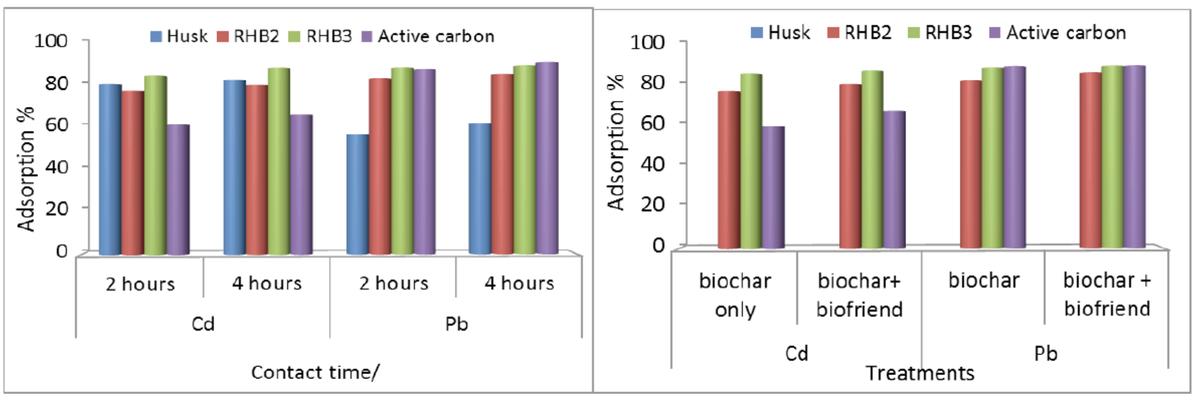
In the case of the solution A, results showed that the adsorption of cadmium and lead from this mixed solution is different than that of their single solutions. The obtained data illustrated that adsorption increase by increasing contact time from 2 to 4 hours in most cases. As in single solutions of cadmium and lead, adding biofriend increases adsorption and gave high degree of purification than that recorded by different types of adsorbents in their single treatments. Data showed that different adsorbents were arranged according to their ability for cadmium adsorption as follow: RHB3 > husk > RHB2 >active carbon, while in the case of lead the arrangement was: active carbon > RHB3 > RHB2 > husk. RHB3 recorded the highest purification value (73.68%) for cadmium, while active carbon recorded the lowest value (48.16%). Active carbon showed the highest ability for adsorption of lead exceeds its ability for cadmium and reached about 80.64% then RHB3 recorded 78.17%. Rice husk recorded the lowest adsorption ability for lead (46.62%) than that of cadmium (64.43%). Data were diagrammatically presented in Figures **7a** and **7b** that the increase of purification values in two different contact times were by 1.41, 2.16, 3.4 and 3.6 in the case of cadmium and 4.09, 1.45, 0.84 and 3.33 in the case of lead with husk, RHB2, RHB3 and commercial active carbon respectively. The increases percentages in purification of cadmium by adding biofriend to different types of adsorbents were by: 3.15, 2.86, 1.28 and 5.65%, while in the case of lead were by: 7.7, 3.24, 0.83 and 0.39% with rice husk, RHB2, RHB3 and active carbon, respectively.

Cadmium and lead adsorbed from solution B were in the same trend as the previous case (solution A) but the adsorption values of cadmium and lead adsorption from this mixed solution were increased with all used treatments compared to that occurred from solution (A). RHB3 recorded the highest purification value (83.66) for cadmium, while active carbon recorded the lowest one. Active carbon showed high ability for adsorption of lead exceeds its ability for cadmium and reached about



(a) (b)

Figure 7: The mean cadmium and lead adsorption in A using husk, RHB2, RHB3 and commercial active carbon, at two contact time, (**a**) and the presence or absence of biofriend (**b**).



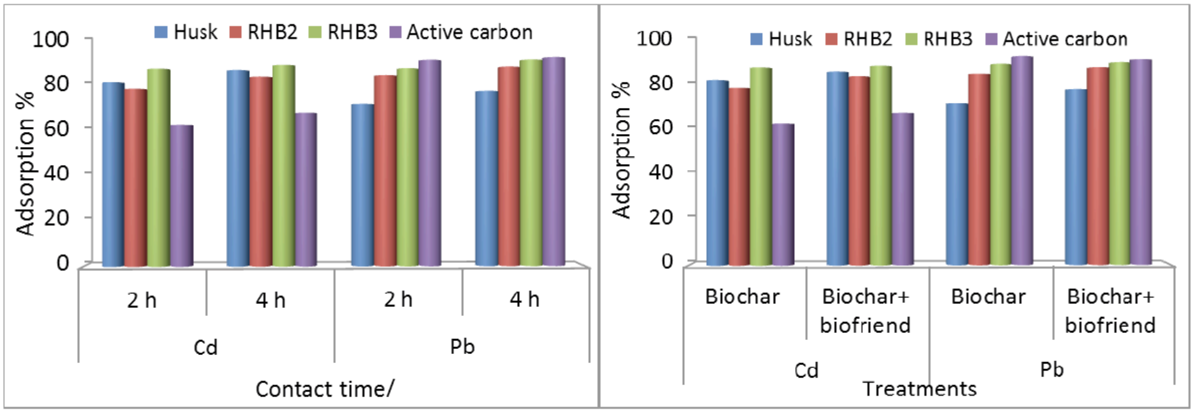
(a) (b)

Figure 8: The mean cadmium and lead adsorption in solution B using husk, RHB2, RHB3 and commercial active carbon, at two contact time (**a**) and the presence or absence of biofriend (**b**).

86.61%, and then RHB3 which recorded 86.25%. Husk recorded the lowest adsorption ability for lead (57.75%) than that of cadmium (78.92%). The increase in mean purification values between adsorbents in the two different contact times in case of cadmium (1.72, 2.7, 3.86 and 4.62) and in the case of lead (5.06, 1.78, 0.93 and 3.58) with rice husk, RHB2, RHB3 and commercial active carbon, respectively. The values for purification of cadmium by adding biofriend to different types of adsorbents were 3.84, 3.59, 1.46 and 7.23%, while in the case of lead were 9.54, 3.99, 0.93 and 0.43% with husk, RHB2, RHB3 and active carbon, respectively (Figure **8a** and **8b**).

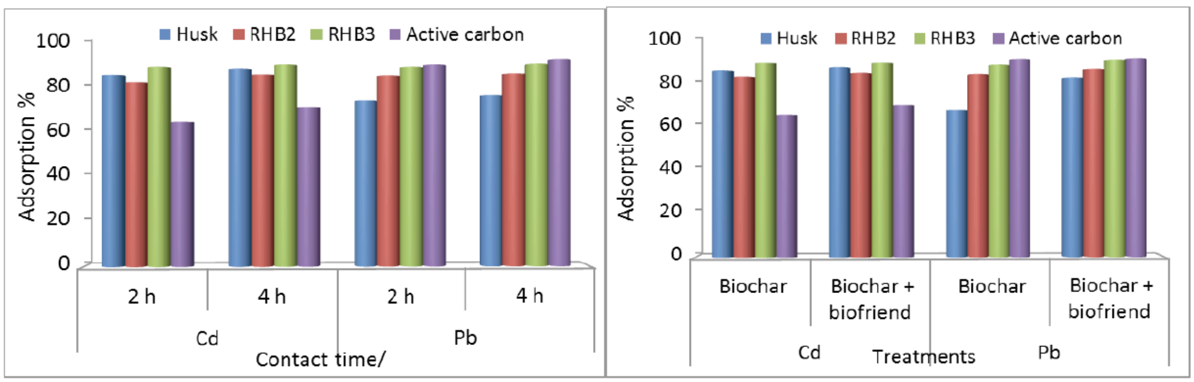
Cadmium and lead adsorbation in solution C increased with all used adsorbents than the previous cases. Different adsorbents were arranged according to their ability for cadmium adsorption as follow: RHB3 > husk > RHB2 > active carbon, while in the case of lead the arrangement were: active carbon > RHB3 > RHB2 > husk. The highest purification value of cadmium was recorded with RHB3 (85.65%) followed by husk (81.70%) but lead recorded different degree of purification, active carbon and RHB3 which showed the highest values (89.81and 87.27%, respectively). Increasing in purification between adsorbents at the two different contact times were by 5.65, 5.68, 1.84 and 6.12 in the case of cadmium and 7.1, 4.06, 4.59 and 1.35% in the case of lead with husk, RHB2, RHB3 and commercial active carbon, respectively. The increases in purification of cadmium by adding biofriend to different types of adsorbents were by: 4.26, 5.47, 0.84 and 5.18% while in the case of lead were by: 6.7, 3.32 and 0.82 with husk, RHB2, RHB3, respectively. From the results it is clear that the adsorption value of lead by active carbon + biofriend is lower (89.20%) than that obtained by using active carbon only (90.43%) as observed in Figure **9a** and **9b**.

In Figure **10**, when solution D was used, decreasing cadmium concentration from 50 to 25 ppm the adsorption increases with all used adsorbents.



(a) (b)

Figure 9: The mean cadmium and lead adsorption in solution C, using husk, RHB2, RHB3 and commercial active carbon, at two contact time (**a**) and the presence or absence of biofriend (**b**).



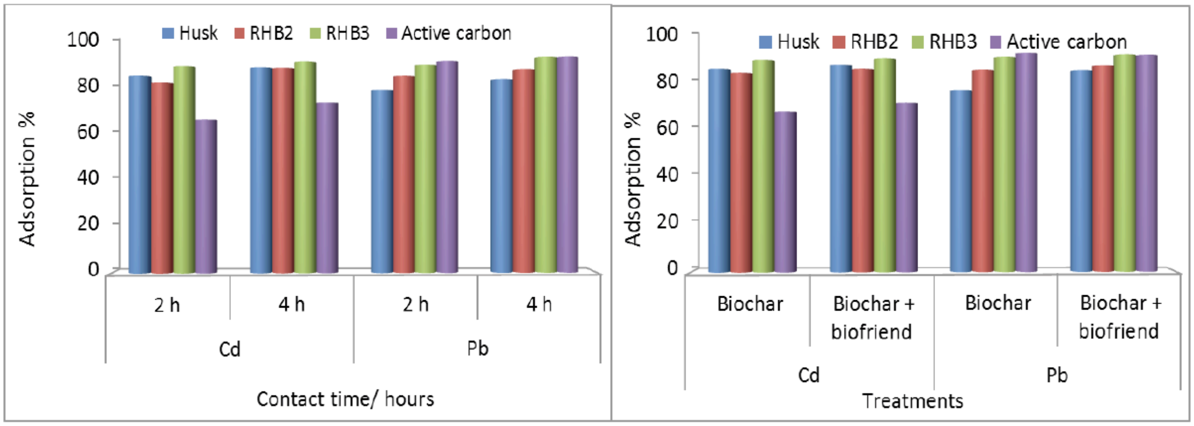
(a) (b)

Figure 10: The mean cadmium and lead adsorption in solution D using husk, RHB2, RHB3 and commercial active carbon, at two contact time (**a**) and the presence or absence of biofriend (**b**).

Adsorption increases with all used adsorbents with cadmium but RHB3 still in the front of the arrangement scoring where it recorded the highest value (86.97). The purification values of lead increase than that occurred with cadmium by all adsorbents except with rice husk where it decreased. In this aoluation, lead was strongly adsorbed on both of active carbon (88.83%) followed by RHB3 (87.30%), RHB2 (83.30%) then rice husk which recorded the lowest purification value (73.15%). The adsorption rate of lead on rice husk is lower than that of cadmium in the same solution. By increasing contact time the adsorption increased in all cases but with different degrees. The adsorption increased by increasing contact time at four hours under all treatments. In the present case the adsorption increased also by addition of befriend.

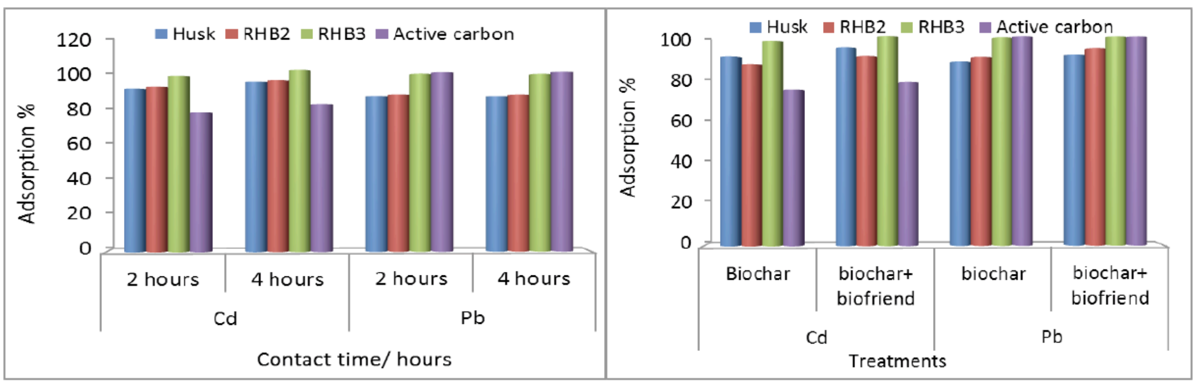
In solution (E), in case of cadmium, RHB3 recorded the highest purification value by about 87.57%, followed by rice husk by about 84.37%, RHB2 by about 82.77%, then finally by active carbon which showed the lowest value (67.89%). Lead exhibited different degree of purification under all adsorbents. Active carbon and RHB3 recorded 89.92 and 89.08% of purification respectively, while rice husk recorded the lowest value by 78.97%. The increase in adsorption values by increasing contact time were by 3.59, 6.7, 2.46 and 8% in the case of cadmium, and were by 4.89, 2.91, 3.61 and 1.98% in the case of lead, with rice husk, RHB2, RHB3 and commercial active carbon, respectively, see Figure **11a** and **11b**.

In the case of natural wastewater (F), cadmium and lead concentrations were measured. The results recorded that wastewater was differed than that of synthetically polluted solution. In the case of cadmium the highest purification value was reached about 99.71% with RHB3. On the other hand, lead purification percentage recorded the highest value with active carbon and reached about 100% followed by RHB3



(**a**) (**b**)

Figure 11: The mean cadmium and lead adsorption in solution E, using husk, RHB2, RHB3 and commercial active carbon, at two contact times (**a**) and the presence or absence of biofriend (**b**).



(**a**) (**b**)

Figure 12: The mean cadmium and lead adsorption in wastewater as affected by using rice husk, RHB2, RHB3 and commercial active carbon, at two contact time (**a**) and the presence or absence of biofriend (**b**).

(99.8%). The results of this treatment were diagrammatically shown in Figure (**12**). The increase in purification values by increasing contact time were recorded 3.52, 3.1, 3.9 and 4.42% in the case of cadmium and 6.92, 4.73, 1.89 and 1.99% in the case of lead, with husk, RHB2, RHB3 and commercial active carbon, respectively. The addition of biofriend increased the adsorption of lead and cadmium from their natural source (wastewater).

4. DISCUSSION

In the first experiment all types of used adsorbents have ability for adsorption of cadmium and lead but with different degrees. Daifullah *et al.* (2003) [42] in their study on utilization of agro-residues (rice husk) in small wastewater treatment plans, they had characterized and evaluated two types of sorbents made from rice husk and found that there are significant different in adsorption. The efficiency of both sorbents in the removal of the complex matrix containing six heavy metals was nearly 100%. These metals were Fe, Mn, Zn, Cu, Cd, and Pb, which were found in the drain containing the agricultural and sewage wastewater.

In the present study it is obviously clear that, pyrolysis of raw rice husk increases adsorption of heavy metals from their single synthetic solution in most cases, although raw rice husk scored relatively high ability of cadmium and lead purification. This can be explained as reported by Taha *et al.*, (2011) [43] who stated that the pyrolysis of rice husk increased its surface area and improving its adsorption properties. Due its high cellulose and lignin contents, rice husk can be utilized as the raw material to prepare activated carbon having highly porous structure in micropores range with high specific surface area.

In the present study, rice husk biochar formed from pyrolysis of raw rice husk at 500ºC (RHB3) scored the highest purification values for cadmium and lead, in all used treatments. In the case of cadmium raw rice husk scored higher adsorption values than that obtained by RHB1 and RHB2. Superiority of RHB3 may be due to well formation of pores on the surface of this adsorbent by increasing temperature of pyrolysis as listed by many researchers. At high temperature the most of organic materials were burnet leaving its place for forming porous structure material (biochar) and this increase also surface area. These findings were agreed with that of Vieira *et al.* (2012) [14], and agreed with Tarley and Arruda (2004) [10] which observed the decomposition of hemicellulose and cellulose between 250 and 360°C and the decomposition of lignin between 360 and 525ºC. The pyrolysis temperature was defined as 500°C, since the entire rice husk had been burnt.

The results of laboratory experiments in the first experiment showed that the adsorption differs with different types of adsorbents, where the adsorption increase with increasing carbonization temperature, but RHB1 (raw rice husk carbonized at 300ºC) resulted the lowest values among all used adsorbents These results were in agreement with that of Nakbanpote *et al*. (2007) [44] whom found the following values of maximum copper adsorption capacity: 0.112mmol of Cu/g of rice husk 0.102mmol of Cu/g of biochar at 300ºC and 0.253mmol of Cu/g of biochar at 500ºC. Also this was agreed with Rahman *et al.* (2004) [45] who reported that the ability to remove metal ion from single metal aqueous solution was found to be improved with the increasing of carbonization temperature. Sample carbonized at 600ºC showed better evolution and development of pores as compared to that carbonized at 400ºC. Also, Arivoli *et al.* (2009) [46] stated that the chemical nature and pore structure usually determines the sorption activity.

Data, in the present study showed that the adsorption of cadmium and lead from the solution increased with increasing contact time and reached its maximum value after 4 hours. This may be due to the fact that, when the contact time increases, the solution spends a longer time with adsorbent material. So the adsorbent materials can uptake a greater amount of heavy metal ions from the synthesized aqueous solution or natural wastewater, therefore, the percentage of removal of heavy metal ions from the aqueous solution increases. Similar results were obtained by Qinggi *et al.* (2004) [47] who reported in the study of adsorption of lead and mercury by rice husk ash. As the contact time increased, the pores were filled. This behavior reflects the fact that the adsorption is a surface phenomenon and that the surfaces are readily accessible to the metal ions in the solution.

Data showed also that, the cadmium and lead adsorption increase with increasing adsorbent dose. Rice husk and all types of biochars showed the highest adsorption values of cadmium and lead by using the highest concentration adsorbent. The adsorption increases with increasing adsorbent dose and reached its maximum value when the third concentration of 3% was used. This may due to the greater availability of the exchangeable sites or surface area at higher dose of the adsorbent. Rio *et al.* (2002) [48] found similar results from their study. Also, Abdel-Ghani *et al.* (2008) [41] studied the effect of adsorbent loading weight on the removal of cations from synthetic wastewater by adsorption by *Eucalyptus camaldulenis*. The percent removal of metal ions increases with increasing weight of *Eucalyptus camaldulenis*. These results were in agreement with previous studies on many other adsorbents as those carried out by Ajmal *et al.* (1998) [49] and Dakiky *et al.* (2002) [50]. The presence of the biofriend (bacterial compound) in mixed treatments with all types of used adsorbents for cadmium and lead adsorption increase their adsorption from solutions in the most cases, but the results of adsorption of cadmium and lead using biofriend only were less than if its mixed with different adsorbents in most treatments. Also Leusch *et al.* (1995) [51] noticed that the presence and activity of microorganisms in biological wastewater treatment are vital to the process with regard to microbial adsorption of heavy metals and biosorption phenomenon is crucial. Roy *et al.* (1993) [52] studied adsorption of heavy metals by green algae and ground rice hulls and they concluded that, metal adsorption by algal and rice hull biomass, from the aqueous test systems, was greater than 90% for all the metals tested (Sr, Cd, Ni, Pb, Zn, Co, Cr, As) except Ni, for which removal was nearly 80%.

It is clear that, in mixed solutions of cadmium and lead the adsorption decreased than that in their single solutions. RHB1 wasn't used in this experiment because of its weak adsorption efficiency for cadmium and lead recorded in the first experiment, in addition commercial active carbon was used. The commercial active carbon used in this experiment was recorded the highest adsorption for lead among all used adsorbents but, it was the lowest one for cadmium. These findings were agreed with Dvorak and Skipton (2013) [53] whom recorded that, activated carbon filtration can effectively reduce certain organic compounds, chlorine and lead but active carbon filters can effectively adsorb other heavy metals.

The metal uptake from solution by adsorbents was strongly affected by the presence of other competing metal ions. The removal percentage decreased by increasing initial concentration of each metal in treatment, this may be due to low available active sits for adsorption on rice husk and rice husk biochar, which would have become saturated at a certain concentration. These findings were in agreed with Huda and Kafia (2013) [39] whom tested the influence of removal of Cu, Ni and Zn and studied ion from a mixture of Cu, Ni and Zn, where the removal percentage of the studied metals was in the following sequence: Zn > Cu > Ni. Removal of Cu and Zn from a mixed solution was found to be lower as compared with their removal from single solution. Higher decrease was found in the efficiency of Ni removal from a mixed solution. Also, similar findings were reported by Abdel-Ghani *et al.* (2008) [41] in the study of the effect of initial metal concentration on the adsorption efficiency of *Eucalyptus camaldulenis*, where the adsorption experiments were carried out at different initial Cu, Zn, Cd and Pb concentrations ranging from 5 to 50mg/l in mixed metal ions solution.

In the case of natural wastewater different results were obtained and the adsorption decreased than expected although low concentration of cadmium and lead in wastewater in this experiment. This may be due to different characteristics of natural wastewater and presence of other organic and non-organic elements that affect adsorption process. A higher concentration level of interfering ions may, however, adversely affect the adsorption capacity of activated carbon, similar findings were obtained by Sreedhar and Anirudhan (1999) [54].

It can be concluded that rice husk biochar carbonized at 500^{o}C (RHB3) can be highly recommended for removal of cadmium and lead from wastewater, followed by rice husk biochar carbonized at 400^{o}C (RHB2) and raw rice husk (RH) mixed with be friend.

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