International Refereed Journal of Engineering and Science (IRJES)
ISSN (Online) 2319-183X, (Print) 2319-1821
Volume 2, Issue 8 (August 2013), PP.18-27

Agro and Horticultural Wastes as Low Cost Adsorbents for Removal of Heavy Metals from Wastewater: A Review

Pushpendra Kumar Sharma[1], Sohail Ayub[2#], Chandra Nath Tripathi[3]
[1]*Asistant professor, Department of Civil Engineering, HCST, Farah, Mathura, UP, India*
[2]*Associate Professor, Department of Civil Engineering, AMU, Aligarh, UP, India*
[3]*Associate Professor, Department of Environmental Engineering, HCST, Farah, Mathura, UP, India*

Abstract:- In recent years the adsorption process has been recognized as an effective and economic method for the removal of heavy metals from wastewaters as it offers flexibility in design and operation so as to produce high quality treated effluents of desired standards for disposal and moreover the adsorbents can be regenerated by suitable desorption. Activated carbon had been the most used adsorbent, nevertheless it is comparatively expensive. Today's demand for safe, eco-friendly, easily available and low cost adsorbents for the removal of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives that is why it is an urgent that all possible sources of agro and horticultural based low cost adsorbents must be explored and their feasibility for the removal of heavy metals should be studied with various affecting parameters. This paper reviews the current methods to explore low cost adsorbents and their utilization techniques for various agro and horticultural waste by-products like sugarcane bagasse, rice husk, orange peels, almond shell, sawdust, soybean hulls, cottonseed hulls, rice bran, coconut tree sawdust, sago waste, banana pitch carbon, coconut husk, palm pressed fibre, clay and some bio adsorbents etc. which are abundantly and easily available in India for the elimination of heavy metals from wastewater.

Keywords:- Adsorbate**,** eco-friendly, adsorption, adsorbents, sorption, agro and horticultural wastes, heavy metals, wastewater, sago waste.

I. INTRODUCTION

Due to rapid industrialization and urbanization in developing countries like India heavy metal pollution is a serious problem today and its treatment is of special concern due to their recalcitrance and persistence in the environment. Like organic pollutants, most of these heavy metals do not undergo biological degradation, resulting into harmless end products [1]. Many industries, like metal plating, mining operations, tanneries, chlor alkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. release these severely toxic heavy metal ions in their wastewaters contaminating natural streams where in disposed, which is a major concern due to toxicity to many life forms [2].Though there are many treatment methods for removal of heavy metals from wastewater like chemical precipitation, membrane filtration, ion exchange, coagulation and flocculation, floatation, electrochemical treatment, adsorption and co-precipitation followed by adsorption etc. yet various researchers have studied and revealed that physical adsorption is a highly effective and economic technique for the removal of heavy metal from waste stream and from ancient times activated carbon has extensively been used as an adsorbent [3] in the water and wastewater treatment plants, but it is found to be an expensive material. Recently, an idea of the production of safe and low cost alternatives to this expensive and commercially available activated carbon has attracted the researchers towards the low cost agro and horticultural wastes and 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 removal of heavy metals from wastewater and it has been investigated successfully.

A low cost adsorbent is one which needs a little processing before use, abundant in nature, a by-product or waste material from another industry. Of course improved sorption capacity may compensate the cost of additional processing [20]. Therefore it becomes very very important to investigate all possible agro and horticultural based inexpensive adsorbents to be explored and their feasibility for the removal of heavy metalsto be studied in all respects. The objective of this study is to contribute in the search for safe and low cost adsorbents and their utilization possibilities for various agro and horticultural waste by-products, which would have been the sources to pollute our natural streams in many cases.

II. RELEVANT LITERATURE

Let us review some agricultural waste by-products used as economic adsorbents for the elimination of heavy metal ions from wastewater in literature.

Rice husk

It is an agricultural waste by-product abundantly available in rice producing countries, especially in Asia continental. It is reported that 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, sugar, etc) and the remainder consists of silica, present in the cellular membrane [21]. Now a day the researchers have focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants [22]. It was reported that tartaric acid modified rice husk is a potentially useful adsorbent in batch studies for the removal of Copper and Lead from aqueous solutions, the various affecting parameters such as pH, initial concentration of adsorbate, particle size, temperature, contact time etc were also studied. The rapid uptake and high adsorption capacity make the rice husk a very attractive and alternative adsorbent. The uptake of Cu and Pb was maximum when pH was increased from 2 to 3, and thereafter remained relatively constant. [11] reported 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]. Removed chromium by rice husk carbon, prepared by carbonization of rice husk with sulphuric acid followed by CO_2 activation resulting 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]. Study 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]. Removed toxic metals from wastewater using rice husk reported, at optimal conditions, the chromium, zinc, copper and cadmium ion from aqueous solution and stated as 79%, 85%, 80% and 85% respectively [23]. Studied adsorption of heavy metals by green algae and ground rice hull and reported that, metal adsorption by algal and rice hull biomass, was greater than 90% for all the metals tested, (Sr, Cd, Ni, Pb, Zn, Co, Cr, As) except Ni, with 80% removal [24]. Studied on adsorption of Cr(VI) on micro- and mesoporous rice husk-based activated carbon and reported that the rice husk carbon is a good sorbent for theremoval of Cr(VI) from aqueous solution rangefrom 5 to 60 mg/l with adsorbent dose of 0.8 g/lat pH < 5 under the minimum equilibration time of 2 hours and above pH 5.0 a sharp decreased adsorption with further higher pH range almost negligible adsorption. Maximum reported adsorption is 95% removal of Cr (VI)[25].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]. 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 and good fit to Freundlich isotherm with 1/n value of 2.863.

Table1. Types of rice husk as adsorbent for heavy metal

Source	Adsorbent	Heavy metal removal efficiency %						
		Cr(V)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**	**Hg(II)**	**Pb(II)**
[9]	Rice husk carbon	>90	-	-	-	-	-	-
[10]	Rice husk							
water and HCl washed		79	-	80	85	85	-	-
[11]	Phosphate-treated	-	-	-	-	>90	-	-
[12]	rice hulls							
Dyestuff-treated (red)		39.7	61.6	78.8	75.1	99.2	92.7	99.8
Dyestuff-treated (yellow)		39.1	60.8	70.0	61.3	83.3	93.3	100
[22]	Rice husk							
Tartaric acid modified		-	-	>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	-	-	-	-	-	-

Sugarcane Bagasse

It is a waste product from sugar mill mainly composed of cellulose, pentosan, and lignin [4]. [27] Reported that the Pb (II) adsorption process obeys Langmuir's model and Cd (II) presents adsorption in multilayer, especially when the temperature >30ºC. When ionic strength increases, the maximum adsorption capacity decreases. The carboxymethylated lignin from sugar cane bagasse can absorb Pb (II) selectively rather than Cd (II) under special conditions (pH 6.0, 30ºC, 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 multicomponent adsorption of cadmium and zinc using activated carbon derived from bagasse and reported that the removal of Cd (II) and 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 20 mg/l at a pH value of 1 but the efficiency reduced sharply to 15% at pH 3. [3] Investigated the effect of solution pH, Cr (VI) concentration, adsorbent dosage and contact time using adsorption based on bagasse and coconut jute in a batch experiment. The removal was 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 reported around 99.8 percent at pH 2. The data for all the adsorbents well fit to the Freundlich isotherm.

Table2. Types of sugar cane bagasse as adsorbent for heavy metal

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

Sawdust

[14] studied that 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) was 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] Removed 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 varying agitation time, initial Cr (VI) 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).

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

Source	Adsorbent	Heavy metal removal Efficiency %			
		Cr (VI)	Ni (II)	Cu (II)	Zn (II)
[14]	Phosphate treated tree sawdust	100	83	86	86.o
[14]	Untreated tree sawdust	-	91	86	75.7
[15]	Coconut tree saw dust carbon	98.84	-	-	-

Soybean hulls, cottonseed hulls, rice bran and straw

[28] adsorbed heavy metals by citric acid modified soybean hulls, extracted with 0.1 N NaOH, modified with different citric acid (CA) concentration (0.1 – 1.2 M) at 120ºC for 90 minutes, with adsorption capacities for Cu2+ from 0.68 to2.44 m moles/g>>unmodified hulls (0.39 m moles/g), probably due to the increase in carboxyl group imparted onto the hulls by reaction with citric acid. [29] analyzed soybean hulls containing (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 and reported adsorption capacities for Zn (II) in decreasing orderas

soybeanhulls, cottonseed hulls, rice straw, sugarcane bagasse with varying capacities from 0.52 to 0.06meq/g dry weight of byproduct. [30] Evaluated defatted rice bran, soybean and cottonseed hulls for both synthetic and metal plating wastewater for theirability to adsorb heavy metals. NaOH and HCl washed soybean and cottonseed hulls were better adsorbents than water-washed (control) hulls, heat treated cottonseed and soybean hulls were inferior adsorbents than water-washed hulls. Reuse of these agricultural wastes after one adsorption/desorption cycle was not satisfactory.

Table 4. Types of soybean hulls, cottonseed hulls, rice bran and straw as adsorbent for heavy metals

Source	Adsorbent	Heavy metals removal Efficiency%			
		Cr (III)	Ni (II)	Cu (II)	Zn (II)
[29]	Soybean hulls	98.1	95.6	99.7	96.40
	Cottonseed hulls	97.6	96.7	98.8	96.60
	Soybean hulls				
	-Water washed	-	53.0	83.0	51.60
	-NaOH washed	-	55.8	61.0	71.40
	-HCl washed	-	69.8	89.6	90.30
	-900heattreat	-	52.5	80.0	59.80
	-1450heat treat	-	31.7	71.0	33.33
	Cottonseed hulls				
	-Water washed	-	47.6	58.8	59.50
	-NaOH washed	-	72.8	37.4	69.50
[30]	-HCl washed	-	51.6	81.5	70.30
	-900heattreat	-	46.5	54.9	56.10
	-1450heattreat	-	44.1	52.6	50.30
	Defated rice brans(pH5)				
	-Non stabilized, defatted at				
	Southern Regional Research	-	29.2	71.5	38.40
	Centre SRRC				
	-extrusion stabilized,				
	defatted at SRRC	-	36.6	83.2	75.00
	-extrusion stabilized,				
	defatted at Riceland Foods Inc.RF	-	38.3	75.6	96.80
	-expander stabilized, defatted at RF	-	20.4	64.7	20.50

[15] Prepared activated carbon from various agricultural solid wastes such as, silk cotton hulls, coconut tree sawdust, sago waste, maize cob, and banana pitch etc. and used for the removal of colour and metal ions from aqueous solution. [17] Used coconut husk and palm pressed fibres in batch and column studies for removal of chromium (VI) from solution and investigated the optimum pH for maximum removal of 80% is 2.0. [32] Prepared activated carbon from waste Parthenium and used as adsorbent for removal of Ni (II) from aqueous solution. They assessed kinetic and equilibrium parameters in batch study, varying time of contact, adsorbate concentration, carbon concentration, pH, temperature and desorption. They modeled sorption data using Langmuir and Freundlich classical isotherm. The adsorption capacity (Qo) from the Langmuir isotherm was 54.35 mg Ni (II) /g of AC at pH 5.0 and temp 20ºC, particle size range 250 – 500 µm. Increase in pH from 2 to 10 increase percent removal of metal ion. [31] Used sago waste, a pollutant as the adsorbent for lead and copper ions from aqueous solutions with respect to the equilibria and kinetics, best fitting the Langmuir and the Freundlich Models, with optimum pH 4-5.5 and reported a considerable adsorption capacity for lead (46.6 mg/g), copper (12.4 mg/g) respectively.

Table5. Other types of agricultural wastes as adsorbent for heavy metal

Source	Adsorbent	Heavy metals removal Efficiency %				
		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	-	96.4	-	100	-
[17]	Coconut husk	>80	-	-	-	-

	Palm pressed fibre	>80	-	-	-	-
[31]	Sago waste	-	-	>75	-	>95

[
33] Investigated the mechanism of the metal biosorption by means of the Langmuir adsorption model with chemically pretreated coniferous barks as adsorbent losing their metal binding capacities. Under the physico-chemical condition the metal affinity of bark was found in the following decreasing order Lead, Chromium, Nickel, Zinc, Copper. [34] Prepared activated carbons from Casurinaequisetifolia leaves carbonised and treated with sulphuric acid (1:1), phosphate salt (10%) or zinc chloride (25%) at different temperatures to removeCr (VI) from wastewater and the conditions optimised for the most effective carbons. The equilibrium data fitted well with the Freundlich adsorption isotherm. Desorption studies showed that 65 – 80% of adsorbed chromium could be desorbed by alkali followed by acid treatment. Activated Carbons could be reused without change in the adsorption capacity.
[35] Reported that the Nile rose plant powder adsorbed 80% and bone powder removed 98.8 % of lead at lead concentration of 4 mg/l and pH 6. [36] Investigated that for single heavy metal ion solutions, phosphoric acid treated peanut shells were better metal ion adsorbents as compared to citric acid treated ones. For multiple metal ion solutions, the metal uptake from solution by adsorbents was strongly dependent on selective affinity to 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. The study revealed that Citric acid-treated samples were significantly better adsorbents as compared to the phosphoric acid-treated samples. [39] Reviewed the adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite. [40] Reviewed agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions.[41] reviewed the removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents.[42] reviewed the use of low cost adsorbents for heavy metals uptake from contaminated water. [43] Investigated the kaolinite clay obtained from Longyan, China to remove heavy metal ions Pb(II), Cd(II), Ni(II) and Cu(II) from wastewater. The uptake is rapid with maximum adsorption being observed within 30 minutes and kaolinite clay was used for removing metal ions from real wastewater containing Pb(II), where its concentration was reduced from 160.00 mg/L to 8.00 mg/L. [44] Reported Zinc and Copper removal from aqueous solutions using brine sediments, sawdust and mixture of both materials. The maximum adsorption capacity was found to be 4.85, 2.58 and 5.59 mg/g for Zinc and 4.69, 2.31 and 4.33 mg/g for Copper respectively, using an adsorbent/solution ratio of 1/40. Biosorption of heavy metals from aqueous solution is a relatively new process that has been confirmed a very promising process for the heavy metal contaminated wastewater treatment. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive bioadsorbents. Biosorption process are particularly suitable to treat dilute heavy metal wastewater [37]. Typical bioadsorbents can be derived from three sources as follows:(1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.; (2) algal biomass; (3) microbial biomass, e.g. bacteria, fungi and yeast[45]. Different forms of inexpensive, non-living plant materials such as potato peels [46], sawdust [47], black gram husk [48], egg shell [49], seed shells [50], coffee husk [51], sugar-beet pectin gels [52], and citrus peels [53] etc., have been widely studied with various affecting parameters in detail and investigated by various researchers as potential biosorbents for heavy metals removal from aqueous solutions. [54] investigated removal efficiency of waste tea from nickel containing aqueous solutions by fixed-bed columns with liquid flow rate (5–20 mL/min), initial Ni(II) concentration (50–200 mg/L), bed height (10–30 cm), pH of feed solution (2.0–5.0) and particle size (0.15–0.25 to 1.0–3.0 mm) of adsorbent using the bed depth service time model and the Thomas models and found that longest breakthrough time and maximum of Ni(II) adsorption was at pH 4.0 with decrease in the particle size from 1.0–3.0 to 0.15–0.25mm resulted in significant increase in the treated volume, breakthrough time and bed capacity. The best results were at lowest flow rate and column bed capacity, exhaustion time increased with increasing bed height. When the initial Ni(II) concentration is increased from 50 to 200 mg/L, the corresponding adsorption bed capacity appeared to increase from 7.31 to 11.17 mg/g. [55] used *Azadirachta indica* (neem) leaf powder as an adsorbent for the removal of chromium from aqueous solutions in a batch process with various process parameters that include agitation time, adsorbent size and dosage, initial chromium concentration, volume of aqueous solution and pH of the aqueous solutions and studied adsorption behavior following Freundlich and Langmuir isotherms. The adsorption mechanism was described by a pseudo second order kinetics. [56] Summarized the performances of various biological compounds, minerals, modified activated carbons, as well as industrial and agricultural wastes as low cost and simple adsorbents in both synthesis and implementation. [57] Reviewed that a number of plant wastes like rice husks, spent grain, sawdust, sugarcane bagasse, fruit wastes, weeds and others modified by numerous chemicals such as mineral and organic acids, bases, oxidizing agent, organic compounds, etc. exhibit higher adsorption capacities than unmodified forms for Cd, Cu, Pb, Zn and Ni. [58] Prepared a low cost adsorbent from tamarind seeds activated by heat treatment and with concentrated sulfuric acid and conducted batch studies for Cr(VI) removal from aqueous solutions and studied the parameters such as initial pH, contact time, initial Cr(VI) concentration, and

adsorbent dosage. The adsorption of Cr (VI) was found to be maximum at low values of initial pH in the range of 1–3. The adsorption process of Cr (VI) was tested with Langmuir and Freundlich isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 29.08 mg g^{-1}. The adsorption process followed second order kinetics and the corresponding rate constant was found to be 0.0026 g mg^{-1} min^{-1}. [59] Karanja Seed Oil Cake, a by-product after oil extraction, which otherwise goes waste or as fertilizers, was used as Precursor for Activated Carbon Preparations. Adsorbent from Karanja seed oil cake was prepared in laboratory by various Chemical and Physical Activation Processes and was studied for adsorptions of Dyes and Waste Water Treatment. [60] Used a *Prunus Amygdalus* (Almond nut shell) as a low cost adsorbent for removal of Cr (VI) from aqueous solutions and the uptake capacity of this adsorbent was studied as a function of contact time, pH, adsorbate concentration and adsorbent dose. From the time variation experiments, the equilibrium contact time was found to be 6 hr. Cr (VI) uptake capacity of the adsorbent increased with decrease in pH with optimum pH 1.8. The adsorption capacity of the adsorbent was found to increase with increase in adsorbate concentration, whereas it decreased with increasing in adsorbent dose. [61] Used thermally synthesized low cost adsorbent i.e aegel marmelos fruit shell which is a waste remains after the conversion of pulp into jam, jelly, squash, marmalade or syrup, etc @ carbonization temperature of 300°C, specific surface area 1.2433±0.0414 m^2/g and studied for adsorption of Cr (VI) from aqueous solution for various concentrations & doses and as a result of experimental analysis concluded that the adsorbent developed in the study was fairly effective. [62] Compared the efficiency of various low cost adsorbents as in the order of PAC>Bagasse>FA>SD>WSD>Coconut coir. The effect of chromium solution PH, contact time , adsorbent dosage, initial chromium concentration and adsorbent mesh size on adsorption were studied in a batch experiment. Fly ash, Bagasse, W.S.D, SD, &Coconut coir were the most active at pH-6 , which is closer to pH of chromium bearing industrial waste as compared to the pH 2.0 of PAC. The equilibrium data for the adsorption of chromium were analysed in the light of Langmuir and Freundlich isotherm models. The ultimate adsorption capacity for the adsorbents PAC, Bagasse, FA, S.D., W.S.D & Coconut coir were found as 4.97 mg/gm, 4.91mg/gm, 4.90mg/gm, 4.89 mg/gm, 4.77mg/gm and 4.56 mg/gm by column studies respectively. [63] Compiled, an extensive list of sorbent literature to summarize available information on a wide range of low-cost agricultural product and by-product sorbent and their modification for removing heavy metals from water and wastewater. [64] Studied the adsorption of hexavalent chromium from aqueous medium by physically activated rice husk carbon and optimised 150 minutes , 20 mg/l , 2 ,and 5g/l for time contact, initial concentration, PH and adsorbent dose respectively along with a result of 95.2% adsorption of Cr(VI). [65] studied the feasibility of sugar cane bagasse to remove chromium (VI) from the aqueous solutions by designed batch experiments evaluating the impact of various parameters, such as adsorbent does, contact time, initial concentration and pH on chromium removal efficiency, the results indicated a prominent effect of pH on the chromium reduction by the adsorbent used. [66] Reviewed the chromium occurrence, transformation, in different environments and the possible and currently practicing remedial measures and the evaluation of their efficacy to minimize the toxic effects.[67] Studied the potential of *Pinus roxburghii* bark as an adsorbent for the removal of heavy metals such as Cr(VI), Ni(II), Cu(II), Cd(II) and Zn(II) from aqueous solution at ambient temperature and found adsorption capacity of the material was found to be 4.15, 3.89, 3.81, 3.53 and 3.01 mg g-1 for Cr(VI), Zn(II), Cu(II), Ni(II) and Cd(II), respectively, at an initial metal ion concentration of 50 mg L-1 at pH 6.5. The effect of concentration, contact time, adsorbent dose, solution pH, adsorbent particle size, salinity and hardness on the adsorption of Cr (VI) were also studied in detail in batch experiments. The equilibrium contact time for Cr (VI) adsorption was found to be 1 h. Adsorption equilibrium data fit well to the Freundlich isotherm in the concentration range studied. The maximum adsorption (96.2%) was recorded at pH 3 for the initial Cr (VI) concentration of 50 mg L-1. The adsorbed metal ions from industrial wastewater were recovered using 0.1 M HCl solution. The column operation was found to be more effective compared to batch process. The percent recovery of Cr (VI) from industrial wastewater by column operation and batch process was found to be 85.8 and 65%, respectively. The results showed that *Pinus roxburghii* bark can be used as a cost-effective adsorbent for the removal and recovery of Cr(VI) from wastewater. [68] compared efficiency of activated coconut shell and activated coconut coir in removing toxic hexavalent chromium from its synthetic solution and tannery industrial effluent in batch mode with respect to pH, adsorbent dose, contact time & initial metal ion concentration and the applicability of adsorption isotherms. Activated coconut shell exhibited more adsorption potential as compared to Activated coconut coir and maximum removal exhibited by ACS was 88% and 83.0 % for 0.3 mm and 1.0 mm in case of synthetic solution & 76%(0.3mm) and 66%(1.0mm) in case of tannery effluent at optimized conditions (pH =2, dose=1.0g/100ml, contact time=60 minutes & initial metal ion concentration=10 ppm). In general ACS was observed to be better adsorbent than ACC while adsorbents of particle size 0.3 mm have greater efficiency than 1.0 mm. On application of adsorption kinetics, Adsorption of Cr (VI) by ACS and ACC followed the pseudo first order and pseudo second order model and investigated that the activated coconut coir is an efficient adsorbent for hexavalent chromium removal. [69] Used Archis Hypogea (ground nut) shells, a lingo cellulosic waste biomass in three different forms natural, beads and activated carbons as low cost adsorbent and evaluated sequestering of Cr (VI) from synthetic wastewater in batch experiments. They investigated that the removal of metal ions was dependent on physic-chemical characteristics of the adsorbent, adsorbate concentration and other process parameters at an optimum pH 2.0. The experimental data were analyzed based on Freundlich and Langmuir adsorption isotherms. Kinetic studies indicated that the adsorption of metal ions followed a pseudo second order equation. [70] Used compost generated from Carnation flowers waste as a low cost adsorbent for removal of chromium (VI) from aqueous solutions and reported 99% removal at pH 2.0 @ 10 mg/l of Cr (VI) solution @ 10 g/l of compost @ 3 hours contact time. Under the above conditions the kinetic adsorption isotherms were examined varying the Cr(VI) concentrations from 15-200 mg/l. The maximum sorption capacity at equilibrium (Q_m) from the Langmuir model was reported to be 6.25 mg/g. To date, though hundreds of studies on the use of low cost adsorbents have been published. Agricultural wastes, horticultural wastes and bye products, industrial by-products and wastes and natural substances have been studied as adsorbents for the heavy metal wastewater treatment. Several reviews are available that discuss the use of low cost adsorbents for the treatment of heavy metals wastewater [37]. Yet, there is a need to explore some further more new low cost adsorbents which are abundant in nature and may cause pollution if released in streams or land without treatment.

III. CONCLUSION

The present literature review study of various agro and horticultural adsorbents over here shows a great potential for the removal of heavy metals from wastewater. The sorption capacity depends on the type of the adsorbent investigated and the nature of the wastewater treated as well. The use of expensive and commercially available activated carbon for the removal of the heavy metals from aqeous solution can possibly be replaced by using low cost, more effective, abandant and readily available agricultural wasteby-products as adsorbents. There is an urgent need of more detailed studies to be carried out so as to better understand the process of more effective and economic adsorption hence therefore to developsuch a technology that matters truly and 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.

To date, though hundreds of studies on the use of low cost adsorbents have been published. Yet, there is a need to explore some further more new low cost adsorbents which are abundant in nature and may cause pollution if released in streams or land without treatment and this way there will be a two way pollution control so called "Aam kea am guthalion ke daam"

REFERENCES

[1] Gupta, V.K., Gupta, M., and Sharma, S., (2001). Process development for the removal of lead and chromium from aqueous solution using red mud – an aluminum industry waste. Water Res. 35(5): 1125 – 1134 pp.

[2] Kadirvelu, K., Thamaraiselvi, K, and Namasivayam, C., (2001). Removal of Heavy Metal from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste. BioresourceTechn., 76: 63-65 pp.

[3] Chand, S., Aggarwal V.K. and Kumar P., (1994).Removal of Hexavalent Chromium from the Wastewater by Adsorption. Indian J Environ. Health, 36(3): 151-158 pp.

[4] Mohan D., and Singh K.P., (2002). Singleand Multi-Component Adsorption of Cadmium and Zinc using Activated Carbon Derived from Bagasse – An Agricultural Waste. Water Research, 36: 2304-2318 pp.

[5] Khan N.A., Ali S.I. and Ayub S., (2001). Effect of pH on the Removal of Chromium (Cr) (VI) by Sugar Cane Baggase,.Science and Tech., 6: 13-19 pp.

[6] Ayub, S.,Ali, S.I., Khan, N.A., and Rao, R.A.K. (1998). Treatment of wastewater byagricultural waste. Environmental ProtectionControl Journal 2(1): 5 – 8 pp.

[7] Ayub, S.,Ali, S.I., and Khan, N.A. (2001). Study on the removal of Cr(VI) by sugarcane bagasse from wastewater. Pollution Research Journal 2(2): 233 – 237 pp.

[8] Ayub, S.,Ali, S.I., and Khan, N.A. (2002). Adsorption studies on the low cost adsorbent for the removal of Cr(VI) from electroplating wastewater. Environmental Pollution Control Journal 5(6): 10 – 20 pp.

[9] Srinivasan K., Balasubramaniam N., and Ramakrishna T.V., (1998). Studies on Chromium Removal by Rice Husk Carbon.Indian Journal Environmental Health, 30(4): 376-387 pp.

[10] Munaf E., and Zein R., (197).The Use of Rice Husk for Removal of Toxic Metals from Wastewater. Environmental Technology, 18: 359-362 pp.

[11] Ajmal, M.,Rao, R.A.K., Anwar, S., Ahmad, J., and Ahmad, R., (2003). Adsorption Studies on Rice Husk: Removal andRecovery of Cd (II) from Wastewater. Bioresource Tech., 86: 147-149 pp.

[12] Suemitsu R., Venishi R., Akashi I., and Nakano M., (1986). The Use of Dyestuff-treated Rice Hulls for Removal of Heavy Metals from Waste Water. Journal of Applied Polymer Science 31: 75-83 pp.

[13] Khan, N.A., Shaaban, M.G., Jamil, Z., (2003). Chromium removal from wastewater through adsorption process. Proc. UM Research Seminar 2003 organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur.

[14] Ajmal, M., Rao, R.A.K., and Siddiqui, B.A., (1996). Studies on Removal and Recovery of Cr (VI) from Electroplating Wastes. Water Res. 30(6): 1478-1482 pp.

[15] Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., and Pattabhi, S., (2003). Utilization of Various Agricultural Wastes for Activated CarbonPreparation and Application for the removalof dyes and metal ions from AqueousSolution.Bioresource Tech. 87: 129-132 pp.

[16] Selvi K.,Pattabhi S., and Kadirvelu K., (2001). Removal of Cr (VI) from Aqueous Solution by Adsorption onto Activated Carbon.Bioresource Technology 80: 87-89 pp.

[17] Tan W.T., Ooi S.T., and Lee C.K., (1993). Removal of Chromium (VI) from Solution by Coconut Husk and palm Pressed Fibre. Environmental Technology, 14: 277-282 pp.

[18] Khan, N.A., Shaaban, M.G., Hassan, MH.A.,(2003). Removal of heavy metal using an inexpensive adsorbent. Proc. UM Research Seminar 2003 organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur.

[19] Ayub, S.,Ali, S.I., and Khan, N.A. (2001). Efficiency evaluation of neem (Azadirachtaindica) bark in treatment of industrial wastewater. Environmental Pollution Control Journal 4(4): 34 – 38 pp.

[20] Bailey, S.E., Olin, T.J., Bricka, R.M., and Adrian, D.D., (1999). A Review of Pontentially Low-Cost Sorbents for Heavy Metals. Water Res. 33(11): 2469-2479 pp.

[21] Vempati, R.K., Musthyala, S.C., Molleh, Y.A., and Cocke, D.L., (1995). Surface Analyses of Pyrolysed Rice Husk using Scanning Force Microscopy. Fuel, 74(11): 1722-1725 pp.

[22] Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., (2003). Removal of Cu and Pb by Tartaric Acid Modified Rice Husk from Malaysian Journal of Science 23 : 43 - 51 (2004) 51 Aqueous Solution. Chemosphere 50: 23-28 pp.

[23] Roy D.,Greenlaw P.N., and Shane B.S., (1993). Adsorption of Heavy Metals by Green Algae and Ground Rice Hulls. J. Environ. Sci. Health A 28(1): 37-50 pp.

[24] Guo, Y., Qi, S., Yang, S., Yu, K., Wang, Z., and Xu, H., (2002). Adsorption of Cr(VI) on Micro- and Mesoporous Rice Husk-Based Active Carbon. Materials Chemistry and Physics 78: 132 – 137 pp.

[25] Daifullah, A.A.M., Girgis, B.S., and Gad, H.M.H, (2003). Utilization of Agro-Residues(Rice Husk) in Small Waste WaterTreatment Plans. Materials Letters 57: 1723– 1731 pp.

[26] Subramaniam, P., Khan, N.A., and Ibrahim, S., (2004). Rice Husk as an Adsorbent for Heavy Metal.Proceedings of International Conference on Water and Wastewater 2004 (ASIAWATER 2004), Kuala Lumpur,Malaysia.

[27] Peternele, W.S., Winkler-Hechenleitner, A.A., and Pineda, E.A.G., (1999). Adsorption of Cd(II) and Pb(II) onto Functionalised Formic Lignin from Sugar Cane Bagasse. Biresource Technology 68: 95-100 pp.

[28] Marshall W.E., Wartelle, L.H., Boler, D.E., Johns, M.M., and Toles, C.A., (1999). Enhanced Metal Adsorption by Soybean Hulls Modified with Citric Acid. Bioresource Tech. 69: 263-268 pp.

[29] Marshall, W.E., and Champagne, E.T., (1995). Agricultural Byproduct as Adsorbents for Metal Ions in Laboratory Prepared Solutions and in Manufacturing Wastewater. Journal of Environ. Science Health A 30(2): 241-261 pp.

[30] Marshall, W.E., and Johns, M.M., (1996). Agricultural By-products as Metal Adsorbents: Sorption Properties and Resistance to Mechanical Abrasion. Journal of Technology and Biotechnology 66: 192-198 pp.

[31] Quek, S.Y., Wase, D.A.J., and Forster, C.F., (1998). The Use of Sago Waste for the Sorption of Lead and Copper. Water S.A. 24(3): 251-256 pp.

[32] Kadirvelu, K.,Senthilkumar, P.,Thamaraiselvi, V., and Subburam, V., (2002). Activated Carbon Prepared from Biomass as Adsorbent: Elimination of Ni (II) from Aqueous Solution. BioresourceTechnology 81: 87-90 pp.

[33] Martin-Dupont, F, Gloaguen, V, Granet, R, Guilloton, M., Morvan, H., and Krausz, P, (2002). Heavy Metal Adsorption by Crude Coniferous Barks: A Modelling Study, A 37(6) : 1063-1073 pp.

[34] Ranganathan, K, (2000). Chromium Removal by Activated Carbons Prepared fromCasurinaequisetifolia Leaves. Bioresource Technology 73: 99-103 pp.

[35] Halim, S.H.A., Shehata, A.M.A., and El- Shahat, M.F., (2003). Removal of lead ions from industrial waste water by different types of natural materials. Water Res. 37:1678 – 1683 pp.

[36] Wofwoyo, W, Chung, W.S., and Marshall, W.E., (1999). Utilization of Peanut Shells as Adsorbents for Selected Metals. Journal of Chemical Technology and Biotechnology 74: 1117-1121 pp.

[37] Fenglian Fu, Qi Wang, (2010). Removal of heavy metal ions from wastewaters; A review. Journal of Environmental Management, xxx 1-12.
[38] Nasim Ahmad Khan, Shaliza Ibrahim and Piarapakaran Subramaniam (2004), Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents, Malaysian Journal of Science 23 : 43 – 51
[39] Bhattacharyya, KG., Gupta S.S., (2008), Adsorption of a few heavy metals on natural and modified kaolinite and montmorllonite: A review, Adv. Colloid Interface Sci.140114-131 pp.
[40] Sud,D., Mahajan, G., Kaur, M.P.,(2008), Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions- A review., Bioresour. Technol,99, 6017-6027 pp.
[41] Wan Ngah, S.W., Hanafiah, M.A.K.M.,(2008), Removal of heavy metal ions from wastewater by chemicalyy modified plant wastes as adsorbents: a review. Bioresour.Technol,99, 3935-3948.
[42] Babel, S., Kurniawan, T.A., (2003), Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J.Hazard. Mater. 97, 219-243pp.
[43] Jiang, M.Q., Jin, X.Y., Lu, X.Q., Chen, Z.L., (2010), Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) on to natural kaolinite clay. Desalination, 252, 33-39 pp.
[44] Agoubordea, L., Navia, R., (2009), Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes.J. Hazard.Mater.167, 536-544 pp.
[45] Apiratikul,R. Pavasant, P., (2008b), Batch and column studies of biosorption of heavy metals by Caulerpalentillifera,Bioresour. Technol, 99, 2766-2777 pp.
[46] Aman, T., Kazi, A.A., Sabri, M.U., Bano, Q., (2008), Potao peels as solid waste for the removal of heavy metal Copper(II) from wastewater/industrial effluent. Colloid Surf.63, 116-121 pp.
[47] Kaczala, F., Marques, M., Hogland, W., (2009), Lead and vanadium removal from a real industrial wastewater gravitational settling/sedimentation and sorption on to Pinussylvestris sawdust. Bioresour.Technol, 100, 235-243 pp.
[48] Saeed, A., Iqbal, M., Akhtar, M.W., (2005), Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn)solution by crop milling waste (black gram husk). J. Hazard Mater.117, 65-73 pp.
[49] Jai, P.H., Wook, J.S., Kyu, Y.J., Cil, K.B., Mok, L.S., (2007), Removal of heavy metals using waste egg shell. J. Environ. Sci., 19, 1436-1441 pp.
[50] Amudaa, O.S., Adelowoa, F.E., ologunde, M.O., (2009), Kinetics and equillibriumstudies of adsorption of chromium (VI), ion from industrial wastewater using Chrysophyliumalbidum (Sapotaceae) seed shell. Colloid Surf.68, 184-192 pp.
[51] Oliveira, L., Franca, A.S., Alves, T.M., Rocha, S.D.F., (2008), Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters. J. Hazard Mater.155, 507-512 pp.
[52] Mata, Y.N., Blazquez, M.L., Ballester, A., Gonzalez, F., Munoz, J.A., (2009), Sugar-beet pulp pectin gels as biosorbent for heavy metals: preparation and determination of biosorption and desorption characteristics. Chem. Eng. J. 150, 289-301 pp.
[53] Schiewer, S., Patil, S.B., (2008), Modeling the effect of pH on biosorption of heavy metals by citrus peels. J. Hazard Mater. 157, 8-17 pp.
[54] E. Malkoc, Y. Nuhoglu(2006) "Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column" Journal of Hazardous Materials, B135 (2006) 328–336.
[55] P. Venkateswarlu, M. Venkata Ratnam, D. Subba Rao and M. Venkateswara Rao (2007), "Removal of chromium from an aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent", International Journal of Physical Sciences, August, 2007, Vol. 2 (8), pp. 188-195.
[56] Oscar Hernandez-Ramirez and Stuart M. Holmes (2008), "Novel and modified materials for wastewater treatment applications", J. Mater. Chem., 2008, 18, 2751–2761
[57] W.S. Wan Ngah , M.A.K.M. Hanafiah (2008), "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review", Bioresource Technology 99 (2008) 3935–3948 pp.
[58] Ashish S. Saksule, Pallavi A. Kude.(2012), "Adsorbents from Karanja Seed Oil Cake and Applications", International Journal of Chemical Engineering and Applied Sciences 2012; 2(3): 13-23 pp.
[59] Mosleh M. Manfe, S. J. Attar, M. Parande and
[60] Niraj S. Topare.(2012), "Treatment of Cr (VI) Contaminated Wastewater Using Biosorbent *Prunus Amygdalus* (Almond) Nut Shell Carbone" Int. J. Chem. Sci.: 10(2), 2012, 609-618 pp.
[61] S.L. Pandharipande, Aarti R. Deshmukh.(2012), "Synthesis, Characterization and Adsorption Studies for Adsorbents Synthesized from Aegel Marmelos Shell for Removal of Cr (VI) from Aqueous Solution", IJAERS/Vol. II/ Issue I/Oct.-Dec.,2012/95-96 pp.

[62] A.Y. Talokar.(2011), "Studies on Removal of Chromium from Wastewater by Adsorption Using Low C Agricultural Biomass as Adsorbent", International Journal of Advanced Biotechnology and Research, Vol. 2, Issue 4, 2011, 452-456 pp
[63] Upendra Kumar (2006), "Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review", Scientific Research and Essay Vol. 1 (2), 033-037 pp, November 2006.
[64] Ismaeel Ahmed, S.J.Attar, M.G.Parande. (2012), Removal of Hexavalent Chromium (Cr (VI)) from Industrial Wastewater by Using Biomass Adsorbent (Rice Husk Carbone). " IJAERS/Vol. I/ Issue II/January-March, 2012, 92-94pp
[65] Nasim Ahmed Khan, Syed Iqbal Ali and Sohail Ayub.(2001), "Effect of pH on the Removal of Chromium (Cr) (VI) by Sugar Cane Bagasse", Science and Technology, 6 (2001) 13-19 pp
[66] Vemula Madhav1, Ambavaram Vijay Bhaskar Reddy, Kalluru Gangadhara Reddy, Gajulapalle Madhavi and Tollamadugu NagaVenkata Krishna Vara Prasad,(2013) "An Overview on Research Trends in Remediation of Chromium"Research Journal of Recent Sciences, Vol. 2(1), 71-83pp, January (2013)
[67] Rais Ahmad, Rifaqat Ali Khan Rao and Mir Mohammad Masood.(2005)," Removal and Recovery of Cr(VI) from Synthetic and Industrial Wastewater using Bark of *Pinus roxburghii* as an Adsorbent" Water Qual. Res. J. Canada, 2005 • Volume 40, No. 4, 462–468pp.
[68] Asha Gupta, Reena Yadav, and Parmila Devi.(2011), "Removal of Hexavalent Chromium Using Activated Coconut Shell and Activated Coconut Coir as Low Cost Adsorbent", The IIOAB Journal, Vol. 2; Issue 3; 2011: 8-12pp.
[69] Garima Mahajan and Dhiraj Sud. (2011), "Kinetics and Equilibrium Studies of Cr(VI) metal ion Remediation by Arachis Hypogea Shells: A Green Approach" Bio Resources, 2011, Vol. 6(3), 3324-3338 pp.
[70] Claudia vargas, pedro F.B. brandao, Jesus Agreda and Elinna castilo.(2012), " Bioadsorption Using Compost: An Alternative for removal of Chromium(VI) from aqueous solutions" BioResources, 2012, 7(3), 2711-2727 pp.