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# Asian Journal of Organic & Medicinal Chemistry

**Special Issue** 

on

Current Research in Chemistry and Nanosciences (CRCNS-2022)

#### Acid-base Modified Biosorbent for Heavy Metal Removal - A Review

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#### ABSTRACT

The heavy metals Cu, Cd, Ni, Cr, Pb, As and Bi removal by modified low cost adsorbents were reviewed in the current article. The present study focuses on enhancement of adsorption of metal by acid-base modification of low cost adsorbent. An acid modification were carried out by H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, citric acid and tartaric acid while base modification were carried out by NaOH, K<sub>2</sub>CO<sub>3</sub> and KOH. The review represents various parameters such as activation agent of adsorbent by acid-base, type of adsorbent, characterization methods viz. SEM, EDS, FTIR, BET and maximum adsorption capacity of heavy metals. Adsorption method is found superior for removal of pollutant from waste water than any other conventional method. The adsorption of metal on adsorbent surface occurred by physical sorption, chemical sorption, complexation, ion exchange and through pore diffusion process. Agricultural waste adsorbents are found good alternative due its negligible cost, easy availability and maximum adsorption capacity.

**KEYWORDS:** Heavy metals; Adsorbent; Acid-base treatment; SEM; BET

#### INTRODUCTION

Heavy metals are major toxic pollutants specially found in waste water discharges from different industries. The process of metal extraction from ore such as mining, roasting, pulverizing, refining greatly contributes the heavy metal accumulation into the waste water while the fertilizer industry, tanneries, pesticides, batteries, electroplating and paper industries also introduces heavy metal into the environment<sup>1</sup>. Heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Cobalt (Co), Lead (Pb), Zinc (Zn), Arsenic (As) Vanadium (V) and Nickel (Ni) shows adverse effect on animals as well as aquatic life<sup>2</sup>. The effluent of industrial waste containing large amount of toxic heavy metals without prior treatment causes hazardous effect to aquatic life. Many of the heavy metals are non-biodegradable and hence accumulate in the food chain which reduces the human life<sup>3</sup>. Cadmium (Cd) is carcinogenic and responsible for Itai-Itai disease, anemia, dyspnea, Chromium causes lungs tumor and allergic dermatitis, Copper (Cu) gives liver illness, diarrhea, headache, Mercury affects on kidney, nervousness, unconsciousness, Nickel (Ni) causes anaphylaxis and damages red blood cells, lead (Pb) affects on appetite loss, kidney failure, high blood pressure, anemia and Zinc (Zn) causes restlessness and metal fume fever<sup>4</sup>.

Nowdays numerous techniques are available for the removal of heavy metals such as precipitation, oxidation, reduction, ultrafiltration, reverse osmosis, electro dialysis and ion exchangers<sup>5</sup>. Due to increase in processing cost, low efficiency, low sensitivity, all these techniques have certain limitations for heavy metal removal from waste water. Adsorption is an advantageous technique over the all of these methods due to low cost and greater removal efficiency of metal from waste water<sup>6</sup>. An activated carbon adsorbent used for heavy metal removal shows greater removal efficiency and easy operating process but due to its high cost it have some limitation. The adsorbent prepared from fly ash, sludge, industrial waste, zeolites and agricultural waste has great significance for heavy metal removal <sup>7-8</sup>.

In the current review article, the surface modification for various low cost adsorbents by acid-base treatment is

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explored. The absorption efficiency of adsorbent can be enhanced by activation viz. physical method and

chemical method<sup>9</sup>. The present work summarizes the effect of modification of various adsorbents by treatment with sulphuric acid, hydrochloric acid, nitric acid, tartaric acid, phosphoric acid while with base sodium hydroxide, potassium hydroxide, potassium carbonate and calcium hydroxide.

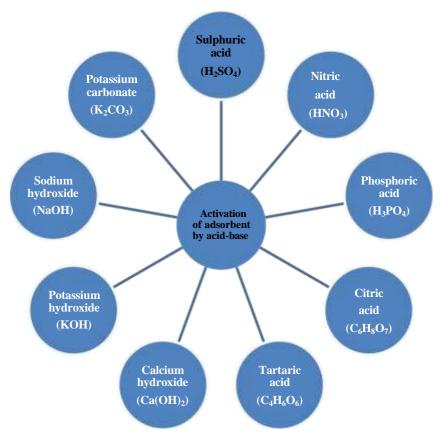


Figure 1. Activation of adsorbent by various Acid-Base treatment

**Modification of adsorbent by acid treatment:** The removal of Cu from agricultural waste adsorbent like bagasse on activation with citric acid was investigated by Meenal Gupta et al.<sup>10</sup>. Sulphuric acid treatment for various adsorbents namely areca catechu <sup>11</sup>, Cynodon Dactylon <sup>12</sup>, Henna leaves <sup>13</sup>, Cashew nut<sup>14</sup> were carried out and found maximum adsorption capacity for Cu 1.33 mg/g, 90.35 mg/g, 3.65 mg/g and 406.6 mg/g respectively. An azadirechta indica leaf <sup>26</sup> on phosphoric acid treatment shows higher adsorption capacity 110.9 mg/g for Cr removal while Macadamia activated carbon<sup>15</sup> on treatment with sulphuric acid, phosphoric acid and nitric acid shows 25.75 mg/g, 25.43 mg/g and 38.59 mg/g respectively. Sorghum bicolor <sup>19</sup> and Cassava peel <sup>28</sup> adsorbents on sulphuric acid modification for Cr shows maximum adsorption capacity 25.64 mg/g and 10.07 mg/g respectively. The adsorption efficiency of toxic metal Cd was investigated by sulphuric acid treated cashew nut shell <sup>14</sup>, phosphoric acid treated azadirechta indica leaf <sup>26</sup> and sulphuric acid modified cassava peel <sup>28</sup>. Lapsi seed stone <sup>21</sup> on activation with mixture of sulphuric acid-nitric acid shows maximum adsorption capacity 47.62 mg/g and 13.51 mg/g respectively.

Ponnusamy Senthil Kumar et al.<sup>14</sup> studied on removal of Zn by using low cost adsorbent Cashew nut shell. The prepared adsorbent was characterized by FTIR and SEM. The maximum adsorption capacity was found 455.7 mg/g while the Palm midrib <sup>23</sup> on citric acid and tartaric acid treatment and azadirechta indica<sup>26</sup> on phosphoric acid treatment shows 5.72 mg/g and 133.3 mg/g respectively. Sartape Ashish et al. explored the use of coconut shell adsorbent <sup>22</sup> on activation with sulphuric acid for the removal of Bi and the activated adsorbent was characterised by FTIR, SEM and BET surface area analyser. The amount of removal of Pb were investigated on sulphuric acid activated maize tassel <sup>25</sup>, phosphoric acid treated azadirechta indica leaf <sup>26</sup>, nitric acid activated baggasse, palm pit, saw dust <sup>27</sup>, sulphuric acid treated cassava peel <sup>28</sup>. An elemental analysis and Boehm method were applied to characterise the prepared adsorbent.

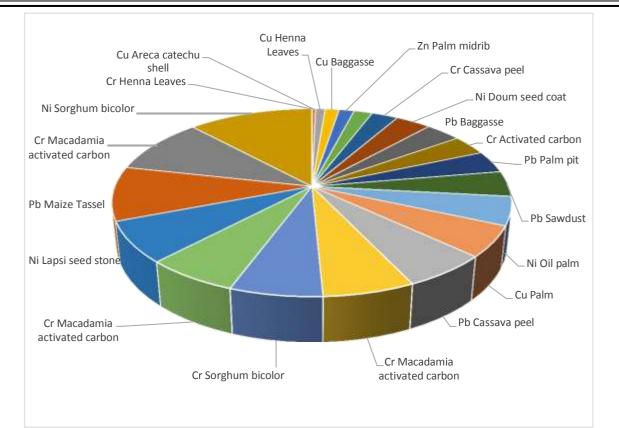


Figure 2. Heavy metal adsorption capacity between 0.078 to 47.62 mg/g by different acid treated adsorbents

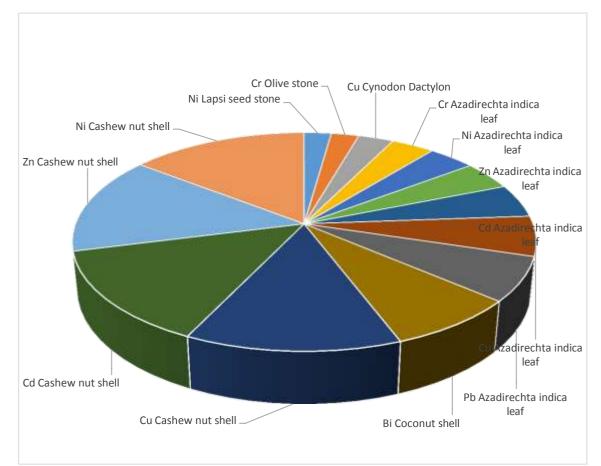


Figure 3. Heavy metal adsorption capacity between 69.49 to 456.3 mg/g by different acid treated adsorbents

Heavy metal	Adsorbent	Modifying agent	Characterizations	Maximum adsorption capacity mg/g	Ref
Cu	Baggasse	Citric acid	FTIR, SEM	5.35	10
Cu	Areca catechu shell	$H_2SO_4$	FTIR, SEM	1.33	11
Cu	Cynodon Dactylon	$H_2SO_4$	FTIR, XRD, SEM	90.35	12
Cu	Henna Leaves	H <sub>2</sub> SO <sub>4</sub>		3.65	13
Cr	Henna Leaves	$H_2SO_4$		0.078	13
Cu	Cashew nut shell	$H_2SO_4$	FTIR, SEM	406.6	14
Cd	Cashew nut shell	H <sub>2</sub> SO <sub>4</sub>	FTIR, SEM	436.7	14
Zn	Cashew nut shell	H <sub>2</sub> SO <sub>4</sub>	FTIR, SEM	455.7	14
Ni	Cashew nut shell	H <sub>2</sub> SO <sub>4</sub>	FTIR, SEM	456.3	14
Cr	Macadamia activated carbon	H <sub>2</sub> SO <sub>4</sub>	FTIR, TGA, EDAX, BET	25.75	15
Cr	Macadamia activated carbon	H <sub>3</sub> PO <sub>4</sub>	FTIR, TGA, EDAX, BET	25.43	15
Cr	Macadamia activated carbon	HNO <sub>3</sub>	FTIR, TGA, EDAX, BET	38.59	15
Cr	Activated carbon	HNO <sub>3</sub>	EAS, Boehm method	13.74	16
Cr	Olive stone	$H_2SO_4$	FTIR	71	17
Ni	Oil palm	H <sub>3</sub> PO <sub>4</sub>		19.6	18
Cr	Sorghum bicolor	$H_2SO_4$	BET, FTIR	25.64	19
Ni	Sorghum bicolor	$H_2SO_4$	BET, FTIR	47.62	19
Ni	Doum seed coat	H <sub>3</sub> PO <sub>4</sub>	FTIR,	13.51	20
Ni	Lapsi seed stone	H <sub>2</sub> SO <sub>4</sub>	FTIR, Boehm method	28.25	21
Ni	Lapsi seed stone	$H_2SO_4$ and $HNO_3$	FTIR, Boehm method	69.49	21

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Bi	Coconut shell	H <sub>2</sub> SO <sub>4</sub>	SEM, FTIR, BET	250	22
Zn	Palm midrib	Citric acid and tartaric acid	SEM	5.72	23
Cu	Palm	H <sub>3</sub> PO <sub>4</sub>	FTIR, BET	21.23	24
Pb	Maize Tassel	$H_2SO_4$	XRD, FTIR	37.31	25
Pb	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	205.6	26
Cu	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	185.8	26
Cd	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	154.5	26
Zn	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	133.3	26
Ni	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	120.6	26
Cr	Azadirechta indica leaf	H <sub>3</sub> PO <sub>4</sub>	BET	110.9	26
Pb	Baggasse	HNO <sub>3</sub>	Element analysis, Boehm method,	13.7	27
Pb	Palm pit	HNO <sub>3</sub>	Element analysis, Boehm method	15.20	27
Pb	Sawdust	HNO <sub>3</sub>	Element analysis, Boehm method	17.5	27
Pb	Cassava peel	$H_2SO_4$	Nitroperchloric digestion method, FAAS	24	28
Cd	Cassava peel	$H_2SO_4$	Nitroperchloric digestion method, FAAS	7.05	28
Cr	Cassava peel	$H_2SO_4$	Nitroperchloric digestion method, FAAS	10.07	28

**Modification of adsorbents by base treatment:** Bagasse <sup>10</sup>, green vegetable waste <sup>29</sup>, rice husk <sup>30</sup> and orange peel <sup>31</sup> have been used as adsorbent for removal of Cu from its solution. Green vegetable waste was modified by potassium hydroxide while other adsorbents were modified with sodium hydroxide. The author carried out the FTIR, SEM, EDS, TGA and BET characterization for the activated biosorbent material. Green vegetable waste biosorbent shows higher adsorption capacity 75 mg/g in comparison with other adsorbent. The removal of Cd by sodium hydroxide treated biosorbent such as sawdust, wheat straw, corn stalk <sup>32</sup> and rice husk <sup>33</sup> shows adsorption capacity 40.78, 38.75, 30.40, 8.50 mg/g respectively. Rice husk <sup>33</sup> on modification with potassium hydroxide and calcium hydroxide changes adsorption capacity 8.24 mg/g and 10.46 mg/g respectively.

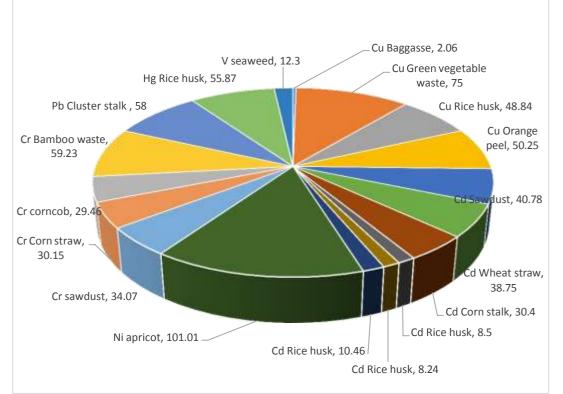


Figure 4. Heavy metal adsorption capacity between 2.06 to 101.01 mg/g by different base treated adsorbents.

S. Erdogan et al. utilised potassium carbonate treated apricot <sup>34</sup> adsorbent for the removal of Ni ion. The prepared biosorbent was characterised by BET and FAAS and shows maximum adsorption capacity 101.01 mg/g. The study of adsorption of Cr by potassium hydroxide activated sawdust, corn straw and corncob <sup>35</sup> were carried out by Shujauddin Khushk et al. The higher adsorption capacity 59.23 mg/g was observed by bamboo waste <sup>36</sup> while corncob shows minimum adsorption capacity 29.46 mg/g. The sawdust and corn straw shows maximum adsorption capacity 34.07 mg/g and 30.15 mg/g respectively. Francisco Jose Alguacil et al. explored the use of cluster stalk <sup>37</sup> on potassium hydroxide activation for Pb ion adsorption.

The poisonous Hg metal adsorption has been investigated by Zhiyuan Liu et al. by rice husk <sup>38</sup> adsorbent on activation with potassium hydroxide. The material was characterised by SEM, FTIR, BET and XPS. The maximum amount of Hg removal by rice husk was found 55.87 mg/g. The seaweed <sup>39</sup> is used as low cost adsorbent on modification with potassium hydroxide and found 12.3 mg/g of maximum adsorption capacity for Vanadium removal.

Heavy metal	Adsorbent	Modifying agent	Characterization	Maximum adsorption capacity mg/g	Ref.
Cu	Baggasse	NaOH	FTIR,SEM	2.06	10
Cu	Green vegetable waste	КОН	SEM, TGA, DSC, FTIR	75	29
Cu	Rice husk	NaOH	FTIR, SEM, EDX	48.84	30
Cu	Orange peel	NaOH	FTIR, SEM, BET	50.25	31
Cd	Sawdust	NaOH	FTIR, SEM, BET, XRD	40.78	32
Cd	Wheat straw	NaOH	FTIR, SEM, BET, XRD	38.75	32
Cd	Corn stalk	NaOH	FTIR, SEM, BET, XRD	30.40	32

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Cd	Rice husk	NaOH	FTIR	8.50	33
Cd	Rice husk	КОН	FTIR	8.24	33
Cd	Rice husk	Ca(OH) <sub>2</sub>	FTIR	10.46	33
Ni	apricot	K <sub>2</sub> CO <sub>3</sub>	BET, FAAS	101.01	34
Cr	sawdust	КОН	SEM, BET, FTIR	34.07	35
Cr	Corn straw	КОН	SEM, BET, FTIR	30.15	35
Cr	corncob	КОН	SEM, BET, FTIR	29.46	35
Cr	Bamboo waste	КОН	FTIR	59.23	36
Pb	Cluster stalk	КОН	FTIR, BET	58	37
Hg	Rice husk	КОН	SEM, FTIR, BET, XPS	55.87	38
V	seaweed	КОН	SEM, EDS, FTIR, BET, XPS	12.3	39

From the literature review it is observed that many researchers applied the acid and base activation method to activate the adsorbent. S. Abdic et al. (2018) studied on the heavy metal removal by modified and unmodified tangerine peel adsorbent <sup>40</sup>. The author reported that 40% of adsorption efficiency enhanced by adsorbent modification. The sulphuric acid is most commonly used acid activating agent for activation of adsorbents. An acid and base activation method is simple, effective, time saving and economical than any other chemical method. The activation of functional group on adsorbent surface found successful and which is identified by adsorbent characterization.

#### CONCLUSION

In the current review, the biosorption of heavy metal on acid-base treated adsorbents have been studied. Agricultural waste material used as low cost adsorbent for heavy metal removal was found highly efficient and environmental healthy. It was observed that the modified adsorbent by acid-base chemical treatment shows better adsorption efficiency than non-modified adsorbents. An acid-base treatment has been most widely used for surface modification because of its specific impact on surface to adsorb target pollutant. Due to surface modification, the increase in pore volume and pore size generates more active sites for adsorption which is characterized by BET surface area analysis. A new functional group binding sites are formed due to activation which results into more uptake of metal ion from solution. The researcher were studied the presence of different functional groups on adsorbent surface and characterized by FTIR while the surface morphology were studied by SEM analysis. The amount of adsorption of metal ion depends on various factors such as adsorbent dose, pH of the solution, temperature, modifying method and nature of adsorbent. These type of modified adsorbent is helpful for industrial waste water treatment and will used to reduce the environmental pollution.

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