

REVIEW ON THE USE OF RICE HUSK IN THE ADSORPTION OF HEAVY METALS FROM WASTEWATER

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ABSTRACT

Rice husk has been used in the removal of heavy metals from wastewater in its modified or unmodified form. This paper reviews the work done by various researchers. Modified or treated rice husk was seen to have an affinity to heavy metals due to the presence of functional groups on its surface such as carboxylic and hydroxyl groups. Its affinity towards the following heavy metals was studied; Cd (II), Pb (II), Zn (II), Hg (II), Cu (II) and Fe (II). The removal of these metals was studied at varying pH, contact time, agitation rate, temperature, adsorbent dose and initial concentration of sorbate. Most of the heavy metals were seen to have a high sorption capacity with increase in sorbate dosage and at a pH of about 6-6.5. Also the types of techniques used were considered and a higher column depth was seen to have a higher sorption capacity.

Keywords: *Rice husk, Heavy metals, Sorption capacity.*

INTRODUCTION

Heavy metals are present abundantly in nature and they can be added to the environment due to human activities such as construction, agriculture, manufacturing and transportation and due to industrial activities such as from refineries, metal plating, mining, metallurgical, textile, tanneries, chemicals and pharmaceutical industries, heavy metals are found in wastewaters produced from this industries(El-Shafey, 2007). Heavy metals present in this these types of wastewater may include lead, copper, cadmium, chromium, mercury, iron, zinc, selenium and arsenic (Feng et al., 2004). The presence of some of these heavy metals even in little amounts can be poisonous to humans, animals and plants. They may cause toxicity at different levels such as acute, chronic, synergistic and mutagenic toxicity due to their level and conditions of intake ingestion.

Lead poisoning may cause irreversible neurological damage, cardiovascular effects, renal diseases, and reproductive toxicity to humans (Naiya et al., 2009). Long-term exposure to copper can cause headaches, dizziness, vomiting, diarrhea, and gastroenteritis symptoms with nausea and high uptake of this copper may lead to liver and kidney damage, ultimately leading to death (Luo et al., 2011). Cadmium builds up slowly in the body mostly through food chain. It causes damage to kidney and bones and it is considered to be carcinogenic (Ye et al., 2010). Processes such as membrane filtration, ion exchange, chemical precipitation and adsorption are used for the removal of heavy metals from wastewater but these processes are expensive (El-Shafey, 2007). Adsorbents such as zeolites, ion exchange resins and nanosorbents have been used in the removal of heavy metals from wastewater. Egashira et al. (2012) used natural zeolite in the removal of copper, zinc and manganese from aqueous solutions. Low cost adsorbents such as sawdust, almond, wool, pine cones and coconut shells have been used also in the removal of heavy metals from aqueous solutions (Politi and Sidiras, 2012). Bozic et al. (2013) used sawdust in the removal of copper, zinc and nickel.

Rice husk, which is a low cost alternative, has been used to remove heavy metals from wastewater in the form of activated carbon or by chemically impregnating the rice husk with chemicals, which changes its chemical properties. The presence of surface functional groups such as the carboxylic and hydroxyl groups helps in the sorption of these heavy metals through chemical processes such as the hydrogen bonding, ion exchange, electrostatic interaction and covalent bonding (Liu and Lee, 2014). The rice husk can be reused after it has reached its equilibrium by removing the heavy metals sorbed on it using heat or acidic solutions (Katsumata et al., 2003). The research on the use of rice husk is mainly because of the cost involved, though the activation or processing of the rice husk to be able to use as an adsorbent requires some added costs but rice husk is a by-product so the cost of obtaining the rice husk is low so it is readily available (Hegazi, 2013). The objective of this review is to check the efficiency of using rice husk as an adsorbent in removing heavy metals.

RICE HUSK

Rice husk is a by-product or waste material obtained from rice mills. Rice is the third highest agriculture product that is produced in the world and it has a production of about 500 million metric tons annually (Hegazi, 2013). The chemical composition and physical properties of rice husk is shown in Table 1. Rice husk in its modified or unmodified form has been used to remove heavy metals from water but the modified rice husk from the researches carried out showed higher sorption capacity for the heavy metals. For example Hegazi (2013) carried out a research using unmodified rice husk for the removal of Cd, a sorption capacity of 67.197 mg/g was achieved which is lower in comparison with the work of Ye et al. (2010) using modified rice husk and achieved a sorption capacity of 125.94 mg/g. Chemicals such as sodium hydroxide, hydrochloric acid, potassium hydroxide, sodium carbonate, hydrogen phosphate,

epichlorohydrin and tartaric acid are used in the treatment of rice husk. These pretreatments can remove lignin, hemicellulose, reduce cellulose crystallinity and increase the surface area or porosity of the rice husk (Wan Ngah and Hanafiah, 2008). Rice husk activated using physical process shows a higher sorption capacity than with chemical treatment. This is in accordance with the work of Masoud et al. (2012), potassium hydroxide was used for the chemical treatment of the rich husk for the removal of Fe (III) and Mn (II), and the sorption capacity attained was less than that for the physical activated rice husk. This may be as a result of higher percentage of ash content since silica is the main constituent of the ash content. The physical activation involves two steps, the first is the carbonization followed by the activation. The carbonization involves the heating of the rice husk in the absence of oxygen to increase its carbon content at a temperature ranging from 600°C to 900°C. The second step, which is the activation involves exposing the rice husk to steam this brings about the formation of pores and fissures on the rice husk. It is then exposed to a temperature between 600°C to 1200°C in the presence of oxygen so that all the non-carbon impurities are burned off. At this point, the rice husk becomes a highly porous material (Masoud et al., 2012). Rice husk ash, which is another form of rice husk is obtained by heating the rice husk at a high temperature of about 700°C, the ash obtained is the rice husk ash and it can also be used in the sorption of heavy metals from aqueous solution (Feng et al., 2004). For example, Naiya et al. (2009) used rice husk ash on the sorption of lead (II) ions, also Srivastava et al. (2008) used rice husk ash in the sorption of cadmium (II) and zinc (II) ions from aqueous solution.

Table 1. Physical structure and chemical composition of Rice husk (6)

Physical structure	Chemical composition	%
Insoluble in water	Cellulose	32.35
Granular structure	Hemicellulose	21.62
Good chemical stability	Lignin	21.55
High mechanical strength	Mineral ash	15.14
	Water	8.06
	Others	1.28
	Chemical composition of mineral ash	
	SiO ₂	96.34
	K ₂ O	2.31
	MgO	0.45
	Fe ₂ O ₃	0.2
	Al ₂ O ₃	0.41
	CaO	0.41

Source: Ye et al., (2010)

EFFECTS OF pH

pH is one of the fundamental physico-chemical property affecting the sorption capacity of adsorbents. The sorption capacity of most heavy metals with rice husk tends to increase with increase in pH to about a pH range of 6-7. Above that, at alkaline situations the metals precipitate to their metallic hydroxide. This is in line with the work of Kumar and Bandyopadhyay (2006), the sorption capacity of epichlorohydrin treated rice husk, sodium hydroxide treated rice husk and sodium bicarbonate treated rice husk on cadmium increased with increasing pH. This findings was further supported by Wong et al (2003). Cu and Pb sorption increased with increasing pH. This can be explained by the high concentration of hydrogen ions during low pH, the hydrogen ions compete with the metal ions to bind to the active sites of the sorbent thus preventing them from binding to the sorbent (Kumar and Bandyopadhyay, 2006).

Effects of pH on sorption were also observed by using rice husk ash as sorbent. Naiya et al. (2009) observed that lead (II) ions had the highest sorption capacity at a pH of about 5. This was in line with Feng et al. (2004) work also on the sorption of lead (II) ions on rice husk ash and at about a pH of 5, maximum sorption capacity was also observed. They attributed this to the competition between the hydrogen ions and the positive ions of the heavy metals at low pH, which brings about the low sorption of the metal ions on the rice husk ash but at a pH of about 5, the concentration of the hydrogen ions is reduced since the pH is approaching an alkaline condition therefore the positively charged metal ions are then sorbed in the surface of the rice husk ash (Feng et al., 2004).

EFFECTS OF SORBENT CONCENTRATION

The rice husk concentration is also a determining factor for sorption capacity. Hegazi (2013) reported that the removal of iron and lead increased with increase in sorbent concentration. This is in line with the work done on Fe (III) and Mn (II) removal (Masoud et al, 2012). Naiya et al (2009) also reported that the sorption of Pb (II) also increased with increase in sorbent concentration but reached equilibrium at 5 g/l and they attributed this to the larger surface area with increase in adsorbent dosage making the active sites to increase thus more sorption occurs. Srivastava et al. (2006) reported that increase in the dosage of rice husk ash increased the amount of cadmium (II), nickel (II) and Zinc (II) ions sorbed on the rice husk ash. Ghorbani et al. (2011) observed the same situation for the sorption of mercury (II) ions but after equilibrium has been reached, further increase in sorbent dosage does not give any increase in the sorption of the metal ion. This can also be explained by the fact that as the size of the sorbent increases, the surface area of the sorbent increases and at a low concentration of the sorbent all the active sites of the sorbents becomes filled leading to the sorbent becoming saturated (Srivastava et al.,

2006). Further increase in the sorbent dosage after reaching equilibrium brings about no relevant change due to the concentration of the sorbate being constant (Ghorbani et al., 2011)

EFFECTS OF INITIAL CONCENTRATION AND CONTACT TIME

Naiya et al. (2009) found that sorption capacity of Pb (II) increased with increment in initial Pb (II) concentration, the contact time was found to be one hour. The initial concentration had little or no effect on the contact time. Hegazi (2013) and Masoud (2012) made no report on the effect of initial concentration but the concentration of heavy metals ions decreased with increase in contact time. But a similar situation of increment in sorption capacity with increase in initial metal concentration was observed for Cd (II) ions (Ye et al., 2010). However, a different report was made by Wong et al. (2003), they reported an increase with a decrease in initial metal concentration and they related this by saying there is less collision in the solution when the metal concentration is lower leading to the sorption of the metal ions on the active sites of the sorbent.

The effect of initial concentration of sorbate during sorption of metal ions on rice husk ash was analyzed by Srivastava et al. (2008) and they found out that increase in initial concentration of the metal ions cause increase in the sorption capacity on the rice husk ash and during the observation for the contact time it was observed that at the first 15 minutes, the rate of uptake of the metal ions on the rice husk ash was higher compared to the remaining time the sorbent was in contact with the solution until equilibrium. This correlates with reported work of Ghorbani et al. (2011), on the removal of mercury from aqueous solution. They also observed that increase in concentration of the mercury ions brought about higher uptake of the ions on the surface of the rice husk ash and rate of uptake increased in the first 20 minutes and then the sorbates were sorbed on the sorbent slowly after that until it reached equilibrium. The effect of initial concentration of sorbate is related to the fact that when the concentration is much the active sites of the sorbent adsorb more sorbates and it does this at a higher uptake rate due to the availability of the active sites on the sorbent (Srivastava et al., 2006).

EFFECTS OF TREATMENT

Acids and bases can be used in the treatment of rice husk before the sorption process is started. This treatment has been seen to increase the sorption capacity of the rice husk. Some researchers have shown that base treatment brings about a higher sorption capacity compared to acid treatment. This situation corresponds with the work done by Asadi et al. (2008), the rice husk was treated with NaOH and HCl acid separately and the NaOH had a higher sorption capacity compared to the HCl treated rice husk. They explained by saying since the rice husk has a carboxylic surface, when treated with NaOH, the base increases the hydroxyl compound

on the surface of the rice husk thereby making it negative which makes it easier for the positively charged heavy metal ions to be sorbed on the surface of the rice husk by electrostatic attraction. The hydrogen in the HCl increases the positivity of the carboxyl by lowering the pH of the solution and at a low pH the hydrogen ions compete with the positively charged metal ions causing less sorption of the metal ions on the surface of the rice husk. This was further supported by the research of Kumar and Bandyopadhyay (2006), NaOH and epichlorohydrin were used to treat rice husk in the sorption of cadmium (II) ions and NaOH exhibited a higher sorption capacity compared to epichlorohydrin although they both exhibited a higher sorption capacity compared to the raw rice husk.

EFFECTS OF AGITATION RATE

According to Srivastava et al. (2006), the sorption process, which is the adsorption of the sorbates on the sorbents, requires four processes. The first step known as the external mass transfer, involves the movement of the solutes to the surface of the boundary layer of the sorbent material, the second is the movements of the solutes pass the boundary layer and this is termed as film diffusion, the third step is the pore diffusion and it is the penetration of the solutes into the porous structure of the sorbent and the last step is the sorption of the sorbates on the active sites of the sorbent and this could be as a result of the electrostatic interactions between the active site and the sorbate. The agitation rate affects the sorption of this sorbates on the surface of the sorbents since the solutes or sorbates have to pass through the boundary layer of the sorbent. The agitation rate helps in breaking of this boundary layer and thus increases the sorption rate of the sorbates on the sorbent (Wong et al., 2003). This effect was demonstrated in Hegazi's (2013) work, he reported that at a higher agitation rate, more of the heavy metal ions were sorbed on the rice husk. Wong et al. (2003) also reported that the sorption of lead and copper increased with increase in agitation rate.

Ghorbani et al. (2011) reported that as the agitation rate was increased for the sorption of mercury (II) on rice husk ash, the sorption of the metal ions increased up to a certain limit at which further increase in agitation rate caused the metal ions to be desorbed from the surface of the sorbents. This may be as a result of the over agitation of the solution.

EFFECTS OF TEMPERATURE

Temperature is one of the fundamental parameters being checked in the adsorption process. Naiya et al. (2009) observed the effect of temperature on the sorption process and according to his report, the percentage removal of rice husk ash for lead (II) increased with increase in temperature from 30°C to 50°C with percentage removal values of 98.82, 99.42, 99.76 for 30°C, 40°C, and 50°C respectively. Also, Feng et al. (2004) observed the sorption capacity for both the Langmuir and Freundlich isotherms and they were both seen to increase with increase in

temperature. This phenomenon may be as a result of the increase in the bond strength between the active site and the sorbate molecule.

BATCH AND FIXED BED COLUMN STUDIES

The laboratory procedure for this experiments usually takes place in the form of a batch technique and it involves the dissolution of a known concentration of the metal salt in a glass flask or conical flask then a known mass of the sorbent which is the rice husk in this case either in its raw form, modified form or activated carbon form is added to the solution and then the glass flask is put in a thermostatic stirrer or shaker at a given temperature for a given period of time. After which the solution is filtered through a filter paper or centrifuged at a certain rotation per minute so that the solids go down and the supernatant is extracted. The supernatant is analyzed using the atomic adsorption spectrometer (AAS), high pressure liquid chromatography(HPLC) or the inductively coupled plasma (ICP). These machines help in knowing the concentration of the heavy metal ions that are left in the solution so that the equilibrium concentration is known and this helps in determining the sorption capacity (Yu et al., 2000).

The fixed bed column technique involves the sorbent being packed in column with specified diameter and length and this column has to be large enough to avoid sidewall effect. The sorbent is packed into the column from the top of the column and the sorbate solution is introduced from the bottom of the column. The solution moves upward through the sorbent material and moves outward through the top of the column. As the solutions move out, the concentration of the heavy metal ions reduces since the sorbent has an affinity for the sorbate so they accumulate on the sorbent. The solution that moves out of the column is analyzed so that the concentration of the heavy metals left in the solution is known (Saeed et al., 2009). According to Luo et al. (2011), increase in the bed height of the column from three centimeters to nine centimeters brought about an increase in the concentration of the heavy metals that were adsorbed in the column, also Mohan and Sreelakshmi (2008) reported that increase in the height of the column from 10 to 30 cm caused an increase in the amount of heavy metal adsorbed on the sorbent material in the column. This is also in line with Ghorbani and Eisazadeh's (2012) work on the removal of zinc, copper, iron and manganese using fixed bed column technique and they also found out that increase in column depth increased the amount of heavy metal ions sorbed on the sorbent in the column. This increase in the amount of heavy metal ions adsorbed on the surface of the sorbent can be attributed to the increase in the quantity of the sorbent at a higher column height thus providing a larger surface area for the heavy metal ions to be sorbed on. Also increase in the column depth gives the sorbate solution more time in the column thereby increase the contact time hence attaining a higher sorption capacity.

SORPTION ISOTHERMS

The types of sorption isotherms models include Linear, Langmuir, Freundlich and BET isotherms but the Langmuir and Freundlich isotherms are mostly used in relating the sorption capacity with the equilibrium sorbate concentration in order to know the sorption capacity at different sorbent dosages. Most of the isotherm data in the studies checked fit into the Langmuir and Freundlich isotherms.

The Langmuir isotherm is represented in its linear form as

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{1}{a}C_e$$

Where a or Q_m is the maximum (sorption capacity forming a single layer) sorbate sorbed per mass sorbent (mg/g), b or K is a coefficient describing the affinity of sorbate on sorbent materials (L/mg), q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium sorbate concentration (mg/L).

The Freundlich isotherm is represented in its linear form as

$$\text{Log } q_e = \text{log } k + \frac{1}{n} \text{log } C_e$$

Where k is an indicator of sorption capacity. The higher the maximum capacity, the higher the value of k . $1/n$ is a measure of intensity of sorption. The higher the $1/n$ value, the more favorable the sorption.

Most of the sorption data in the studies fit into both models of isotherm but was well suited for the Langmuir model compared to the Freundlich model. Kumar and Bandyopadhyay (2006) reported that the data for the sorption of cadmium was well fitted for the Langmuir isotherm and also El-Shafey (2010) reported the same for the sorption data of zinc and mercury. The same was observed for the sorption of Fe (III) and Mn (II) using physically activated rice husk but the situation was the reverse for Mn (II) using chemically treated activated rice husk (Masoud et al., 2012). The Langmuir isotherm operates under the assumption that each active site on the sorbent holds one sorbate molecule and all the active sites are energetically equivalent.

The Freundlich isotherm was observed to be the best fit for the sorption of lead (II) ions on the rice husk ash (Naiya et al., 2009). Also a Freundlich isotherm was observed for the sorption of cadmium (II) ions and Zinc (II) ions on rice husk ash (Srivastava et al., 2006). From this, it is seen that the sorption of heavy metals on rice husk ash is well fitted on the Freundlich isotherm

compared to the Langmuir isotherm and this can be linked to the fact that the Freundlich isotherm leads to a multilayer process of adsorption (Naiya et al., 2009).

CONCLUSION

From the review, it is seen that rice husk can be used in the removal of some heavy metals from wastewater. Changing the parameters such as pH, sorbent dose, temperature and initial concentration of sorbate give a different sorbate capacity. Modified rice husk shows more potential in the removal of heavy metals compared to raw rice husk and this is as a result of change in the surface functionality of the rice husk.

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