

Agricultural and agro-processing wastes as low cost adsorbents for metal removal from wastewater: A review

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This study reviews the use of agricultural and agro-processing industry wastes as metal adsorbents from wastewater. Modified materials displayed better adsorption capacity and capability of some was comparable with that of commercial activated carbons and synthetic resins. Agricultural wastes are low-cost adsorbents and can be viable alternatives to activated carbon for treatment of metal-contaminated wastewater.

Keywords: Adsorption, Agricultural waste, Low-cost adsorbents, Metals

Introduction

Heavy metals discharge into aquatic ecosystems is a matter of concern. Eleven metals [lead (Pb), chromium (Cr), mercury (Hg), uranium (U), selenium (Se), zinc (Zn), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni)], out of 20 classified metals as toxic, are emitted into environment in quantities that pose risks to human health¹. Inputs of these trace metals into ecosystem are largely as a result of mining operations, refining ores, sludge disposal, fly ash from incinerators, processing of radioactive materials, metal plating, or manufacture of electrical equipment, paints, alloys, batteries, pesticides and preservatives². Presence of heavy metals in environment has become a major threat due to their bio-accumulating tendency and toxicity. Hence, it is necessary to remove these metals from industrial effluents before discharging aqueous waste into environment.

Traditional metal removal methods³ (chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction) have certain disadvantages (incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products). Most of these methods are often ineffective or uneconomical when heavy metal

concentration is higher (10-100 mg l⁻¹) than permissible concentration⁴ (< 1 mg l⁻¹).

Studies⁵⁻¹³ are available on use of adsorbents for removal of metal ions from effluents. Commercial activated carbon (CAC) is widely used for adsorbing various substances from industrial wastewater¹⁴⁻¹⁶. However, CAC is expensive material for heavy metal removal¹⁷. Mofa¹⁸ found plant based phytochelatin and proteins bind metals and reduce toxicity. Live biological systems work well for low concentrations but cannot survive high concentrations in highly contaminated areas and industrial effluents¹⁹. Use of non-living bio-materials as metal-binding agents or natural biopolymers are industrially attractive because of their capability in lowering metal ion concentration to parts per billion (ppb) levels due to their high affinity for cationic metals^{9,20}. Natural materials and certain wastes from agricultural operations have potential to be used as low cost adsorbents²¹.

Wide variety of agricultural wastes studied as adsorbent for decontaminating industrial/domestic wastewaters from toxic metals, include walnut waste²², apple waste²³, maize cobs²⁴, peanut shell^{25, 26}, cassava waste^{27, 28}, jackfruit peels²⁹, fluted pumpkin waste^{30, 31}, olive pomace³², wheat bran³³, coconut shell⁷, coir pith³⁴⁻³⁷, rice husk and bagasse³⁸. This paper reviews the use of agricultural wastes as metal adsorbents (Tables 1-6)..

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Table 1—Cadmium (II) adsorption capacities (q_m) of agricultural waste materials

Material	q_m , mg/g	E/K model
Bengal gram husk ⁴¹	39.99	F, L
Bengal gram husk ⁴²	42.24	L
Cassava tuber bark wastes ⁴⁴	45.61	
Cassava waste ⁴⁴ (thioglycolic acid modified)	18.05	
Cocoa shell ¹²⁶	4.94	
Coffee residues ¹²⁴ (pyrolyzed)	39.5	L
Coffee wastes ¹³⁵	1.48	
Coir pith activated carbon ³⁷	93.4	L
Corncoobs ¹³⁶	8.89	
Cornstarch ¹³⁷	8.88	L
Jack fruit peel ²⁹	52.08	Rs, L-F (Sips)
Palm sheath ¹³⁸ (petiolar felt-sheath)	10.8	
Peanut hulls ²⁵	5.96	
Peanut hulls pellets ²⁵	6.0	
Pinus pinaster bark ¹³⁹	8.0	
Rice husk ⁹⁶	2.0	L
Rice husk ⁹³	8.58	Ps, L
Rice husk ⁹³ (NaOH treated)	20.2	Ps, L
Rice husk ⁹³ (epichlorohydrin treated)	11.1	Ps, L
Rice husk ⁹³ (NaHCO ₃ treated)	16.2	Ps, L
Sawdust of <i>Pinus silvestris</i> ¹⁴⁰	9.29	Ps, L
Spent grain ¹⁴¹	17.3	Ps, L
Sterculia lychnophora seeds ¹⁴²	17.5	
Sugar beet pulp ¹⁴³	17.2	P, L
Sugar cane bagasse pith ¹⁴⁴	24.7	Ps, L
Tea wastes ¹¹³	11.3	F
Tea wastes ¹¹³ (binary system)	2.59	F
Wheat bran ³³	0.70	L

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir; Rs, Modified Ritchie second-order; Ps, Pseudo second order

Agricultural Wastes as Low Cost Metal Adsorbents

Bagasse

Bagasse, an agricultural waste from sugar industry, has been found as low cost metal adsorbent. Mohan & Singh³⁹ studied potentiality of activated carbon (AC) derived from bagasse for removal of Cd (II) and Zn (II) from aqueous solutions in single as well as multi-metal systems. Cd (II) adsorption was slightly more than Zn (II) and increased sorption capacity was reported with increase in temperature. Adsorption on bagasse-based AC occurs through a film diffusion mechanism at all concentrations³⁹. Using bagasse-based carbon, Ayyappan⁴⁰ studied adsorbent of Pb (II) under batch adsorption. Desorption of Pb (II) from sorbed carbon was achieved by eluting with 0.1M HNO₃. Carbon was

Table 2 — Chromium adsorption capacities (q_m) of agricultural waste materials

Material	q_m^a , mg/g	E/K model
Chitosan on acid treated palm shell charcoal ¹⁷	154*	L
Coir pith ⁵⁵	11.56*	Ps, L
Rice husk ⁹⁹	0.5*	
Rice husk ash ⁹⁹ (heated at 300°C)	19.09*	
Rice husk ash ⁹⁹ (heated at 600°C)	6.49*	
Rice whole with husk ⁹⁹	0.12*	
Cocoa shell ¹²⁶	2.52**	
Almond shell ¹¹⁵	10.62	F, L
Bagasse ⁸⁷	0.03	F, L
Bengal gram husk ²	91.64	F, L
Coconut husk fibers ¹⁴⁵	29	
Coconut shell activated carbon ⁴⁸ (HNO ₃ oxidized)	15.47	F, L
Coconut shell activated carbon ⁴⁸ (H ₂ SO ₄ oxidized)	8.94	F, L
Coconut shell charcoal ⁴⁸ (chitosan coated)	3.65	F, L
Coconut shell charcoal ⁴⁸ (HNO ₃ oxidized)	10.88	F, L
Coconut shell charcoal ⁴⁸ (H ₂ SO ₄ oxidized)	4.05	F, L
Eucalyptus bark ³⁸	45	Fo(L), F
Hazelnut shell activated carbon ¹¹⁸	170	L
Olive cake ¹¹⁵	33.44	F, L
Palm pressed fibers ¹⁴⁶	15	
Pine needles ¹¹⁵	5.36	F, L
Rice husk ⁹⁵	0.79	F
Rice husk ⁹⁸ (ethylene diamine modified)	23.4	
Saw dust ¹⁴⁷	39.7	
Sawdust of maple ¹⁴⁸	5.1	F, L
Saw dust ¹¹⁵	15.82	F, L
Soya cake ¹⁴⁹	0.28	F, L
Sugar beet pulp ¹⁴⁷	17.2	
Sugar cane Bagasse ¹⁴⁷	13.4	
Tamarind hull ¹³²	81	Pf, F, R-P, F-S
Tamarind seed ¹³³ (crushed)	90	Forkf, F

^aValues indicate maximum amount of Cr (VI) adsorbed (qm) at equilibrium unless otherwise mentioned, *Values for total chromium - Cr (III) + Cr (VI), **Values for Cr (III)

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir; Rs, Modified Ritchie second-order; Pf, Pseudo-first-order; Ps, Pseudo second order; R-P, Redlich-Peterson; F-S, Fritz-Schlunder; Fo(L), First order (Lagergren); Forkf, First order reversible kinetic fit model

retrieved by washing with 0.1M CaCl₂ solution and reused. Similar studies were carried with chromium also³⁸.

Bengal Gram Husk

Use of bengal gram husk (BGH) (*Cicer arietinum* L.), a milling agro waste, in single, binary and ternary

Table 3 — Copper (II) adsorption capacities (q_m) of agricultural waste materials

Material	q_m , mg/g	E/K model
Banana peel ⁷⁹	4.75	F
Banana pith carbon ¹⁵⁰	13.50	L
Bengal gram husk ⁴¹	25.73	F, L
Cassava tuber bark wastes ⁴⁴	54.21	
Cassava waste ⁴⁴ (thioglycolic acid modified)	56.82	
Cocoa shell ¹²⁶	2.87	
Coir activated ¹⁵¹	227	L
Coconut husk ¹⁵²	3.07	
Coir pith ³⁵	10.22	
Cotton seed hull carbon ¹⁵³	19.1	
Oil Palm fiber ¹⁵⁴	2.00	
Orange peel ⁷⁹	3.65	F
Peanut hull carbon ⁸⁶	65.6	L
Peanut hulls ²⁵	10.17	
Peanut hulls pellets ²⁵	9.11	
Pecan shells ¹²¹ (phosphoric modified)	95.00	
Pecan shell carbon ¹²⁰ (H ₃ PO ₄ activated)	6.84	F
Pecan shell carbon ¹²⁰ (CO ₂ activated)	0.001	F
Pecan shell carbon ¹²⁰ (steam-activated)	18.10	F
Sago industry waste ¹²⁹	12.40	Ps
Sawdust ¹⁰⁴	1.74	
Soybean hull ¹³¹ (citric acid modified)	154.90	
Sugar beet pulp ¹⁰⁹	30.90	F, L
Tea wastes ¹¹³	8.64	F
Tea wastes ¹¹³ (binary system)	6.65	F

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir; Ps, Pseudo second order

systems of metal solutions was investigated^{41,42}. Adsorbent removed heavy metal ions (Pb>Cd>Zn>Cu>Ni) efficiently from aqueous solutions and adsorption of metal increased with increasing atomic weight and ionic radii⁴². Adsorption of metal ions increased with increase in initial metal concentration. Maximum concentration of heavy metals adsorbed at equilibrium (30 min) was: Pb, 49.97; Cd, 39.99; Zn, 33.81; Cu, 25.73; and Ni, 19.56 mg g⁻¹ BGH biomass. Maximum adsorption occurred at pH 5. Efficiency of adsorbent to remove Pb (II) from binary and ternary solutions with Cd, Cu, Ni and Zn was of the same level as it was with single solution. Ahalya *et al*² demonstrated removal of 99.9% of chromium in 10 mg l⁻¹ chromium solution using 1 g BGH. Adsorption equilibrium reached within 180 min

Table 4 — Nickel (II) adsorption capacities (q_m) of agricultural waste materials

Material	q_m , mg/g	E/K model
Almond husk activated carbon ¹¹⁴	37.17	L
Bagasse ⁸⁷	0.001	F, L
Banana peel ⁷⁹	6.88	F
Bengal gram husk ⁴¹	19.56	F, L
Cocoa shell ¹²⁶	2.63	
Coir fibers ⁵⁰	2.51	L
Coir fibers ⁵⁰ (H ₂ O ₂ oxidized)	4.33	L
Coir pith ³⁵	91.63	
Coir pith activated carbon ³⁶	62.5	L
Coir pith ⁵⁵	15.95	Ps, L
Corncobs ⁷⁶	57.5	
Fluted pumpkin waste ³⁰	12.69	L
Fluted pumpkin waste ³⁰ (0.5 N 2-mercaptoethanoic acid modified)	40	L
Fluted pumpkin waste ³⁰ (1 N 2-mercaptoethanoic acid modified)	42.19	L
Hazelnut shell activated carbon ¹¹⁷	10.11	L
Orange peel ⁷⁹	6.01	F
Orange peel ⁷⁸	158	Pf
Peanut hulls ⁸⁴	53.65	L, La
Tea wastes ¹¹²	15.26	L, F
Wheat bran ¹⁵⁵	12	
Wood ash of rubber tree ¹⁵⁶	28.88	L, F, Pf

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir; La, Lagergren; Pf, Pseudo first order; Ps, Pseudo second order

at optimum pH (2). Adsorption capacity increased with increase in agitation speed. Fourier transform infrared spectroscopy (FTIR) study revealed dominance of hydroxyl and carboxyl groups in adsorption process.

Cassava Waste

Cassava tuber, a major staple food in Africa and many other parts of world⁴³, generates enormous waste biomass. Pure activated and differentially thiolated cassava waste biomass¹⁹ (0.5 M and 1 M thiolation level respectively), studied using equilibrium sorption, removed metals from aqueous solutions at following sorption rates: Cd (II), 0.2303, 0.109; Cu (II), 0.0051, 0.0069; and Zn (II), 0.0040 min⁻¹, 0.0367 min⁻¹. Increased thiolation led to increased incorporation or availability of more binding groups onto cellulosic matrix, which improved adsorptivity of cassava waste biomass. Cassava tuber bark wastes⁴⁴⁻⁴⁶ (CTBW) in pure and chemically modified forms had good potential as metal ion adsorbents from aqueous solutions and industrial effluents. From solutions containing 100 mg l⁻¹ of metal, CTBW removed: Cd, 45.61; Cu, 54.21; and Zn, 28.95 mg g⁻¹. Acid treatment of biomass enhanced sorption capacity⁴⁶ (> 50%).

Sorption of Cd (II), Cu (II) and Zn (II) on to pure and thioglycolic acid treated CTBW, studied using batch sorption technique⁴⁶ at 30°C, was fast and stable. Monolayer sorption capacity for Langmuir isotherm ranged as follows: Cd (II), 5.88-26.3; Cu (II), 33.3-90.9; and Zn (II), 22.2-83.3 mg g⁻¹.

Coconut Wastes

Coconut Shell and Fibre

Coconut shell based AC⁴⁷ removed 66% Cd (II) from water within 80 min at pH 6. Coconut shell charcoal (CSC) oxidized with nitric acid had higher Cr adsorption capacities (10.88 mg g⁻¹) than that oxidized with sulfuric acid (4.05 mg g⁻¹) or coated with chitosan (3.65 mg g⁻¹). Surface modification of CSC with a strong oxidizing agent and treatment of chitosan generated more adsorption sites on its surface for metal adsorption⁴⁸. Regeneration of CSC with NaOH and HNO₃ enabled the same column for multiple uses in subsequent cycle with more than 95% regeneration efficiency⁴⁹. Shukla *et al*⁵⁰ found that metal uptake of H₂O₂ modified coir fibres was 4.33, 7.88 and 7.49 mg g⁻¹ for Ni (II), Zn (II) and Fe (II), respectively as against 2.51, 1.83 and 2.84 mg g⁻¹ respectively for unmodified ones due to generation of carboxylic acid groups on fibre. Lowering of pH decrease metal uptake. Unground and unmodified coir⁵¹ in batch sorption removed Zn (91%) and Pb (97%).

Coir Pith

Adsorption of Cu (II) from aqueous solutions on carbonized coirpith⁵² was highest at 25 min [initial Cu (II) concentrations, 20-50 mg l⁻¹]. Removal increased from 50% to 90% with increase of pH from 2.0 to 4.0 and remained constant upto pH 10 for a Cu (II) concentration of 20 mg l⁻¹. Adsorption of metals on coirpith AC from real industrial wastewater was also studied^{35,53}. Using industrial wastewater containing Cd (II), Ni (II) and Cu (II) ions, maximum metal adsorption³⁵ occurred at pH 4.0-5.0. At initial pH (5.0) at 30°C for particle size 250-500 μm, adsorption capacities were: Ni (II)³⁶, 62.5; and Cd (II)³⁷, 93.4 mg g⁻¹. Adsorption of Ni (II) and Cd (II) increased with pH from 2.0 to 7.0 and remained constant up to 10.0. At adsorbate concentration of 20 mg l⁻¹, ZnCl₂ activated coir pith carbon⁵⁴ is an effective sorbent of Cr (VI), V (V), Ni (II) and Hg (II). Coir pith was also used for adsorption of Co (II), Cr (III) and Ni (II) from single-ion solutions as well as from a mixture⁵⁵. Optimum pH for maximum metal-ion adsorption was determined as 4.3 for Co (II), 3.3 for Cr (III) and 5.3 for Ni (II).

Table 5 — Lead (II) adsorption capacities (q_m) of agricultural waste materials

Material	q_m , mg/g	E/K model
Barley straw ¹⁵⁷	15.2	
Bengal gram husk ⁴²	49.97	L
Bengal gram husk ⁴¹	49.97	F, L
Coir ¹⁵⁸ (L)	48.84	F, L, Ps, Fo
Coir fibers ⁵¹	18.9	F, L
Hazelnut shell ¹⁵⁹	1.78	F, L
Hop leaf & stem biomass ¹²⁷	74.2	
Maize bran ¹³⁴	142.86	L
Oil palm shell activated carbon ⁶⁸	95.2	Dlsc
Rice husk ¹⁶⁰	4	
Rice husk ¹⁰²	8.6	
Sago industry waste ¹²⁹	46.6	Ps
<i>Sterculia lychmophera</i> seeds ¹⁴²	27.1	

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir; First order (Lagergren); Pf, Pseudo first order; Ps, Pseudo second order; Dlsc, Diffuse layer surface complexation model

Table 6 — Zinc (II) adsorption capacities (q_m) of agricultural waste materials

Material	q_m , mg/g	E/K model
Almond husk activated carbon ¹¹⁶ (with H ₂ SO ₄)	35.34	F, L
Almond husk activated carbon with heat ¹¹⁶	30.86	F, L
Banana peel ⁷⁹	5.8	F
Barley straw ¹⁵⁷	5.3	
Bengal gram husk ⁴¹	33.81	F, L
Cassava tuber bark wastes ⁴⁴	28.95	
Cassava waste ⁴⁴ (thioglycolic acid modified)	11.06	
Cocoa shell ¹²⁶	2.92	
Coir fibers ⁵¹	8.6	
Coir fibers ⁵⁰	1.83	L
Coir fibers ⁵⁰ (H ₂ O ₂ oxidized)	7.88	L
Orange peel ⁷⁹	5.25	F
Peanut hulls ²⁵	9	
Peanut hulls pellets ²⁵	10	
Pecan shell carbon ¹²⁰ (H ₃ PO ₄ activated)	13.9	F
Pecan shell carbon ¹²⁰ (CO ₂ activated)	6.62	F
Pecan shell carbon ¹²⁰ (steam-activated)	7.38	F
Sugar beet pulp ¹⁰⁹	35.6	F

E/K, Equilibrium/ Kinetic; F, Freundlich; L, Langmuir

Maximum adsorption capacity of coir pith was found to be: Co, 12.82; Cr, 11.56; and Ni, 15.95 mg g⁻¹.

Oil Palm Waste

Palm oil industry generates huge amounts of palm shell. Most research on palm shell carbon is focused on carbonization and activation⁵⁶⁻⁶³. Oil palm shell, because of inherent high densities and carbon content^{56,58,59,64}, produced high quality AC. Othman *et al*⁶⁵ investigated adsorption of Cd (II) and Pb on modified oil palm shell. Chu & Hashim⁶⁶⁻⁶⁷ reported application of palm oil fuel ash for removal of Cr and Zn (II) from aqueous solutions. Biosorbent prepared by coating chitosan onto acid treated oil palm shell charcoal (AOPSC) was studied for Cr removal from industrial wastewater¹⁷. AOPSC (particle size 100-150 µm) with approx. 21% w/w chitosan loading gave sorption of 154 mg Cr g⁻¹ of chitosan used at 25°C. Palm shell AC⁶⁸ showed high adsorption capacity for Pb ions (95.2 mg g⁻¹) at pH 5.0. Addition of boric acid to the solution improved total metal uptake, while malonic acid decreased uptake due to formation of Pb-malonate complex.

Olive Waste from Oil Production

Adsorption efficiency of dried olive husks has been found up to 90% for Zn (II) and Cu (II) ions⁶⁹. Increase in initial pH and decrease in particle size enhanced adsorption process. Presence of high concentration of sodium ions strongly suppressed uptake of Zn (II) ions. Pagnanelli *et al*⁷⁰ conducted preliminary studies for removal of different heavy metals (Hg, Pb, Cu, Zn and Cd), effect of pre-treatments by water and n-hexane on metal removal and regeneration possibility. Adsorption followed an affinity series reflecting hydrolytic properties of metallic ions, and particular affinity for Cu (II), which suggests a general ion exchange mechanism combined with a specific complexation reaction for Cu (II) ions. Adsorbent characterization using potentiometric titration, IR analyses and selective extractions titration modeling suggested carboxylic and phenolic groups as main active sites involved in metal removal^{32,71}.

Under equilibrium and dynamic conditions⁷², metal sorption capacity of husk was found in the sequence Pb>Cd>Cu>Zn. In dynamic tests, except for Cu (II), a significant reduction in sorption capacity (Pb, 77%; Cd, 93%; Zn, 68%) was recorded. Sorption tests with suspended olive mill residues evidenced 60% Cu (II) removal from solution⁷³. Acid regenerated residues

achieved about 40% Cu (II) removal in same experimental conditions. Regeneration with EDTA at different concentrations damaged active sites of adsorption. Malkoc⁷⁴ found maximum Cr (VI) adsorption by olive pomace at pH 2.0; total sorbed Cr (VI) and equilibrium Cr (VI) uptake decreased with increasing flow rate, and increased with increasing inlet Cr (VI) concentration. Olive stone waste⁷⁵ used as biosorbent for Pb (II), Ni (II), Cu (II) and Cd (II), gave maximum metal sorption at pH 5.5-6.0. Highest uptake was found for Cd (II) (6.88×10^{-5} molg⁻¹) followed by Pb (II) (4.47×10^{-5} molg⁻¹), Ni (II) (3.63×10^{-5} molg⁻¹) and Cu (II) (3.19×10^{-5} molg⁻¹). An increase in ionic strength concentration caused a decrease in metal removal.

Orange Wastes

Orange peel adsorbed heavy metals from wastewater^{76,77}. Ajmal *et al*⁷⁸ employed orange peel for Ni (II) removal from simulated wastewater. Maximum metal removal (158 mg g⁻¹) occurred at pH 6.0 and 50°C. This result was significantly higher than a similar study by Annadurai *et al*⁷⁹, suggesting that adsorption capacity of an adsorbent depends on initial concentration of adsorbate. Pavan *et al*⁸⁰ using Ponkan mandarin (*Citrus reticulata* Blanco) peel as biosorbent got maximum adsorption at pH 4.8 from aqueous solutions as follows: Ni (II), 1.92; Co (II), 1.37; and Cu (II) 1.31 mmol g⁻¹. Dhakal *et al*⁸¹ used orange juice residues to prepare adsorption gel (Ca²⁺ form and H⁺ form gels) for metal ions by simple chemical modification. Ca²⁺ form gel was effective for complete and selective removal of Pb (II), Cu (II) and Fe (III) compared with other divalent metal ions [selectivity order of gel: Pb (II)>Fe (III)>Cu (II)>Cd (II)>Zn (II)>Mn (II)]. Maximum loading capacities for divalent metal ions [Pb (II), Cd (II) and Zn (II)] were evaluated as 1.1 mol/kg dry gel, while 1.55 mol/kg dry gel for Fe (III). The H⁺ form gel showed a different adsorption profile for Fe (III) compared to Ca²⁺ form gel. Both gels were effective at acidic pH.

Peanut Waste

Peanut shells AC can be used to adsorb various metal ions⁸²⁻⁸⁶. Peanut hulls removed Ni (II) maximum (53.65 mg g⁻¹) at pH 4-5 from synthetic solution⁸⁵. In column studies, Periasamy & Namasivayam⁸⁶ observed maximum Cu (II) removal (65.57 mg g⁻¹) at pH 6-10 Cu (II) from synthetic solution using peanut hull. Metal removal by peanut hull in column studies was higher than that in batch studies^{25,87}. Cu (II) uptake onto peanut hulls and peanut hull pellets was optimum within pH range

5.0-7.5 in batch systems and column studies²⁶. The capacity of palletized peanut hulls was higher than that of unmodified peanut hulls. Brown *et al*²⁵ reported a slight reduction in rate of Cu (II) adsorption on to pellets than on raw peanut hulls but equilibrium capacity was found to be unaffected.

Acid treated peanut shells for metal [Cu (II), Ni (II), Zn (II), Cd (II) and Pb (II)] showed higher adsorption (19-34%) from aqueous solution as compared with only 5.7% for non-acid treated samples⁹⁰. Chamrathy *et al*⁹¹ reported that adsorption efficiencies of individual metal ions on modified peanut shells for Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) ions were at par/ higher than commercial resins Duolite GT-73, Amberlite IRC-718 and carboxymethylcellulose. Wilson *et al*⁸⁸ used peanut shells for adsorption of Cd (II), Cu (II), Pb (II), Ni (II) and Zn (II). Johns *et al*⁸⁹ reported that granular AC produced from peanuts by a combination of CO₂ or steam activation followed by air oxidation, was excellent adsorbent for metal pollutants. Granular AC made from peanut shells adsorbed Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) ions to a greater extent than comparable CACs.

Amounts of Cu (II), Zn (II) and Ni (II) ions adsorbed onto peanut shell⁹² increased while that of Cr (VI) ions decreased with increasing equilibrium pH of solution. Maximum uptake of Cr (VI) ions was found at a pH below the point of zero charge of adsorbent (pH[pzc]) and vice versa for Cu (II), Zn (II) and Ni (II). The amount of metal cation adsorbed at given equilibrium concentration increased in the order: Ni (II) < Zn (II) < Cu (II). Peanut shell AC is effective for metal cations at pH $e \geq$ pH[pzc] and anions at pH $d \geq$ pH[pzc].

Rice Husk

Rice husk has good metal affinity and has potential for use as a low cost sorbent⁹³. Roy *et al*⁹⁴ demonstrated applicability of ground rice hulls for adsorption of heavy metals [As, Cd, Cr, Pb (>99%) and Sr (94%)]. Maximum Cr (VI) removal (23.4 mg g⁻¹) by rice husk AC from aqueous solution is reported⁹⁵ at pH 2.0. Chemical pretreatment of rice husk showed varied degree of effects in adsorbing heavy metal from solution^{95,96}. Daifullah *et al*⁹⁷ used rice husk in removal of metals from a complex matrix containing six heavy metals (Fe, Mn, Zn, Cu, Cd and Pb) and metal removal efficiency of sorbent was approx. 100%. Modified rice husk was investigated for Cr (VI) removal from simulated solution⁹⁸. Maximum adsorption capacities of untreated rice with husk (URH), rice husk (RH), rice husk ash heated at 300°C (RHA-

300) and 600°C (RHA-600) were 0.12, 0.50, 19.09 and 6.49 mgCr g⁻¹ adsorbent, respectively and 0.47, 294, 18.34 and 4.90 mgBi g⁻¹ adsorbent, respectively, showing RHA-300 as the most effective adsorbent⁹⁹. At optimum conditions (pH 4.0, flow rate 8.0 ml min⁻¹ and particle size $d=355 \frac{1}{4}m$), 30 g of husks was necessary to attain permissible limits¹⁰⁰ for effluent release for Al, Cd, Cu, Pb and Zn. Batch adsorption of Cd (II) from wastewater with modified rice husk⁹³ showed that sorption capacity increased from 8.58 mg g⁻¹ (raw rice husk, RRH) to 11.12, 20.24 and 16.18 mg g⁻¹ and reduced equilibrium time from 10 h for RRH to 2, 4 and 1 h for epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH) and sodium bicarbonate treated rice husk (NCRH) respectively. Bhattacharya *et al*¹⁰¹ observed that adsorption of Zn (II) was maximum with 10 g l⁻¹ rice husk at pH 5-7. Zulkali *et al*¹⁰² investigated optimum conditions (initial metal concentration, 50 mg l⁻¹; temperature, 60°C; biomass loading, 0.2 g; and pH, 5.0) for maximum uptake (98.11%) of Pb (II).

Sawdust

Several researchers¹⁰³⁻¹⁰⁵ reviewed sawdust as adsorbent for metals and other pollutants from water. Ajmal *et al*¹⁰⁶ observed that phosphate treatment of sawdust from mango tree, used for Cr (VI) removal from electroplating wastewater, improved adsorption capacity (100% adsorption at pH<2 and initial concentration of 8-50 mg l⁻¹). Almost 87% of sorbed chromium was recovered by treating with 0.01 M NaOH. Adsorption-desorption cycles¹⁰⁷ showed that Cu (II) binding capacity of sawdust stabilized at 3.1×10^{-2} meq g⁻¹. Competitive ion exchange exhibited in adsorption from mixture of ions showed order of affinity for sawdust as Ni (II) < Zn (II) < Cd (II) < Cu (II) < Pb (II). Desorption of Pb (II) from sorbed carbon from sawdust⁴⁰ was achieved by eluting with 0.1 M HNO₃. Carbon could be retrieved by washing with 0.1 M CaCl₂ solution and reused. Sciban *et al*¹⁰⁸ examined kinetics of Cu (II), Zn (II) and Cd (II) adsorption on poplar wood sawdust from electroplating wastewater. Adsorption of Cu (II) ions from a mixture was better than that from a single metal solution. Zn (II) showed no change while Cd (II) adsorption was lower in mixture than in single metal solution, due to a difference in binding affinity between ions that reinforces competitive nature of adsorption¹⁰⁷.

Sugarbeet Pulp

Batch adsorption of sugarbeet pulp¹⁰⁹ (SBP) reached equilibrium by 60 min of contact and achieved 60%

removal of Cu (II) and Zn (II); a highest up to 30.9 mg g⁻¹ for Cu (II) at pH 5.5 and 35.6 mg g⁻¹ for Zn (II) at pH 6.0. In another study¹¹⁰, sugarbeet pulp AC, with initial Cd concentrations of 100, 250 and 500 mg l⁻¹ at 120 min, 20°C, pH 6.3 and adsorbent dose of 2.5 g l⁻¹, removed Cd as 99.0, 78.2 and 57.0% respectively. Reddad *et al.*¹¹¹ studied Ni (II) and Cu (II) binding properties of raw and sugar beetpulp modified by saponification, hot 0.05 M HCl and cold 0.05 M NaOH extractions. Base-extracted pulp and saponified pulp exhibited highest Ni (II) and Cu (II) ion removal.

Tea Factory Waste

Malkoc & Nuhoglu¹¹² observed 15.26 mg Ni (II) g⁻¹ adsorption on tea waste at 25°C and initial pH of 4.0. Adsorption reactions were spontaneous ($\Delta G < 0$), slightly endothermic ($\Delta H > 0$) and irreversible ($\Delta S > 0$). Maximum adsorption capacities of Cu (II) and Cd (II) of Turkish tea waste¹¹³ were 8.64±0.51 and 11.29±0.48 mg/g for single and 6.65±0.31 and 2.59±0.28 mg/g for binary systems, respectively.

Wastes from Tree Nuts

Hasar¹¹⁴ found maximum Ni (II) adsorption (37.17 mg g⁻¹) from simulated solution using almond husk AC at pH 5.0. Ni (II) adsorption capacity of almond husk (37.17 mg g⁻¹) was almost four times than that of Cr (VI) adsorption by almond shell¹¹⁵ (10.67 mg g⁻¹) because cell walls of almond husk contain a higher concentration of cellulose, silica and lignin than those of almond shell. Almond husk has more hydroxyl and carboxylic groups than almond shell for metal adsorption, resulting in higher metal removal by almond husk¹¹⁴. AC from almond husks¹¹⁶ at optimum conditions (initial metal conc. 20 mg l⁻¹, pH 5.5, temp. 70°C, contact time 60 min and adsorbent conc. 4 g l⁻¹) removed 92% of Zn (II) ions

Demirbas *et al.*¹¹⁷ observed that hazelnut shell AC removed from simulated solution maximum Ni (II) (initial metal conc. 15 mg l⁻¹) at pH 3.0 with metal adsorption capacity of 10.11 mg g⁻¹. In another study¹¹⁸, hazelnut shell was also employed for Cr (VI) adsorption from simulated solution [pH 1, initial Cr (VI) conc. 1000 mg l⁻¹]. Kinetic models for adsorption of Ni (II) ions on to hazelnut shell AC have been compared¹¹⁹. Pseudo-second order kinetic model correlated better to the data from batch reactions (initial metal ion conc., 11.87-92.34 mg dm⁻³; agitation speed, 50-200 rpm; and particle size, 0.90-1.60 mm).

Treated pecan shells¹²⁰ [PSA (phosphoric acid-activated pecan shell carbon), PSC (carbon dioxide-activated pecan shell carbon); PSS (steam-activated pecan shell carbon)] have good removal capacities for Cu (II) and Zn (II) ions removal from real wastewater. At pH 3.6, adsorption capacity of pecan shells¹²¹ for Cu (II) (95 mg g⁻¹) was higher than that of SR5 resins (80 mg g⁻¹). At pH higher than 8.5, pecan shells had an adsorption capacity of 180 mg g⁻¹, almost two times higher than that at pH 3.6. This measured Cu (II) adsorption capacity was not a reliable result since, at pH higher than 8.5, Cu (II) ions precipitated in the form of hydroxide, thus increasing metal removal from solution.

Miscellaneous Materials

Jatropha (*Jatropha curcas* L.) seed coat¹²², due to electrostatic attraction of Cu (II) towards lignocellulosic polar groups, removed Cu (II) (82-89%) in 80 min. *Jatropha* oil cake¹²³ showed maximum Cr (VI) adsorption at pH 2. Pyrolyzed coffee residue¹²⁴ removed from synthetic solution of metals in the order of Cd (II) > Cu (II) > Zn (II) > Ni (II). Sorption on 2% grape stalks encapsulated in calcium alginate beads was examined in a continuous packed bed column¹²⁵. Total uptake decreased with increasing flow rate and increased with increasing inlet Cr (VI) concentration. Charred jackfruit peel made by sulphuric acid treatment was used to study Cd (II) removal from aqueous solution²⁹. Cocoa shells¹²⁶ (15 g l⁻¹) adsorbed 161 mmol kg⁻¹ of Pb from aqueous solutions. Horsfall & Spiff³⁰ assessed differential sorption behaviour of pure and acid treated fluted pumpkin (*Telfairia occidentalis* Hook. f.) waste biomass on the adsorption of Ni (II) ion from aqueous solution. Hop plant (*Humulus lupulus* L.) was employed for removal of lead (II) ions from contaminated aqueous solutions¹²⁷. Batch adsorption study was carried for Cd (II) removal using shelled moringa (*Moringa oleifera* Lam.) seed powder¹²⁸. Sago processing waste was used to adsorb Pb (II), Cu (II)¹²⁹ and Hg (II)¹³⁰ ions from aqueous solution. Soybean hull¹³¹ pretreated with NaOH and citric acid, remarkably improved its metal removal capacity. Using tamarind hull¹³², removal of chromium enhanced from 33% to 99% with a pH change from 5.0 to 1.0. Crushed tamarind seeds have been used as chromium biosorbent¹³³. Singh *et al.*³³ reported that wheat bran removed maximum Cd (II) (87.15%) at pH 8.6, initial Cd (II) concentration of 12.5 mg l⁻¹ and temperature 20°C. Singh *et al.*¹³⁴ used maize bran for optimum removal of Pb (II) (98.4%) at 20°C, pH 6.5 and initial metal concentration 100 mg l⁻¹.

Comparison of Metal Adsorption Capacities of Adsorbents from Agro-wastes with CAC

Adsorption capacities of low cost adsorbents were found to be comparable and in some cases better than that of CAC. Materials like citric acid modified soybean hull¹³¹ [Cr (VI), 154.9 mg g⁻¹], maize bran (142.86 mg Pb(II) g⁻¹)¹³⁴, orange peel (158 mg Ni(II) g⁻¹)⁷⁸, chitosan coated on acid treated palm shell charcoal (154 mg Cr(VI) g⁻¹)¹⁷, oil palm shell AC (95.2 mg Pb(II) g⁻¹)⁶⁸, coir pith (91.63 Ni(II) g⁻¹)³⁵ coir pith AC (93.4 mg Cd(II) g⁻¹)³⁷ are found to have superior metal adsorbing capabilities when compared with CAC [Cd(II) 146 mg g⁻¹, Cr(VI) 145 mg g⁻¹, Cu(II) 15.47 mg g⁻¹, Pb(II) 41 mg g⁻¹, Zn(II) 20 mg g⁻¹]^{120,147,161,163}. Thus, low cost adsorbents from agricultural wastes are good for substituting CAC.

Conclusions

Agricultural wastes, being porous and lightweight due to fibrous nature, are non-conventional low cost adsorbents for metal adsorption. Carboxylic and hydroxyl functional groups on surface of agricultural wastes have high affinity for heavy metal ions. Physico-chemical modifications of wastes can enlarge surface area, type of adsorbing sites, porosity etc, thus improving sorptive capacity, which may compensate for the cost of additional processing. Regeneration of spent adsorbent has become a cost effective and sound environmental option. Desorption and regeneration can be done to recover valuable metal from spent adsorbent. Hydroxyl and carboxylic groups in agricultural wastes make them amenable to easy desorption and regeneration with basic or acid solutions.

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