

## Activated carbon derived from lignocellulosic materials as a bioadsorbent for heavy metal removal: A review

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**Abstract:** Adsorption is one of the upcoming techniques for waste water remediation due its non-destructive properties and its ability to target wide range of contaminants. Different types of adsorbents include agro-based adsorbents, raw or modified minerals, polymeric materials, nanomaterials and so on. Modification of agro-based adsorbents or lignocellulosic materials using acids, alkali, surfactants, copolymers, nanomaterials leads to increase in adsorption capacity and improve its textural properties. Activated carbon posses larger surface area, chemical inertness, mechanical stability and hence are one of the promising adsorbents for removal of heavy metals from waste water. Also conversion of lignocellulosic materials to activated carbon helps to convert it to valuable useful substances. The present review includes various lignocellulosic materials for fabrication of activated carbon, effect of activating agent and carbonization temperature on surface properties, and their applicability in adsorption of heavy metals from aqueous phase.

**Keywords:** Adsorption, Activated carbon, physical activation, chemical activation, heavy metals.

### 1. Introduction

Activated carbon is defined as carboniferous solid material obtained from animals, plants or minerals by chemical, physical or microwave assisted treatment via pyrolysis [1-2]. Activated carbons are most adaptable adsorbents due to its enormous surface area, enhanced adsorption capacity, erratic surface chemical composition, polymodal porous arrangement, chemical inertness and superior mechanical stability [3-4]. The favorable adsorption of heavy metals onto the activated carbon occurs due its larger surface area, microporous ability and chemical intricacy of its peripheral area [5]. Adsorption onto contemporary solids is one of the upcoming methods for waste water remediation. Adsorption process is non-destructive, technologically compliant and highly efficient for wide range of target contaminants [6]. The production of activated carbon from agricultural byproducts results in conversion of superfluous profitless materials to valuable adsorbents [7]. The preparation of activated carbon comprise of two different steps: First, carbonization or pyrolysis of the precursor and second activation [8]. Activation process mainly involves physical or chemical activation. In physical activation, carbonization of carboniferous substance is done to confiscate the bulk of volatile matter after which the activation of resulting char is done in the presence of activating agents like carbon dioxide, steam, air or combination of these agents. In chemical activation, precursor is impregnated with chemicals such as NaOH, KOH, H<sub>2</sub>SO<sub>4</sub>, ZnCl<sub>2</sub> and then pyrolyzed in an inert atmosphere as single step process [9]. Chemical activation results in uniformity of pore distribution and higher carbon yields [10]. However physical activation process is cost effective; it also eliminates the usage of chemicals and post washing process. Physical activation process requires high consumption of energy as compared to chemical activation and results in lower carbon yields. In contrast to it chemical activation results improved surface chemistry and textural characteristics [11]. This review includes preparation of activated carbon from various lignocellulosic materials, effect of chemical activating agents and carbonization temperature on properties of activating carbon,

removal of heavy metals by adsorption onto them, adsorption isotherms and kinetic models applicable to the uptake.

### 2. Heavy metal removal from wastewater by adsorption onto activated carbon derived from lignocellulosic materials

Soliman et al. studied the uptake of Pb<sup>2+</sup> from aqueous solution by adsorption onto activated carbon derived from H<sub>2</sub>SO<sub>4</sub> impregnated palm leaves. The study revealed that the alkalinity of carbon samples increased with increase in temperature due to decomposition of functional groups analogous to carboxylic acid and partial calcination of inorganic components. Thus, activated carbon derived at 250°C was utilized for further batch experiments. The optimum conditions for uptake of Pb<sup>2+</sup> from aqueous solution were found to be pH= 5.5, adsorbent dosage 5g/L, concentration of Pb<sup>2+</sup> solution = 100 ppm and equilibrium time= 3h. The evaluation of thermodynamic parameters revealed chemisorption and endothermic nature of adsorption process; langmuir model best fitted the adsorption process (Table 1) [12]. Lalhruiatluanga et al. carried out chemical activation of *M. baccifera* charcoal using H<sub>3</sub>PO<sub>4</sub> and KOH and studied its effect on adsorption capacity to uptake Pb<sup>2+</sup> from aqueous solution. The chemical activation using 60% KOH showed highest adsorption of Pb<sup>2+</sup>. The chemical activation using alkali results in the formation of enhanced carboxylate (-COO) and hydroxyl group (-OH) due to hydrolysis and hence adsorption capacity increases. The adsorption of Pb<sup>2+</sup> on raw and modified *M. baccifera* charcoal was best described by pseudo second order kinetic model and Langmuir adsorption isotherm (Table 1) [16]. Similarly, activated carbon derived from cassava peels using H<sub>3</sub>PO<sub>4</sub> acid activation was evaluated for their adsorption potential to uptake Pb<sup>2+</sup> and Cu<sup>2+</sup> from aqueous solution (Tables 1 and 2) [17]. The uptake of Pb<sup>2+</sup> from wastewater by activated carbon derived from waste cluster stalks was best described by Langmuir adsorption isotherm and pseudo second order kinetic model. N<sub>2</sub> adsorption-desorption isotherm confirms the microporous structure of activated carbon derived from waste cluster stalks (Table 1) [18]. Moyo et al. demonstrated Pb<sup>2+</sup> uptake from aqueous solution using

**Table 1.** Precursors and activating agents for activated carbon preparation from lignocellulosic materials for adsorption of Pb<sup>2+</sup> onto them.

Sr.no	Lignocellulosic precursor	Activating agent	Activation temperature(°C)	Specific surface area m <sup>2</sup> /g	reference
1	Date palm	H <sub>2</sub> SO <sub>4</sub>	250-450	64.12	[12]
2	<i>Cicer arietinum</i>	KOH, K <sub>2</sub> CO <sub>3</sub>	850	2082	[13]
3	<i>Melocanna baccifera</i>	H <sub>3</sub> PO <sub>4</sub> , KOH	----	-----	[16]
4	Cassava	H <sub>3</sub> PO <sub>4</sub>	300	----	[17]
5	Cluster stalks	KOH	799.85	1194	[18]
6	Maize tassel	H <sub>2</sub> SO <sub>4</sub>	---	250	[20]
7	Doum palm	ZnCl <sub>2</sub> , NaOH, KOH	500	0.84, 226.41, 5.41	[21]
8	African palm fruit	H <sub>3</sub> PO <sub>4</sub>	300	-----	[23]
9	<i>Albizia lebbbeck</i>	HCl	550	-----	[29]
10	<i>Melia azedarach</i>	HCl	550	----	[29]
11	<i>Zea Mays L</i>	H <sub>3</sub> PO <sub>4</sub>	300	-----	[30]
12	<i>Salix matsudana</i>	H <sub>3</sub> PO <sub>4</sub>	550	435.65	[31]
13	<i>Ulva lactuca</i>	KOH	800	345.40	[32]
14	<i>Bambusa vulgaris striata</i>	Water stream	650	608	[33]
15	Hazelnut husk	K <sub>2</sub> CO <sub>3</sub>	600	980.9	[34]
16	<i>PhoenixDactylifera</i> bead	ZnCl <sub>2</sub>	300	850	[38]

**Table 2.** Precursors and activating agents for activated carbon preparation from lignocellulosic materials for adsorption of Cu<sup>2+</sup> onto them.

Sr.no	Lignocellulosic precursor	Activating agent	Activation temperature(°C)	Specific surface area m <sup>2</sup> /g	Reference
1	<i>Cicer arietinum</i>	KOH, K <sub>2</sub> CO <sub>3</sub>	850	2082	[13]
2	Grape bagasse	H <sub>3</sub> PO <sub>4</sub>	400-600	1455	[14]
3	<i>Phoenix Dactylifera</i>	CaO	499.85	645.5	[15]
4	Cassava	H <sub>3</sub> PO <sub>4</sub>	300	-----	[17]
5	African palm fruit	H <sub>3</sub> PO <sub>4</sub>	300	-----	[23]
6	<i>Ulva lactuca</i>	KOH	800	345.40	[32]
7	Rice hulls	ZnCl <sub>2</sub>	749.85	-----	[35]
8	Chestnut shell	ZnCl <sub>2</sub>	549.85	1319	[36]
9	Grape seed	ZnCl <sub>2</sub>	549.85	916	[36]
10	<i>Ceiba pentandra</i> hulls	Steam	200	521	[39]

maize tassel derived activated carbon (Table 1) [20]. Imamgolu et al. demonstrated the effectiveness of hazelnut activated carbon prepared using K<sub>2</sub>CO<sub>3</sub> activation to uptake Pb<sup>2+</sup> from aqueous solution. The adsorption behavior of Pb<sup>2+</sup> onto hazelnut activated was best described by pseudo second order kinetic model and langmuir adsorption isotherm (Table 1) [34]. The adsorption of Pb<sup>2+</sup> onto *Phoenix Dactylifera L.* beads derived activated carbon followed pseudo second order kinetic model and Langmuir adsorption isotherm (Table 1) [38].

Gaya et al. demonstrated the effectiveness of activated carbon prepared from doum palm shell to adsorb Cd<sup>2+</sup> and Pb<sup>2+</sup> from industrial effluents. Thus, it can be concluded that chemical activating agents has profound effect on the porosity of activated carbons. NaOH activated carbon and ZnCl<sub>2</sub> activated carbon were found to be consisting of mesopores while KOH activated carbon consisted of macropores (Tables 1 and 3) [21]. The uptake of Pb<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution by activated carbon derived from *Albizia lebbbeck* and *Melia azedarach* using HCl activation was best described langmuir and Freundlich adsorption isotherms (Tables 1 and 3) [29]. Shu et al. studied the effectiveness of *Salix Matsudana Kiodz* to adsorb Cd<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solution. *Salix Matsudana Kiodz* activated carbon showed preferential selective adsorption of Pb<sup>2+</sup> as compared to that of Cd<sup>2+</sup> (Tables 1 and 3) [31].

Activated carbon prepared from chickpea husk by chemical activation with KOH and K<sub>2</sub>CO<sub>3</sub> in different proportions was analyzed for their potential to uptake Pb<sup>2+</sup>, Cr<sup>6+</sup> and Cu<sup>2+</sup> from aqueous solutions. The activated carbon prepared with KOH activation ratio 50% wt possessed highest BET surface area and was utilized for adjoining batch experiments. The decrease in BET surface area after 50 and 75% wt KOH and K<sub>2</sub>CO<sub>3</sub> led to

enhanced activation reactions resulting in the formation of larger pores. The results of batch experiment revealed favorable adsorption of Pb<sup>2+</sup> as compared to Cr<sup>6+</sup> and Cu<sup>2+</sup>. The adsorption process was best described by Freundlich adsorption isotherm and pseudo second order kinetic model (Tables 1, 2 and 5) [13]. Similarly, activated carbon prepared from grape bagasse by chemical activation with H<sub>3</sub>PO<sub>4</sub> was utilized for the uptake of Cu<sup>2+</sup> from the aqueous solutions. The surface area, micropore volume and total pore volume increased with increase in impregnation ratio at activation temperature 400°C due to increase in amount of embedded phosphates and polyphosphates that result in larger pore volume and pore size. Also surface area, micropore volume and total pore volume at H<sub>3</sub>PO<sub>4</sub>: grape bagasse impregnation ratio 3 decreased with increase in activation temperature from 400 to 600°C due to tumbling of pores at higher temperatures leading to fall in porosity growth. Also, the spent adsorbent could be reused effectively up to at least 4 times after desorption and regeneration with 0.2 M HCl. Langmuir isotherm, Dubinin-Raduskevich isotherm and pseudo second kinetic model best described adsorption of Cu<sup>2+</sup> onto the activated carbon (Table 2) [14]. *Ulva lactuca* activated carbon prepared using KOH activation showed preferential removal of Cu<sup>2+</sup> as compared to Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cr<sup>3+</sup> form aqueous solutions (Tables 1-3 and 5) [32]. The maximum adsorption capacities of Cd<sup>2+</sup>, Hg<sup>2+</sup> and Zn<sup>2+</sup> onto *Bambusa vulgaris striata* activated carbon were found to be 239.45 mg/g, 248.05 mg/g and 254.39 mg/g respectively (Tables 3 and 5) [33]. Chick pea activated carbon prepared using KOH and K<sub>2</sub>CO<sub>3</sub> activation showed its effectiveness to adsorb Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>6+</sup> from aqueous solutions. Chickpea activated carbon prepared using impregnation with 50% KOH showed highest BET surface area and hence was employed in batch experiment studies (Tables

1, 2 and 5) [13]. Activated carbon derived from grape seed and chestnut shells using  $ZnCl_2$  activation demonstrated its potential to adsorb  $Cu^{2+}$  from aqueous solution (Table 2) [36]. The adsorption of  $Cd^{2+}$  and  $Cu^{2+}$  onto *Ceiba pentandra* activated carbon obeyed Freundlich adsorption isotherm and pseudo second order kinetic model (Tables 2 and 3) [39]. *Typha angustifolia* and *Salix matsudana* activated carbon showed its effectiveness to adsorb  $Cd^{2+}$  and  $Pb^{2+}$  from aqueous solutions (Tables 1 and 2) [28].

Danish et al. investigated the adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  onto calcium oxide activated date stone (ADS). CaO furnishes strong basic sites on the surface of adsorbent due to its low charge to radius ratio. The adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  was dependent upon chemical interactions with adsorbent. Langmuir adsorption isotherm and pseudo second order kinetic model best described the adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  on ADS (Tables 2 and 4) [15]. Abdulrazak et al. carried out batch experiments to analyze heavy metal removal efficiency of activated carbon derived from African palm fruit using phosphoric acid activation. The optimum conditions for removal  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Pb^{2+}$  were found to be 80°C and contact time 60 minutes. At optimum contact time of 60 minutes African palm fruit activated carbon showed highest removal efficiency for  $Cd^{2+}$  ion (99.23%) and lowest removal efficiency for  $Ni^{2+}$  ion (95.34%) (Tables 1- 4) [23]. Nale et al. demonstrated the effectiveness of activated carbon derived from maize cob using  $H_3PO_4$  activation to uptake  $Ni^{2+}$  and  $Pb^{2+}$  from aqueous solution (Tables 1 and 4) [30]. Huang et al. evaluated the

uptake of  $Ni^{2+}$  from aqueous solutions using activated carbon derived from lotus stalks using phosphoric acid activation (Table 4) [37].

Hettiarachchi et al. reported desalination application of activated coconut coir produced from raw coconut coir pretreated with 50% wt phosphoric acid (Table 5) [19]. Abbas et al. evaluated the effectiveness of activated carbon derived from apricot stone to uptake  $Co^{2+}$  from aqueous solutions (Table 5) [22]. The optimum conditions for removal  $Cr^{6+}$  from aqueous media using apple peel activated carbon were found to be pH=2, concentration of  $Cr^{6+}$ = 50 mg/l, adsorbent dose = 0.05 g/50 ml and contact time 4hours (Table 5) [24]. *Aegle Marmelos* activated carbon fabricated using  $ZnCl_2$  activation showed maximum uptake of  $Cr^{6+}$  from aqueous solution at pH=2 and highest adsorption capacity was found to be 43.54 mg/g (Table 5) [25]. Activated carbon prepared from potato peel using HCl and  $H_3PO_4$  activation was evaluated for its potential to uptake  $Fe^{2+}$  from waste water. The adsorption capacity of HCl treated potato peel activated carbon was found to be higher than that of  $H_3PO_4$  treated and untreated activated carbon (Table 5) [26]. The adsorption of  $As^{3+}$  onto *Dialium Guineense* activated carbon was best described by Freundlich adsorption isotherm. *Dialium Guineense* activated carbon prepared using  $ZnCl_2$  activated carbon possessed highest iodine number as compared to that of untreated and activated with  $H_3PO_4$  and  $HNO_3$  respectively and hence it was utilized in batch experiment studies (Table 5) [27].

**Table 3.** Precursors and activating agents for activated carbon preparation from lignocellulosic materials and adsorption of  $Cd^{2+}$  onto them.

Sr.no	Lignocellulosic precursor	Activating agent	Activation temperature (°C)	Specific surface area m <sup>2</sup> /g	Reference
1	Doum palm	$ZnCl_2$ , NaOH, KOH	500	0.84, 226.41, 5.41	[21]
2	<i>Salix matsudana</i>	$H_3PO_4$	400	234.42	[28]
3	<i>Typha angustifolia</i>	$H_3PO_4$	400	130.42	[28]
4	<i>Albizia lebbek</i>	HCl	550	-----	[29]
5	<i>Melia azedarach</i>	HCl	550	-----	[29]
6	<i>Salix matsudana</i>	$H_3PO_4$	550	435.65	[31]
7	<i>Ulva lactuca</i>	KOH	800	345.40	[32]
8	<i>Bambusa vulgaris striata</i>	Water stream	650	608	[33]
9	Rice hulls	$ZnCl_2$	749.85	-----	[35]
10	<i>Ceiba pentandra</i> hulls	Steam	200	521	[39]
11	<i>Phoenix Dactylifera</i> stone	$H_3PO_4$	450	54.93	[40]

**Table 4.** Precursors and activating agents for activated carbon preparation from lignocellulosic materials and adsorption of  $Ni^{2+}$  onto them.

Sr.no	Lignocellulosic precursor	Activating agent	Activation temperature (°C)	Specific surface area m <sup>2</sup> /g	Reference
1	<i>Phoenix Dactylifera</i>	CaO	499.85	645.5	[15]
2	African palm fruit	$H_3PO_4$	300	-----	[23]
3	<i>Zea Mays L</i>	$H_3PO_4$	300	-----	[30]
4	Lotus stalks	$H_3PO_4$	450	1220	[37]

**Table 5.** Precursors and activating agents for activated carbon preparation from lignocellulosic materials and other heavy metal ions adsorption onto them.

Sr.no	Lignocellulosic precursor	Activating agent	Activation temperature (°C)	Heavy metal adsorbed	Reference
1	<i>Cicer arietinum</i>	KOH, $K_2CO_3$	850	$Cr^{6+}$	[13]
2	Coconut coir	$H_3PO_4$	450	$Na^+$ , $Mg^{2+}$	[19]
3	Apricot stones	$H_3PO_4$	250	$Co^{2+}$	[22]
4	Apple peels	$H_3PO_4$	619	$Cr^{6+}$	[24]
5	<i>Aegle Marmelos</i> fruit shell	$ZnCl_2$	400-700	$Cr^{6+}$	[25]
6	Potato peel	$H_3PO_4$ , HCl	699.85	$Fe^{2+}$	[26]
7	<i>Dialium guineense</i> seed	$ZnCl_2$	400	$As^{3+}$	[27]
8	<i>Ulva lactuca</i>	KOH	800	$Cr^{3+}$	[32]
9	<i>Bambusa vulgaris striata</i>	Water stream	650	$Zn^{2+}$ , $Hg^{2+}$	[33]

### 3. Conclusion

The present review concludes that activated carbon derived from lignocellulosic materials can be served as promising low cost adsorbents for adsorption of heavy metals from aqueous phase. The surface properties of activated carbon can be controlled by effect of activating agent and/or activation temperature. The chemical activating agents utilized in fabrication of activated carbon include NaOH, KOH, HNO<sub>3</sub>, CaO, ZnCl<sub>2</sub>, and so on. Chemical activation is preferred over physical activation due to lower energy consumption and higher carbon yields.

### 4. References

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