Rice Husk as Biosorbent: A Review

Noor Syuhadah S*, Rohasliney H

School of Health Sciences, Universiti Sains Malaysia, 16150 Kubang kerian, Kelantan, Malaysia

*Coresponding author email: syuhadah_subki@yahoo.com
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ABSTRACT: Over the last three decades, the concern about the environment protection has increased tremendously. Presently, several attempts were carried out for the conversion of by-products of natural materials, especially agricultural wastes into a biosorbent material. Rice husk is one of the low-value agricultural by-products which have been used as a sorbent material especially to absorb heavy metals. Previous studies have found that rice husk were capable to absorb heavy metals such as lead, cadmium, selenium, copper, zinc and mercury in the wastewater. Rice husk is also used to treat textile wastewater that contains reactive blue 2, reactive orange 16 and reactive yellow. This review highlights the capability of modified and unmodified rice husks as biosorbent. Factors that affect the biosorbent (i.e. pH, initial concentration, agitation rate, sorbent dosage and temperature) were discussed. Generally, chemically modified rice husks exhibit higher absorption capacities than unmodified rise husks.

Keywords: rice husks, heavy metals, wastewater, low-cost sorbent

Introduction

Rice husks are the hard protecting coverings of grains of rice. The husk is made of hard materials, including opaline silica and lignin in order to protect the seed during the growing season. The husk is mostly indigestible to humans. During the milling process, the husks are removed from the grain to create brown rice; the brown rice is then milled further to remove the bran layer to become white rice.

Rice husks are a class "A" insulating material because they are difficult to burn and less likely to allow moisture to propagate mould or fungi. When burned, rice husk produces significant amounts of silica element. The very high content in amorphous silica of the husks confer to them and to their ash (SiO_2 ~ 20 wt.%) after combustion are very valuable properties for excellent thermal insulation. Besides, rice husk contains abundant floristic fibre, protein and some functional groups such as carboxyl and amidogen (Nakbanpote Woranan *et al.*, 2007). Reported physicochemical characteristic of rice husk is shown in the **TABLE** 1.

The worldwide annual rice husk output is about 80 million tones and over 97% of the husk is generated in the developing countries. Malaysia is one of them. According to the statistics compiled by the Malaysian Ministry of Agriculture, 408,000 metric tonnes of rice husk are produced in Malaysia each year. Generally, farmers and rice processor often burn the rice husk as wastes, and this which releases carbon dioxide (CO_2) into the atmosphere. CO_2 is a well-known greenhouse gas. The increase volume of CO_2 gas in the atmosphere is believed to cause global warming commonly known as greenhouse effect. The CO_2 gas does not only elevate global temperature; it also gives negative impact to human health because its higher concentrations can affect respiratory function. Large volume of CO_2 displaces oxygen in the air, resulting in lower oxygen concentrations for breathing.

TABLE 1 Physicochemical characteristic of rice husk (Malik, 2003)

Characteristic	Unit	Value
Bulk density	g/ml	0.73
Solid density	g/ml	1.5
Moisture content	%	6.62
Ash content	%	45.97
Particle size	mesh	200-16
Surface area	m^2/g	272.5
Surface acidity	meq/gm	0.1
Surface basicity	meq/gm	0.45

Major rice producing countries shall conduct research on the usage of rice husks application for various industries. Research on fully utilize the agriculture waste means to avoid burning the rice husks as wastes are worthlike. Rice husk is a very cost-effective raw material to be used and it is very easy to obtain. A few current implementations on the usages of the rice husks are building material, pillow staffing and fertilizer. Foo and Hameed (2009) showed that utilizing of the rice husk will provide twofold advantage to the environmental management. First, the large volume of rice husk waste could be partly reduced, converted to useful, value added adsorbent. Second, the development of the low-cost adsorbent may overcome the wastewaters and air pollution at a reasonable cost.

Contamination of ground and surface water by different organic and inorganic pollutants are a major factor of environmental problems for the numbers of years. The pollutants are usually discharged by the industries into natural water streams and could have contaminated the ground water. The presence of toxic compounds in different industrial effluents often represents a risk to the environment. Different methods such as chemical oxidation, coagulation, chlorination, solvent attraction, liquid membrane permeation and adsorption, have previously been employed to remove pollutant in the wastewater. However, these treatment methods involve expensing materials and operating cost.

There has been a great deal of research into finding the cost-effective methods for the removal of contaminants from waste water. The abundance and availability of agricultural by-products such as rice husk make them good sources of cheap raw material for natural adsorbents. Many carbonaceous materials such as fly ash (Basava Rao and Ram Mohan Rao, 2006), hen feathers (Gupta *et al.*, 2006) and de-oiled soya (Mittal *et al.*, 2006) are used as an absorbance. Rice husk (contains about 20% silica) has been reported as a good adsorbent for many metals and basic dyes

(Kumar *et al.*, 1987; Chuah *et al.*, 2005; Wan Ngah and Hanafiah, 2008).

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants (industrial wastewater). Some researchers found that the modified rice husk exhibited higher adsorption capacities than unmodified rice husk (E.I. El-Shafey, 2007; Sahu *et al.*, 2009). The major components of rice husk which may be responsible for sorption are carbon and silica (Nakbanpote *et al.*, 2000). Note that silica is composed of $SiO_4.4H_2O$ in which each oxygen atom is shared between two adjacent tetrahedrons. The Si-O bond is about 50% ionic owing to the large difference in the electro negativity of oxygen and silicon (Kumar *et al.*, 1987). In this review, we are concern about the use of rice husks as an absorbance to remove dyes, heavy metals and some other chemicals that present in the industrial wastewaters.

Rice husk as a sorbent in wastewater

Rice husk as a sorbent in removing dyes, heavy metals and some other chemicals have been reported. Its application to absorb lead (Wong *et al.*, 2003a; Wong *et al.*, 2003b; Naiya *et al.*, 2009b), cadmium (El-Shafey, 2007; Naiya *et al.*, 2009a; Ye *et al.*, 2010), selenium (El-Shafey, 2007), copper (Wong *et al.*, 2003a; Wong *et al.*, 2003b), zink (El-Shafey, 2010), mercury (El-Shafey, 2010), reactive blue 2 (Low and Lee, 1997), reactive orange 16 (Low and Lee, 1997), reactive yellow 2 (Low and Lee, 1997), paraquat (Hsu and Pan, 2007; Hsu *et al.*, 2009) and 2,4-dichlorophenol (Akhtar *et al.*, 2006) have been reported. The capability or the rate of absorption of modified or unmodified rice husk is depend on few factors such as the effect of pH, initial concentration, agitation rate, sorbent dosage, temperature which could be further researched for more efficient applications.

Effect of pH

The change in pH affects the adsorption process because the pH of the solution affects the charge in the surface of the adsorbent where the hydronium ion, H^+ concentration may react with the functional groups on the active sites on the adsorption surface. Wong *et al.* (2003) reported that the uptake of Pb(II) and Cu(II) by tartaric acid modified rice husk increased when the pH increased from 2 to 3. The effect of pH on adsorption of Cd (II) and Se(IV) by rice husk was studied by El-Shafey *et al*. (2007) and they showed that in the pH range 1.5-2.0, Cd(II) sorption was extremely low, and with the rise in the initial pH, Cd (II) uptake increased. The sorption of Cd (II) almost showed no significant change between pH 4 and 7 (El-Shafey *et al*. 2007). Adsorption capacity elevated with increasing pH values as reported by Roy *et al*. (1993). The sorption of Se (IV) was high at pH 1.5, and the sorption decreased with the initial pH increase (El-Shafey, 2007). Study on pH effect on Zn (II) and Hg(II) was reported by El-Shafey *et al*. (2010) who found that the Zn (II) uptake, has no significant change appeared between pH 3.5 and 6, while maximum Hg (II) uptake took place at pH 5-6.

Verma and Mishra (2010) reported that the sorption capacity also increase with the increase of pH value when rice husk is used as dyes absorbrnt. The authors found that the removal of crystal violet at pH 2 is 80% and at pH 10 is 85%. For direct orange, the removal was increased from 62% to 85% at pH 2 and pH 10. The equilibrium reached in the acidic medium at pH 6 for both of the dyes. However, in the case of magenta, the removal was observed to be 45% to 73% in the same condition and equilibrium obtained at pH 8.

Akhtar *et al*. (2006) found that the percent sorption of 2,4-dichlorophenol (DPD) onto rice husk is higher at low pH. At low pH, there is a reasonably strong interaction between the sorbent and the polar resonance contributed phenol structure.

Temperature

Verma and Mishra (2010) investigated the effect of temperature on the removal of dyes (crystal violet, direct orange and magenta) at temperature varying from 20°C to 100 °C. It was observed that the removal of crystal violet, direct orange and magenta was increased from 80% to 87.5%, 69.2% to 85% and 50% to 80% respectively. The temperature can affect the rate of removal of dyes by altering the molecular interactions and solubility of dyes (Pandey *et al.*, 1989).

According to El-Shafey (2007 & 2010), elevated temperature has increased the sorption of heavy metals such as Zn(II), Hg(II), Cd(II) and Se(IV). This is probably due to some swelling of the carbon sorbent prepared from flax shive via sulphuric acid treatment (Tanzil H. Usmani *et al.*, 1993; Cox *et al.*, 1999; Cox *et al.*, 2000; El-Shafey *et al.*, 2002).

Effect of initial concentration

The study by Wong *et al.*, (2003) showed that the initial sorption rate increased with a decrease in the initial Pb(II) and Cu(II) concentration. Breakthrough of Cu(II) could occur faster than Pb(II) and the total metal removed was less for Cu(II) than for Pb(II). Verma and Mishra (2010) had also studied the effect of the initial concentration of dyes removal by the rice husk with a constant dose of adsorbent. They found that the adsorption of dyes was much dependent on concentration of solution and removal decreases with the increment in initial concentration of the dyes.

Effect of agitation rate and time

Wong *et al.* (2003) found that the uptake of Pb(II) and Cu(II) increased with the increase in agitation rate. Increasing agitation rate could reduce the film boundary layer surrounding the sorbent particles. Agitation also increases the external film mass transfer coefficient and hence the ion uptake rate.

Verma and Mishra (2010) had explored the effect of agitation time to the removal of dyes using the rice husk carbon. They found that in 15 min, the removal of crystal violet was 70% and increased to 82.5% in 60 minutes. The removal of direct orange and magenta were 47% and 54% in 15 min respectively and increased up to 77% and 84% in 45 min respectively. The increase of the removal of dyes with the increasing of agitation time is largely due to the formation of monolayers on the surface of adsorbent. This is and it is controlled by the rate of transport of the adsorbate species from the outer sites to the interior site of the adsorbent. Ola Abdelwahab *et al.* (2005) found that the amount of adsorbed dye increase with the increase in agitation time. He reported that the time required for direct F. Scarlet due to attain equilibrium was 120 min for untreated rice husk and 90 min for activated rice husk.

Effect of sorbent dosage

Sorption was generally found to be attained more rapidly at lower adsorbent dosage. Akhtar *et al.* (2006) reported that the percent sorption of 2, 4-dichlorophenol by the rice husk increases very rapidly up to 66% by increasing amount of the sorbent from 0.025 to 0.1g and thus stayed almost constant up to 1 g of sorbent dosage. A fixed ratio between sorbent dose and sorbate concentration, which represent maximum percentage of sorption is important (Perrin and Dempsey, 1974).

The removal of dyes increased with the adsorbent dose varied from 0.5g to 2.5g as observed by Verma and Mishra, (2010). In the case of crystal violet, direct orange and magenta, the removal of dyes were increased from 70% to 77.5%, 54% to 69% and 67% to 89% respectively (Verma and Mishra, 2010). For direct F. Scarlet dye, Ola Abdelwahab *et al.* (2005) reported that an incremental of 10% was observed for every 2.5g/l increase biomass of citric acid treated rice husk.

Conclusion

For the past few years, there is increasing interest in the preparation of low-cost adsorbent as an alternative to wastewater treatment process. Presently, rice husk has shown its potential to be a bioabsorbent material in solving wastewater pollution at a cost-effective way. The usage of the rice husk might help to overcome part of the excessive agricultural wastes in some part of the world. Our review shows that rice husks possess different characteristic following methods of treatment or. Physical and chemical modification improves the adsorption capacity of active binding sites. More comprehensive research should be done to find the most cost-effective method of rice husks treatment to improve its adsorption efficiency.

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