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Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents

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ABSTRACT The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. The objective of this study is to contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products such as sugarcane bagasse, rice husk, oil palm shell, coconut shell, coconut husk etc. for the elimination of heavy metals from wastewater.

ABSTRAK Penjerapan adalah teknik yang digunakan secara meluas oleh para penyelidik untuk perawatan air sisa yang dicemari oleh logam berat dan karbon teraktif banyak digunakan sebagai penjerap. Walaupun karbon ini banyak kegunaannya dalam perawatan air dan air sisa industri, ianya masih suatu bahan yang mahal. Baru-baru ini keperluan untuk kaedah yang selamat dan ekonomi untuk perawatan logam berat telah menumpukan minat penyelidik-penyelidik ke arah bahan yang lebih murah dan kedapatan karbon teraktif yang komersial. Satu keperluan untuk mengkaji sisa pertanian sebagai bahan ganti karbon teraktif komersial telah wujud dan penyelidikan yang terperinci akan tindakan mereka terhadap logam berat mesti dilakukan. Objektif kajian ini adalah untuk menyumbang kepada kajian dalam mencari penjerap yang murah dan kebolehgunaan bahan ini seperti hampas tebu, hampas padi, tempurung kelapa sawit, tempurung kelapa dil. untuk merawat logam berat dalam air sisa.

(adsorption, adsorbents, agricultural wastes, heavy metals, wastewater)

INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1]. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and

storage batteries industries, etc. [2]. Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and coprecipitation/adsorption. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent [3]. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research

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interest towards the production of low cost alternatives to commercially available activated 5 carbon.

The low cost agricultural waste by-products such as sugarcane bagasse [3, 4, 5, 6, 7 and 8], rice husk [9, 10, 11, 12 and 13], sawdust [14, 15 and 16], coconut husk [3, 17], oil palm shell [18], neem bark [19], etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course improved sorption capacity may compensate the cost of additional processing [20]. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. The objective of this study is to contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products, which are in many cases also pollution sources.

RELEVANT LITERATURE

Reviews of some agricultural adsorbents for the removal of heavy metals from wastewater are ' presented as follows.

Rice husk

Rice husk is an agricultural waste material generated in rice producing countries, especially in Asia. The annual world rice production is approximately 500 million metric tons, of which 10 – 20% is rice husk. Dry rice husk contains 70 -.85% of organic matter (lignin, cellulose, sugars, etc) and the remainder consists of silica, which is present in the cellular membrane [21]. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. [22] using tartaric acid modified rice husk as adsorbent have carried out batch studies for the removal of lead and copper and reported the effects of various parameters such as pH, initial concentration of adsorbate, particle size, temperature etc. It was reported that modified

rice husk is a potentially useful material for the removal of Cu and Pb from aqueous solutions. The rapid uptake and high adsorption capacity make it a very attractive alternative adsorption material. It was also shown that the uptake of Cu and Pb was maximum when pH was increased from 2 to 3, thereafter remained relatively constant. Adsorption behaviour of Ni (II), Zn (II), Cd (II), and Cr (VI) on untreated and phosphate treated rice husk (PRH) by [11] showed that adsorption of Ni (II) and Cd (II) was greater when PRH was used as adsorbent. Adsorption of Cd (II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution. It was also reported that the maximum adsorption (> 90%) was obtained at a pH value of 12. [9] studied on chromium removal by rice husk carbon. The activated carbon prepared by carbonization of rice husk with sulphuric acid followed by CO2 activation showed 88% removal of total chromium and greater than 99% removal of hexavalent chromium. Column studies showed capacity of 8.9 mg/g and 6.3 mg/g for rice husk and commercial carbons respectively, for Cr (VI) removal.

[12] studied on the use of dyestuff-treated rice husk for removal of heavy metal from waste water. Rice hulls, when coated with the reactive dye of Procion Red or Procion Yellow, was found to be highly effective for removal of many metal ions from aqueous solutions both in batch and column methods. The high removals for red dyestuff-treated husk are on lead (II) and cadmium (II) at 99.8% and 99.2% respectively, for yellow dyestuff-treated husk are on lead (II) and mercury (II) at 100% and 93.3% respectively. [10] studied the use of rice husk for removal of toxic metals from wastewater. They have reported, at optimal conditions, the chromium, zinc, copper and cadmium ion removals from aqueous solution and stated as 79%, 85%, 80% and 85% respectively. [23] studied on adsorption of heavy metals by green algae and ground rice hulls. 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%. [24] studied on adsorption of Cr(VI) on micro- and mesoporous rice husk-based activated carbon. They have concluded that the rice husk carbon is a good sorbent for the removal of Cr(VI) from aqueous solution range

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from 5 to 60 mg/l with adsorbent dose of 0.8 g/l at pH < 5 under the minimum equilibration time of 2 hours. There is a sharp decrease in adsorption above pH 5.0 and the adsorption in the higher pH range would be negligible. Maximum reported adsorption is > 95% removal of Cr(VI). A study on utilization of agro-residues (rice husk) in small waste water treatment plans was done by [25]. They have characterized and evaluated two types of sorbents made from rice husk. The efficiency of both sorbents in the removal of the complex matrix containing six heavy metal was

nearly 100%. These metals are Fe, Mn, Zn, Cu, Cd, and Pb, which are found in the drain containing the agricultural and sewage wastewater. [26] studied on raw rice on the removal of Cr(VI). The overall result indicated that the maximum removal (66%) of Cr(VI) for raw rice husk was obtained at pH 2, when it is given adsorbent dose of 70 g/l for 2 hours. It has also showed good fit to Freundlich isotherm with 1/n value of 2.863. (Table 1) summarizes the usage of types of rice husk as an adsorbent.

Table 1 . Types of rice husk as adsorbent for	heavy	metal
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Source	Adsorbent	Heavy metal removal efficiency (%)						
		Cr(VI)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Pb(II)
[9]	Rice husk carbon	> 99	-	-	-	-	-	-
[10]	Rice husk (water and HCl washed)	79	-	80	85	85	-	-
[11]	Phosphate-treated rice husk	-	-	-	-	> 90	-	-
[12]	Dyestuff-treated rice hulls (red) Dyestuff-treated rice hulls (yellow)	39.7 39.1	61.6 60.8	78.8 70.0	75.1 61.3	99.2 83.3	92.7 93.3	99.8 100.0
[22]	Tartaric acid modified rice husk	-		> 80	-	-	-	> 95
[23]	Rice hull biomass	98.93		- *	-	97.96	-	99.43
[25]	Rice husk carbon	-	. *	≈100	≈100	≈100	-	≈100
[26]	Raw rice husk	66	-	-		-	,	1

Sugarcane Bagasse

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Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch is composed largely of cellulose, pentosan, and lignin [4]. [27] studied on adsorption of Cd (II) and Pb(II) onto functionalized formic lignin from sugar cane bagasse. They have stated that the Pb (II) adsorption process obeys Langmuir's model and Cd (II) presents adsorption in multilayer, especially when the temperature is higher than 30°C. When ionic strength increases, the maximum adsorption capacity diminishes. The carboxymethylated lignin from sugar cane bagasse can adsorb Pb(II) selectively rather than Cd(II) under special conditions (pH 6.0, 30°C, and ionic strength of 0.1 mol/dm³), when both ions are present in the mixture. Factorial analysis of Pb(II) adsorption suggests that temperature is the most important factor in single system and adsorption increases with increasing temperature. [4] carried out research on single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse. They have reported that the removal of Cd(II) and

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Zn(II) is found to increase as pH increases beyond 2 and at pH > 8.0 the uptake is 100%. It is also evident that the sorption affinity of the derived activated carbon towards Cd(II) and Zn(II) is comparable or better than other available adsorbents. Therefore cost wise the activated carbon prepared would be cheaper than the commercially available ones. [5] reported that at an adsorbent dose of 0.8 g / 50 ml is sufficient to remove 80 - 100% Cr(VI) from aqueous solution having an initial metal concentration of 20mg/l at a pH value of 1 but the efficiency reduced sharply to 15% at pH 3. [3] studied the of hexavalent chromium from removal wastewater by adsorption. Removal of chromium (VI) from aqueous waste was investigated using adsorption based on bagasse and coconut jute. The effect of solution pH, Cr(VI) concentration, adsorbent dosage and contact time were studied in a batch experiment. The removal was in general most effective at low pH values and low Cr(VI) concentration. Activated coconut jute carbon was the most active among the four adsorbents studied. It was fairly stable even at higher pH. This was followed by activated bagasse carbon, raw bagasse and bagasse ash respectively. The maximum removal obtained was around 99.8 percent at pH 2. The data for all the adsorbents fit well to the Freundlich isotherm. The utilization types of sugar cane bagasse as adsorbent is summarized in (Table 2).

Sawdust

Studies on removal and recovery of Cr(VI) from electroplating waste were carried out by [14]. Phosphate treated sawdust (PSD) showed remarkable increase in sorption capacity of Cr (VI) as compared to untreated sawdust. Adsorption of Cr (VI) on PSD is highly pH dependent. The maximum adsorption of Cr (VI) is observed at pH 2. The adsorption of Cr (VI) remains at maximum (100%) even at a pH less than 2. The adsorption densities in general decrease as the adsorbent dose is increased from 0.2 to 3g. 100% removal of Cr (VI) from synthetic wastewater as well as from actual electroplating waste containing 50 mg/l Cr (VI) was achieved by batch as well as by column process. The adsorbed chromium can be recovered by using 0.01 M NaOH solution. [16] studied the removal of Cr(VI) from aqueous solution by adsorption onto activated carbon prepared from coconut tree sawdust for the removal of Cr (VI) from aqueous solution. Batch mode adsorption studies were carried out by

Cr(VI) initial time, agitation varving concentration, carbon concentration and pH. Langmuir and Freundlich adsorption isotherms were applied to model the adsorption data. Adsorption capacity was calculated from the Langmuir isotherm and was 3.46 mg/g at initial pH of 3.0 for particle size 125-250 µm. The adsorption of Cr(VI) was pH dependent and maximum removal was observed in the acidic pH range. Saw dust types and its efficiency summarized in (Table 3).

Soybean hulls, cottonseed hulls, rice bran and straw

[28] did a study on metal adsorption by soybean hulls modified with citric acid. A method was developed to enhance metal ion adsorption of soybean hulls for wastewater treatment using copper ion (Cu^{2+}) as a typical metal ion. Hulls, extracted with 0.1 N NaOH, were modified with different citric acid (CA) concentration (0.1 - 1.2)M) at 120°C for 90 minutes. CA-modified hulls had adsorption capacities for Cu^{2+} from 0.68 to 2.44 m moles/g, which was much higher than for unmodified hulls (0.39 m moles/g). They have also concluded that, soybean hulls treated with sodium hydroxide and modified with citric acid, especially at concentration of 0.6 M and above removed over 1.7 m moles of copper ion from solution per g of hulls. This is due to the increase in carboxyl group imparted onto the hulls by reaction with citric acid. [29] stated that soybean hulls contains (mg/g dry weight basis) protein, lipid ash, lignin, cellulose, hemicelluloses and silica which are 109, 10.0, 36.4, 49.1, 676, 137, and < 10 respectively They studied on agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in Byproduct of manufacturing wastewaster. soybean and cottonseed hulls, rice straw and sugarcane bagasse were evaluated as metal ion adsorbents in aqueous solutions. Adsorption capacities were determined by adsorption isotherms using the Langmuir model. Their adsorption capacities for Zn (II) were: soybean hulls > cottonseed hulls > rice straw > sugarcane bagasse. Capacities varied from 0.52 to 0.06 meq/g dry weight of byproduct. [30] did a study on agricultural by-products as metal adsorbents to find the sorption properties and resistance to mechanical abrasion. Defatted rice bran, soybean and cottonseed hulls were evaluated for their sorption properties and resistance to mechanical abrasion in consideration of their potential use as commercial metal adsorbents. These by-product

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were evaluated using both laboratory prepared solution and metal plating wastewater for their ability to adsorb Zn (II) and/or Cu (II) and Ni (II). Extrusion stabilized, pilot plant-prepared brans had greater adsorption capacities and adsorption efficiencies than expander stabilized, commercially available bran. NaOH- and HClwashed soybean and cottonseed hulls had generally higher adsorption efficiencies than water-washed (control) hulls, but had higher or lower adsorption capacities, respectively, than water-washed hulls. Heat treated cottonseed and soybean hulls had lower adsorption properties than water-washed hulls. Reuse of hulls after one adsorption/desorption cycle resulted in a large decrease in adsorption capacity which classified hulls as single-use adsorbents when desorbed with HCl.

Other agricultural waste by-products

[31] in their study on the use of sago waste for the sorption of lead and copper. Sago processing waste, which is both a waste and a pollutant, was used to adsorb lead and copper ions from solution. The sorption process was examined in terms of its equilibria and kinetics. The most

effective pH range was found to be 4 to 5.5 for both metals. The equilibria data for both metals fitted both the Langmuir and the Freundlich models and based on the Langmuir constants, the sago waste had a greater sorption capacity for lead (46.6 mg/g) than copper (12.4 mg/g). The kinetic studies showed that the sorption rates could be described well by a second-order expression than by the more commonly applied Lagergren equation. [15] studied on utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution. Mercury (II) and nickel (II) were used in the study for various adsorbents. Activated carbon was prepared from agricultural solid wastes such as, silk cotton hulls, coconut tree sawdust, sago waste, maize cob, and banana pitch. [17] studied on removal of chromium (VI) from solution by coconut husk and palm pressed fibres and it was investigated using batch and column techniques. For both substrates, the optimum pH for maximum removal is at 2.0 which corresponds to > 80% removal. [32] studied on activated carbon prepared from waste Parthenium as adsorbent in treating Ni (II) from aqueous solution.

Table 2. Types of sugar cane bagasse as adsorbent for heavy metal

Source	Adsorbent	Heavy metal removal efficiency (%)			
		Cr(VI)	Zn(II)	Cd(II)	
	Bagasse ash	53.4			
[3]	Activated bagasse carbon	99.97	-	-	
	Raw bagasse	93.5	-		
	Activated coconut jute carbon	99.7	-	· _ '	
[4]	Sugarcane bagasse activated carbon	-	100	100	
[5]	Raw sugarcane bagasse	80 - 100	-	-	
		pH 1			

 Table 3.
 Types of saw dust as adsorbent for heavy metal

ource	Adsorbent		Heavy metal removal efficiency (%)			
		Cr(VI)	Ni(II)	Cu(II)	Zn(II)	
[14]	Phosphate treated tree sawdust	100	83	86	86	
	Untreated tree sawdust	-	91	86	75.7	
[16]	Coconut tree saw dust carbon	98,84	-		_	

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Batch mode adsorption experiments are carried out, by varying contact time, metal ion concentration, carbon concentration, pH and desorption to assess kinetic and equilibrium parameters. The adsorption data were modelled by using both Langmuir and Freundlich classical isotherm. The adsorption capacity (Q_o) calculated from the Langmuir isotherm was 54.35 mg Ni (II) /g of AC at initial pH of 5.0 and 20°C, for the particle size range $250 - 500 \ \mu$ m. Increase in pH from 2 to 10 increase percent removal of metal ion.

Martin Dupat et. al [33] have studied on heavy metal adsorption by crude coniferous barks. This paper reports an extensive study on the biosorption abilities of coniferous barks. A chemical pretreatment of the barks caused a decrease in their metal binding capacities. The mechanism of the metal biosorption by barks was approached by the means of the Langmuir adsorption model and seems quite complex. The selective affinity of barks for the metals tested, in the physico-chemical condition defined by their study, is: $Pb^{2+} > Cr^{3+} > Ni^{2+} > Zn^{2+} > Cu^{2+}$. [34] studied on chromium removal by activated carbons prepared from Casurina equisetifolia leaves. Casurina equisetifolia leaves were carbonised and activated after treatment with sulphuric acid (1:1), phosphate salt (10%) or zinc chloride (25%) at different temperatures. Prepared activated carbons were used to remove Cr (VI) from wastewater and the conditions optimised for the most effective carbons. The equilibrium data fitted well with the Freundlich adsorption isotherm. Desorption studies show that 65 - 80% of adsorbed chromium could be desorbed by alkali followed by acid treatment. Recycling of the carbons could be carried out without change in the adsorption efficiency. The carbons were also tested for the removal of chromium (VI) and total chromium from plating effluent. [35] studied on removal of lead ions from industrial wastewater by different types of natural materials. From the research done it was reported that at lead concentration of 4 mg/l and $p\hat{H}$ 6 the adsorption capacity is maximum for Nile rose plant powder at 80% removal and at the same concentration and pH it was also reported that bone powder removed 98.8 % of lead.

Wofwoyo et. al [36] carried out studies on the utilization of peanut shells as adsorbents for selected metals. The results showed that for single metal ion solutions, treatment with phosphoric or citric acid increased the amount of metal ions adsorbed by peanut shells for the metals (Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II)) studied. Base wash increased the effectiveness of citric acid-treated samples in single metal ion solutions while it had no effect on phosphoric acid-treated or untreated samples. Overall, phosphoric acid treatment resulted in higher metal ion adsorption than citric acid treatment. For multiple metal ion solutions, the metal uptake from solution by adsorbents was strongly dependent on the presence and type of other competing metal ions. The acid-treated samples exhibited a high selectivity for Cu(II) ions; 42% for citric acid-treated and 28% phosphoric acid-treated. Citric acid-treated samples were significantly more effective than the phosphoric acid-treated samples as well as commercial resin Amberlite, the removal of Cu(II) ions from multiple ion solution. Peanut shells show promise for use as metal adsorbents from aqueous solutions. Other types of adsorbents and its efficiency in (Table 5).

CONCLUSION

A review of various agricultural adsorbents presented herein shows a great potential for the elimination of heavy metals from wastewater. The sorption capacity is dependent on the type of the adsorbent investigated and the nature of the wastewater treated. The use of commercially available activated carbon for the removal of the heavy metals can be replaced by the utilization of inexpensive, effective, and readily available agricultural by-products as adsorbents. More studies should be carried out to better understand the process of low-cost adsorption and to demonstrate the technology effectively.

As presented through (Tables 1 to 5), various agricultural adsorbents show a high degree of removal efficiency for heavy metals such as chromium, nickel, lead, copper, mercury, zinc, cadmium etc.

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Table 4.	Types of soybean hulls	, cottonseed hulls, rice bran an	d straw as adsorbent for heavy metal
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ource	Adsorbent		Heavy metal removal efficiency (%)			
		Cr(III)	Ni(II)	Cu(II)	Zn(II)	
[29]	Soybean hulls	98.1	95.6	99.7	96.4	
	Cottonseed hulls	97.6	96.7	98.8	96.6	
	Soybean hulls		$\zeta_{e,\sigma}^{d',\gamma}$			
	-water washed	-	53.0	83.3	51.6	
	-NaOH washed	-	55.8	61.0	71.4	
	-HCl washed	-	69.8	89.6	90.3	
	-90°C – heat treated	· -	52.5	80.0	59.8	
	-145°C – heat treated	-	31.7	71.0	33.3	
	Cottonseed hulls					
	-water washed	-	47.6	58.8	59.5	
	-NaOH washed	-	72.8	37.4	69.5	
[30]	-HCl washed	-	51.6	81.5	70.3	
	-90°C – heat treated	-	46.5	54.9	56.1	
	-145°C – heat treated	-	44.1	52.6	50.3	
	Defatted rice brans (pH 5.0)					
	-Non stabilized, defatted at Southern Regional Research	-	29.2	71.5	38.4	
	Center (SRRC)					
	-extrusion stabilized, defatted at SRRC	-	36.6	83.2	75.0	
	-extrusion stabilized, defatted at Riceland Foods Inc.					
	(RF)	-	38.3	75.6	96.8	
	-expander stabilized, defatted at RF	-	20.4	64.7	20.5	

Table 5. Other types of agricultural wastes as adsorbent for heavy metal

Sources	Adsorbent	Heavy metal removal efficiency (%)					
						, 1	
		Cr(VI)	Ni(II)	Cu(II)	Hg(II)	Pb(II	
[15]	Silk cotton carbon	-	64	•	100	-	
	Coconut tree sawdust carbon	-	84.3	-	100	-	
	Sago waste carbon	-	100	-	100	-	
	Maize cob carbon	-	100	-	100	-	
	Banana pitch carbon	-	96.40	-	100	-	
[17]	Coconut husk	> 80	-	-	-	-	
	Palm pressed fibre	> 80	-	-	-	-	
[31]	Sago waste		-	> 75	-	> 95	

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