A systematic study for removal of heavy metals from aqueous media using *Sorghum bicolor*: an efficient biosorbent

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**ABSTRACT**

This review is based on the adsorption characteristics of sorghum (*Sorghum bicolor*) for removal of heavy metals from aqueous media. Different parameters like pH, temperature of the medium, sorghum concentration, sorghum particle size, contact time, stirring speed and heavy metal concentration control the adsorption efficiency of sorghum biomass for heavy metal ions. Sorghum biomass showed maximum efficiency for removal of heavy metal ions in the pH range of 5 to 6. It is an agricultural waste and is regarded as the cheapest biosorbent, having high adsorption capacity for heavy metals as compared to other reported adsorbents, for the treatment of heavy metal polluted wastewater. Adsorption of heavy metal ions onto sorghum biomass follows pseudo second order kinetics. Best fitted adsorption isotherm models for removal of heavy metal ions on sorghum biomass are Langmuir and Freundlich adsorption isotherm models. Thermodynamic aspects of heavy metal ions adsorption onto sorghum biomass have also been elaborated in this review article. How adsorption efficiency of sorghum biomass can be improved by different physical and chemical treatments in future has also been elaborated. This review article will be highly useful for researchers working in the field of water treatment via biosorption processing. The quantitative demonstrated efficiency of sorghum biomass for various heavy metal ions has also been highlighted in different sections of this review article.

**Key words** | biosorbent, effluents, heavy metals, kinetics, pseudo second order, thermodynamics

**INTRODUCTION**

High concentrations of heavy metals are harmful to the environment and living things (Imaga & Abia 2015a). In developing countries, toxic heavy metals enter water bodies or the environment from coal, mining, smelting of metals, dyeing, electroplating, paper mills, electro-osmosis, plastic industries, chemical industries, fertilizers, metallurgy, batteries and refining process which cause serious environmental pollution and toxicity in water bodies (Salman et al. 2015a). When this wastewater enters the human body, it causes various diseases (Wang & Chen 2006; Ahluwalia & Goyal 2007). Different conventional methods like precipitation (Charternanyarak 1999; Papadopoulos et al. 2004; Ghosh et al. 2011), ion exchange (Kang et al. 2004; Alyuz & Veli 2009), electrocoagulation (Heidmann & Calmano 2008), electro-flotation (Casqueira et al. 2006), filtration (Ferella et al. 2007), reverse osmosis (Csefalvay et al. 2009) and adsorption (Cojocaru et al. 2009; Salman et al. 2014) have been employed for the removal of heavy metals from wastewater.
Among them, adsorption is the most effective, cheap, and commonly used physiochemical method for removing heavy metals from wastewater as compared to other methods, which produce large amounts of sludge. The adsorption process involves physical or chemical interactions between the adsorbent and heavy metal ions present in wastewater.

Agricultural wastes, living organisms and different chemical agents have been reported as adsorbents for the removal of heavy metal ions from aqueous media (Gurgel & Gil 2009; Salman et al. 2013a; Choudhary et al. 2015). Agricultural residue or agricultural waste materials are preferable for the removal of heavy metal ions from aqueous media because they are more efficient, easily available and cost effective adsorbents (Gurgel & Gil 2009; Dong et al. 2015). Among them, *Sorghum bicolor* is an efficient biosorbent which carries various active functional groups that interact with metal ions to remove them from aqueous media. It is also a low cost, easily available and plentiful biosorbent. It has recently been reported for the removal of toxic heavy metal ions from wastewater (Choudhary et al. 2015). This biosorbent can be recycled and reused because of it maintains its desorption capacity through many cycles (Choudhary et al. 2015).

### Toxicity of Heavy Metals in Wastewater

Heavy metals are deleterious for humans, animals and the environment. Some heavy metals that have been removed from wastewater using *Sorghum bicolor* biomass as the adsorbent are given as below.

#### Nickel

Nickel is not harmful for humans in small quantities but exposure in high quantities can be fatal. High concentrations of nickel cause several symptoms such as skin rashes, headache, dizziness, nausea and vomiting. It also causes several lung diseases. The delayed effects of nickel on humans include chest pain, coughing, shortness of breath and even death (Imaga & Abia 2013a). The main exposure to nickel comes from battery manufacturing industries and the use of nickel as a catalyst in different reactions. Thus, nickel is released in water and contaminates it. Imaga & Abia (2015a) reported the use of *Sorghum bicolor* having particle diameters of 150 and 250 μm for the removal of nickel (II) ions from wastewater. The adsorption capacity was found to be 38.354 and 38.173 mg/L, respectively. The optimum time for adsorption of Ni^{2+} ions on sorghum biomass was found to be 80 min, and the adsorption process followed the pseudo second order kinetic model.

#### Lead

Lead is also a heavy metal, persistent environmental pollutant and highly toxic to humans as well as animals when ingested even in small quantities (Salman et al. 2014). It is harmful to the nervous system and causes brain and blood disorders. It is stored in soft body tissues and bones, thus disturbs the normal functioning of the body (Imaga & Abia 2015d). Inorganic lead is released into the environment due to industrial and mining processes. It is divalent (Pb^{2+}) in water and causes water pollution. If ingested, it disturbs the digestive and nervous systems. Its presence even in small quantities can destroy aquatic life. The acceptable level for divalent lead in water set by United States Environmental Protection Agency (USEPA) is 5 μg/L and increases in this level in water are not permissible, so its removal becomes necessary (Salman et al. 2013b). Imaga & Abia (2015d) and Salman et al. (2013b) used sorghum biomass for removal of lead (II) from wastewater. The adsorption process followed pseudo second order kinetics and the adsorption capacity was found to be 32.581 and 39.31 mg/L for sorghum biomass with particle diameters of 150 and 250 μm, respectively.

#### Cadmium

Cadmium is a highly toxic water pollutant. The environment and water sources are exposed to cadmium through different processes like electroplating, battery manufacturing, refining of metals and mining. Cadmium exposure causes flu, fever and muscle ache in humans (Imaga & Abia 2015b). It is a cancer-causing agent in the human body and also induces hypertension. The EPA’s suggested acceptable level of cadmium (II) in water is 5 μg/L (Salman et al. 2013b). Salman et al. (2013b) reported the removal of Cd^{2+} from aqueous media onto sorghum hull biomass. They observed that sorghum biomass is highly effective for the removal of Cd^{2+} ions from aqueous media. Imaga & Abia (2015b) studied the adsorption of cadmium (II) from aqueous solutions onto sorghum hull biomass with particles with diameters of 150 and 250 μm. The optimum time for adsorption of Cd^{2+} ions onto sorghum hull biomass having particle size 150 and 250 μm was found to be 80 and 40 min while maximum adsorption was found to be 54.89 and 58.87 mg/L, respectively. Marchiol et al. (2007) observed the uptake capacity of sorghum roots and leaves for Cd^{2+}...
ions removal. The uptake of Cd$^{2+}$ ions by sorghum root biomass was found to be higher than by the leaves.

**Zinc**

The environment and water sources are exposed to zinc by natural processes as well as human activities like electroplating, cell battery manufacturing, coal burning, burning of waste materials and alloy formation (Imaga & Abia 2015c). The permissible concentration of zinc (II) for the human body is 0.4 mg/day, but it becomes toxic at higher concentrations. Zinc intake in large amounts, even for short periods, causes nausea, vomiting and several other stomach diseases. For long-term exposure causes anemia, damages the pancreas and decreases the level of high density lipoprotein (HDLP) which is good form of cholesterol and essential in the body (Imaga & Abia 2015c). It has been observed that zinc concentration in water depends upon the concentration of other minerals and the pH of the water. Researchers found that zinc can be readily removed from wastewater at pH > 7 as compared to low pH. Imaga & Abia (2015c) reported the removal of zinc (II) ions from wastewater using Sorghum bicolor biomass as an adsorbent. The maximum adsorption of zinc (II) ions was found to be 55.152 and 55.196 mg/L for sorghum biomass particles having diameters of 150 and 250 μm, respectively.

**Chromium**

Chromium is added into the environment by electroplating, dyeing of leather, mining and pigment manufacturing processes (Salman et al. 2015a). Chromium is present in wastewater in different oxidation states (III, VI). The permissible concentration of chromium in drinking water suggested by USEPA is 0.1 mg/L (Salman et al. 2015a). The WHO sets the limit of chromium in wastewater at 0.05 mg/L (Choudhary et al. 2015). Due to mutagenic and carcinogenic effects, Cr$^{6+}$ is more toxic for human health as compared to Cr$^{3+}$. Cr$^{6+}$ causes ulcers, asthma, cancer, liver and kidney failure. However, long-term exposure to Cr$^{3+}$ also induces skin allergies and cancer in humans. Cr$^{3+}$ can change into the more carcinogenic Cr$^{6+}$ by bacterial and manganese oxide action present in the environment (Garcia-Reyes & Rangel-Mendez 2010). Cr$^{3+}$ affects human erythrocyte membranes and decreases immunity levels in the body (Garcia-Reyes & Rangel-Mendez 2009). Choudary et al. (2015) used sorghum root powder for the removal of Cr$^{6+}$ from aqueous media and the maximum adsorption capacity was found to be 18.39 mg/g while Salman et al. (2015a) reported the use of sorghum leaf biomass unmodified and modified with urea for the removal of Cr$^{3+}$ from aqueous media. Maximum adsorption capacities were found to be 7.03 and 16.36 mg/g for unmodified and urea-modified sorghum biomass, respectively.

**Copper**

Water sources are exposed to copper from different processes like mining, electroplating, dyeing and refineries etc. (Choudhary et al. 2015). Although copper is essential for health, its excessive uptake causes gastrointestinal bleeding, headache, dizziness, anemia and eventually death (Imaga & Abia 2014). Long-term exposure also causes lung cancer and disorders of the nervous system. The World Health Organization (WHO) set the limit of copper in wastewater as 1 mg/L (Choudhary et al. 2015) while the EPA has suggested the limit of cupric ions should be 1.3 ppm in industrial wastewater (Ahluwalia & Goyal 2007). Salman et al. (2013b) and Choudhry et al. (2015) reported the removal of Cu$^{2+}$ ions from aqueous media by biosorption using sorghum biomass adsorbent, and the maximum adsorption capacity was found to be 4.34 and 18.6 mg/g, respectively. Dong et al. (2015) reported the grafting of sorghum stalk biomass with acrylic acid (Ac) by γ irradiation and used it for the removal of Cu$^{2+}$ ions from aqueous medium. The Langmuir model showed the best fit for the adsorption process for Cu$^{2+}$ ion removal, with the maximum adsorption capacity found to be 13.32 mg/g.

**Arsenic**

Arsenic is highly toxic heavy metal and shows adverse effects on human health (Cano-Aguilera et al. 2005). The presence of arsenic in drinking water up to 100 μg/L induces several health problems including skin and lung cancer (Haque et al. 2007). Inorganic arsenic is a well-known human poison, while long-term exposure to arsenic also causes black foot disease in humans. Cano-Aguilera et al. (2005) reported the use of sorghum biomass for removal of As(III) from aqueous media in the presence of several interfering species such as CaCl$_2$, MgCl$_2$, FeSO$_4$, MgSO$_4$ and Fe(NO$_3$)$_3$. Only the iron salts showed a positive effect on the adsorption capacity of sorghum biomass for As$^{3+}$ adsorption, while all the other salts reduced the adsorption capacity of biomass for As$^{3+}$ ions.

Sorghum and modified sorghum biomass as efficient biosorbent

Sorghum is a grass species that produces grains used worldwide as a food for animals and humans (Choudhary et al. 2015). Sorghum is a rich source of phytates, which can remove various heavy metals in aqueous media.

1. **High phytate concentration**
2. ** Efficient adsorption**
3. **No toxicity**

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These grains also find applications in syrup preparation, ethanol and fuel production (Ucar et al. 2014). As sorghum plant leaves, shoots and roots are usually waste materials which are dumped into the soil, these are plentiful agricultural waste materials (Salman et al. 2013b). The main components of sorghum biomass are cellulose, hemicellulose and lignin (Dong et al. 2013). They contain different functional groups like carboxyl (COOH), aliphatic hydroxyl (Salman et al. 2013a), aromatic hydroxyl (OH) (Dong et al. 2013), phenolic hydroxyl (Dong et al. 2013), carbonyl (CO) (Salman et al. 2013b) methoxyl (OR) (Dong et al. 2013) and amino (NH2) groups (Choudhary et al. 2015). These active functional groups participate in binding and removing heavy metals from wastewater (Salman et al. 2013b). Sorghum biomass has been used unmodified or modified by different reagents like urea (Salman et al. 2013a), thiourea (Salman et al. 2014), mercapto acetic acid (Imaga & Abia 2015a, 2015b), phosphoric acid (Ucar et al. 2014), sulfuric acid (Adewoye et al. 2017) or grafted with acrylic acid (Dong et al. 2013) to improve its adsorption capacity for extraction of heavy metals from aqueous media. The purpose of modification is to enhance the binding sites or to increase the number of functional groups of sorghum for metal ion adsorption. Haque et al. (2007) investigated the functional groups of unmodified sorghum biomass involved in the extraction of As3+ ions from aqueous media by potentiometric titration (PT) and Fourier transform infrared (FTIR) spectroscopy. It was observed that the main functional groups involved in the removal of As3+ ions from aqueous media were carboxyl and hydroxyl groups. Garcia-Reyes & Rangel-Mendez (2009) reported the use of sorghum straw biomass for removal of Cr3+ ions from aqueous media and showed that hemicellulose and lignin are the major components of sorghum biomass which contributed to their removal from aqueous media. Salman et al. (2013a) observed that the treatment of sorghum biomass with urea actually introduces amide groups which enhance its adsorption capacity for different heavy metals. Elemental analysis showed that the nitrogen content was increased from 0.86 to 8.24% in sorghum biomass treated with urea under microwave irradiation. It was observed that the adsorption efficiency of urea-modified sorghum for Cr3+ ions was increased from 49.62 to 72.31% under the same environmental conditions. High nitrogen content in modified sorghum increased its binding sites for the extraction of heavy metal ions. Salman et al. (2013b) used unmodified and urea-modified sorghum to remove Cr3+ ions from wastewater. Ucar et al. (2014) studied the adsorption capacity of natural and phosphoric acid modified sorghum biomass for simultaneous removal of Pb2+, Cd2+, Cu2+ and Mn2+ ions from aqueous media. They also employed unmodified and modified sorghum biomass on river water and investigated their adsorption capacities for different heavy metal ions. Imaga & Abia (2015a) carbonized the sorghum hull biomass in a muffle furnace at 250 °C for 1 hour and then treated the cooled carbonized sorghum with mercapto acetic acid (HSCCH2COOH) to enhance its adsorption capacity. Results showed that different biosorption mechanisms like ion exchange, electrostatic attraction or complexation might have contributed to the adsorption of heavy metal ions onto sorghum biomass (Choudhary et al. 2015). FTIR analysis showed that large shifts in the peak positions of functional groups of sorghum occurred after loading of metals.

Thus, researchers have found that Sorghum bicolor has a very impressive biosorption capacity as it has the ability to remove maximum heavy metals from aqueous media. Sorghum biomass interacts via weak forces with the heavy metals, which is advantageous for its regeneration and reuse (Salman et al. 2013b). Uptake of metal ions from aqueous solutions onto sorghum biomass is influenced by several factors which affect its biosorption capacity. These factors (process conditions) are given below.

### Effect of sorghum dose on metal ion adsorption

The concentration of sorghum biomass used during the adsorption process also affects its adsorption capacity for different metals (Salman et al. 2013b; Choudhary et al. 2015). Increases in sorghum biomass dose increase the percentage removal of different metals but only up to a certain limit. High concentration of sorghum biomass provide a high number of active sites for adsorption of metal ions and as a result the percentage removal is increased. After a certain biomass dose, further increases in its concentration do not affect the percentage removal of heavy metal ions. The reason is the coagulation of biomass at its high concentration leading to active sites.

Salman et al. (2013b) studied the effect of sorghum biomass dose on the removal of Pb2+, Cd2+ and Cu2+ ions from aqueous media. The concentration of sorghum biomass was changed from 0.2 to 1.8 g while the concentration of metal ions solution, pH, and agitation time was kept as 50 mg/L, 7 and 25 min respectively. The optimum dose for adsorption of Pb2+ and Cd2+ ions was found to be 1.0 g/50 mL, while for Cu2+ ions its value was found to be 0.8 g/50 mL. The same group of researchers observed the effect of unmodified sorghum and urea-modified sorghum
biomass dose by changing its concentration from 0.1 to 0.9 g/50 mL for removal of Cr$^{3+}$ ions from aqueous media (Salman et al. 2013a). The percentage removal of Cr$^{3+}$ ions was increased with increasing sorghum dose but up to a certain point. After that limit, its value became constant or decreased. At high absorbent doses, its particles coagulate or aggregate among themselves and their binding sites available for metal ions were found to have decreased. A decrease in the percentage removal of metal ions by increasing the sorghum dose to high concentrations may also occur due to the unavailability of sufficient metal ions for adsorption.

**Effect of agitation speed on metal ion adsorption**

The agitation speed also affects the adsorption of metal ions onto sorghum biomass (Choudhary et al. 2015). At low speeds, biosorbent particles coagulate at the bottom of the flask during the adsorption process and their active sites become unavailable for the uptake of metal ions. Also at high speeds, centrifugal forces overcome the electrostatic interactions between functional groups of the sorghum biomass and metal ions. As a result, the metal ion adsorption rate is decreased. Thus, medium speeds are required for maximum uptake of metal ions by sorghum biomass (Salman et al. 2013b). Salman et al. (2013a, 2013b) studied the effect of agitation speed for the adsorption of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Cr$^{2+}$ ions onto unmodified and modified sorghum biomass and observed that adsorption of metal ions was influenced by agitation speed. Optimum agitation speed for Pb$^{2+}$, Cu$^{2+}$ and Cr$^{2+}$ ions adsorption was found to be 150 rpm while for Cd$^{2+}$ ions it was found to be 125 rpm.

**Effect of concentration of metal ions**

The initial metal ions concentration also affects the adsorption capacity of sorghum biomass. It acts as a driving force to bring these ions to the surface of the solid absorbent and overcomes all mass transfer resistances. High metal ion concentrations enforce the interaction between these ions and sorghum biomass functional groups. As a result, adsorption capacity ($q_e$) of sorghum biomass increases with increase of metal ion concentration. Choudhary et al. (2015) studied the effect of initial concentration of Cu$^{2+}$ and Cr$^{6+}$ ions on adsorption capacity of sorghum root powder. Adsorption capacity of sorghum root biomass was increased from 1.96 to 18.60 mg/L for Cu$^{2+}$ ions and 1.98 to 18.39 mg/L for Cr$^{6+}$ ions by increasing their initial concentration from 5 to 50 mg/L, respectively. Percentage removal of Cu$^{2+}$ and Cr$^{6+}$ ions changed from 98.13 to 93.0% and 99.12 to 91.98% when their initial concentrations were changed from 5 to 50 mg/L, respectively while all other parameters were kept constant. The decrease in percentage removal with increase in initial metal ion concentration can be due to unavailability of binding sites of biomass for metal ion adsorption. Other researchers also studied the effect of initial metal ion concentration for the removal of metal ions using sorghum biomass and observed the same results (Salman et al. 2013a, 2013b).

**Effect of pH on metal ion adsorption by sorghum biomass**

The pH of the medium is the key parameter which controls the metal-sorghum biomass interaction during the biosorption process. Salman et al. (2013b) studied the effect of pH on the adsorption of Pb$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$ ions onto sorghum biomass and observed that high percentage removal of all heavy metal ions on sorghum biomass was attained in the pH range of 5–6. At pH > 7, the hydroxide of relevant metal ions interfered in the adsorption process and decreased the uptake capacity of sorghum biomass for metal ions. At acidic pH, due to protonation of functional groups of sorghum biomass, adsorption of metal ions was decreased. They also observed the effect of the pH of the medium on adsorption capacity of sorghum biomass and microwave-irradiated urea-modified sorghum biomass for Cr$^{3+}$ ions (Salman et al. 2013a). It was observed that optimum adsorption of Cr$^{3+}$ ions was attained in the pH range of 5–6. The reason was that at pH < 6, chromium existed as Cr$^{3+}$ ions, so a maximum number of ions were available to be adsorbed onto sorghum biomass. At pH > 6, Cr$^{3+}$ ions precipitated out as Cr(OH)$_3$ and available Cr$^{3+}$ ions for adsorption were reduced. As a result, percentage removal of metal ions also decreased. At very low pH, H$^+$ ions were present in solution in excess and competed with Cr$^{3+}$ ions to be adsorbed and as a result the amount of adsorbed Cr$^{3+}$ ions was also decreased. Other researchers have also studied the effect of the pH of the medium on the adsorption capacity of sorghum biomass for removal of different metal ions from aqueous media (Imaga & Abia 2014; Salman et al. 2014; Adewoye et al. 2017).

**Effect of size of sorghum biomass particles on metal ion adsorption**

The size of sorghum biomass particles also affects their adsorption capacity for different metal ions. Small sorghum
particles provide high surface to volume ratio. As adsorption is a surface phenomenon, a large surface area means greater interaction between high numbers of metal ions and sorghum biomass functional groups (Imaga & Abia 2015a, 2015b, 2015c, 2015d). Thus, large surface area leads to the uptake of high amounts of metal ions. Imaga & Abia (2015a, 2015b) observed the effect of sorghum particles size on their adsorption capacity for different metal ions and the results are given in Table 1. Results in Table 1 show that small particles of carbonized and mercapto acetic acid modified sorghum hull (MSb) biomass have high adsorption capacity for Ni\textsuperscript{2+} and Cd\textsuperscript{2+} ions as compared to Zn\textsuperscript{2+} and Pb\textsuperscript{2+} ions. The same group of researchers also studied the effect of the size of untreated sorghum biomass particles and mercapto acetic acid treated particles on adsorption of Ni\textsuperscript{2+} and Cu\textsuperscript{2+} ions from aqueous media (Imaga & Abia 2014). Unmodified and modified biomass particles with a diameter of 106 \(\mu\)m showed high adsorption capacity for Ni\textsuperscript{2+} and Cu\textsuperscript{2+} ions as compared to particles with a diameter of 250 \(\mu\)m. The reason was the availability of high surface area/active sites for adsorption of heavy metal ions.

**Effect of contact time on metal ions adsorption**

Contact time or agitation time is also an important factor which affects the metal ions-sorghum adsorption process (Choudhary et al. 2015; Imaga & Abia 2015a, 2015b, 2015c, 2015d). Sorghum biomass shows maximum metal ion adsorption capacity at specific times. Imaga & Abia (2015a) studied the effect of agitation time on adsorption of Ni\textsuperscript{2+} ions by carbonized and mercapto acetic acid modified sorghum hull (MSb) biomass particles with two different values of diameter (150 and 250 \(\mu\)m). By changing the agitation time from 20 to 100 min, the amount of Ni\textsuperscript{2+} ions adsorbed (\(C_c\)) was changed for both MSb-150 and MSb-250 sorghum biomass at pH 7 when 30 mL of 60 mg/L Ni\textsuperscript{2+} ion solution and 0.2 g adsorbent was used for experimentation. The optimum time for adsorption of Ni\textsuperscript{2+} ions onto MSb-150 and MSb-250 biomass was found to be 80 min. At optimum agitation time, biomass particles with 150 \(\mu\)m diameter showed high Ni\textsuperscript{2+} ion uptake efficiency as compared to 250 \(\mu\)m sorghum particles. The amount of Ni\textsuperscript{2+} ions adsorbed at the optimum time was found to be 58.24 and 58.17 mg/L for 150 and 250 \(\mu\)m sized MSb particles, respectively. The reason is high surface area for small adsorbent particles as compared to large particles. Small biomass particles provide a large surface area for metal ion adsorption. Alternatively, adsorption of metal ions increases with decrease in size of adsorbent particles. These results indicate that the adsorption process depends both upon the contact time of the process as well as the size of adsorbent particles. They also reported the use of carbonized and chemically modified sorghum hull biomass with particle diameters of 150 and 250 \(\mu\)m for removal of Zn\textsuperscript{2+} ions from aqueous media (Imaga & Abia 2015c).

Contact time for optimum adsorption of Zn\textsuperscript{2+} ions was found to be 40 and 60 min for MSb-150 and MSb-250 sorghum biomass, respectively, under the same adsorption conditions. At the optimum time, the amount of adsorbed Zn\textsuperscript{2+} ions was found to be 55.15 and 55.19 mg/L for MSb-150 and MSb-250, respectively. The same group of researchers also studied the effect of adsorption time on the removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} ions from aqueous solutions onto mercapto acetic acid modified sorghum hull biomass having two different pore size particles (Imaga & Abia 2015b, 2015d). They observed that modified sorghum biomass have high capacity to remove heavy metal ions from aqueous media. Values of optimum time and maximum amount of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} ions (\(C_a\)) adsorbed onto MSb-150 and MSb-250 biomass are given in Table 1.

The mechanism for adsorption of Cu\textsuperscript{2+} ions onto sorghum biomass due to involvement of carboxyl groups (COOH) at high pH explained by Dong et al. (2013) is shown in Figure 1.

<table>
<thead>
<tr>
<th>Metals</th>
<th>MSb-150 (\mu)m</th>
<th>Optimum time (min)</th>
<th>Adsorbed metal ions (mg/L)</th>
<th>MSb-250 (\mu)m</th>
<th>Optimum time (min)</th>
<th>Adsorbed metal ions (mg/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsuperscript{2+}</td>
<td>80</td>
<td>38.24</td>
<td></td>
<td>80</td>
<td>38.17</td>
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<td>Imaga &amp; Abia (2015a)</td>
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<tr>
<td>Zn\textsuperscript{2+}</td>
<td>40</td>
<td>55.15</td>
<td></td>
<td>60</td>
<td>55.19</td>
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<td>Imaga &amp; Abia (2015c)</td>
</tr>
<tr>
<td>Pb\textsuperscript{2+}</td>
<td>40</td>
<td>32.58</td>
<td></td>
<td>80</td>
<td>39.30</td>
<td></td>
<td>Imaga &amp; Abia (2015d)</td>
</tr>
<tr>
<td>Cd\textsuperscript{2+}</td>
<td>80</td>
<td>54.89</td>
<td></td>
<td>40</td>
<td>58.87</td>
<td></td>
<td>Imaga &amp; Abia (2015b)</td>
</tr>
</tbody>
</table>
They explained that the ion exchange mechanism was important to interpreting the adsorption process between Ac-grafted sorghum stalk biomass and Cu$^{2+}$ ions. Raw lignocellulosic materials have small amounts of sodium on the surface. Cu$^{2+}$ ions were displaced by sodium ions present on the surface of carboxylate sodium grafted biomass. The adsorbed amount of Cu$^{2+}$ ions was found to be higher than the amount of Cu$^{2+}$ ions adsorbed by displacement of sodium ions. These results showed that it is not only ion exchange mechanism involved in the adsorption process but functional groups like hydroxyl groups also contributed to the adsorption of Cu$^{2+}$ ions.

**Biomass Desorption and Recyclability**

Desorption of sorghum biomass and its reusability is an important aspect of recent research from a commercial and economic point of view. Heavy metals can be desorbed from sorghum biomass using different eluting agents like hydrochloric acid (HCl) (Choudhary *et al.* 2013), sodium hydroxide (NaOH) (Bernardo & Rene 2009), ethylene diamine tetra acetic acid (EDTA) (Bernardo & Rene 2009) and nitric acid (HNO$_3$) (Choudhary *et al.* 2013). In this way, sorghum biomass can be used repeatedly for removal of heavy metal ions from wastewater. Choudhary *et al.* (2013) used sorghum root biomass for removal of Cu$^{2+}$ and Cr$^{6+}$ ions from aqueous media. They desorbed these metal ions from sorghum root biomass using HCl and HNO$_3$ as eluting agents. For this purpose, metal-ion-loaded biomass was shaken with desorbing agents in a thermostat machine under specific conditions. Desorption efficiency of sorghum root biomass was calculated by using the following formula:

$$\text{Desorption efficiency} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100$$ (1)

Desorption efficiency of Cu$^{2+}$ and Cr$^{6+}$ ions from sorghum root biomass using HCl as the eluting agent was found to be 93 and 96%, while using HNO$_3$ as the eluting agent, their desorption efficiency was found to be 84 and 89% respectively. Thus it was observed that elution capacity of HNO$_3$ was greater than that of HCl for Cu$^{2+}$ and Cr$^{6+}$ ions. They also observed that regenerated sorghum biomass retained its adsorption capacity to best extent for four to five cycles and that the regeneration process was cost effective.

Bernardo & Rene (2009) reported the use of NaOH, HNO$_3$ and EDTA as eluting agents for desorption of Cr$^{3+}$ ions from sorghum stalk biomass. It was observed that EDTA showed high eluting efficiency as compared to NaOH and HNO$_3$ for Cr$^{3+}$ ions from sorghum biomass depending upon the nature of metal-sorghum bonding. 0.05 M EDTA showed 75% desorption percentage for Cr$^{3+}$ ions from sorghum biomass while the desorption percentage using HNO$_3$ (1.0 and 0.1 M), NaOH (1.0 and 0.1 M) and 0.1 M EDTA eluting agents was found to be 55, 22, 72, 41, 71%, respectively, at 55 °C.

**Isotherm Models for Adsorption Process**

Adsorption isotherms are the curves which describe the relationship between the adsorbed amount of a substance from an aqueous medium (bulk) to a solid surface at a given temperature (Salman *et al.* 2013a). Adsorption equilibrium (ratio of adsorbed amount of adsorbate to the amount remaining in solution) is established when adsorbate concentration in bulk comes in dynamic equilibrium with its concentration adsorbed onto the surface of the adsorbent while both are kept in contact with each other for sufficient time under suitable conditions (Choudhary *et al.* 2013). These models also provide information about adsorption mechanism, surface properties of different adsorbents as well as their adsorption affinity for metals and other pollutants. Different models including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (DR) have been employed to interpret the adsorption process between metal ions and sorghum biomass. These models differentiate between the surface morphology as well as the nature of adsorption process. Details of adsorption isotherm models with characteristic parameters are given below.
Langmuir adsorption isotherm model

The Langmuir adsorption isotherm model was initially developed to explain the adsorption of gas to solid surface but it was further extended to liquid-solid adsorption processes. In this model, it is assumed that only one molecule of adsorbate gets adsorbed onto a single active site of the adsorbent, thus leading to single-layer adsorption process (Choudhary et al. 2015). It also assumes that the adsorption process is homogenous in nature, which means all molecules of adsorbate have equal potential to get adsorbed onto the available active sites of the adsorbent. Linear form of Langmuir isotherm equation is given as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{q_m}{q_m} C_e
\]  

(2)

In Equation (2) \( q_e \) (mg/g) is the amount of metal ions adsorbed onto sorghum biomass at equilibrium while \( C_e \) (mg/L) is its concentration present in solution at equilibrium. \( q_m \) (mg/g) and \( b \) (L/mg) are Langmuir constants and represent the maximum adsorption capacity of sorghum biomass and adsorption energy, respectively. The value of \( q_m \) and \( b \) can be calculated from the slope and intercept of the plot of \( C_e/q_e \) vs \( C_e \). The value of \( b \) can be used to find another dimensionless parameter called the separation factor (\( R_L \)) which shows the nature of the adsorption process. The separation factor in the form of \( b \) is given as follows:

\[
R_L = \frac{1}{(1 + bC_e)}
\]  

(3)

Possible values of \( R_L \) for the adsorption process can be found in the range of 0 to 1 which shows favorable adsorption. When the value of \( b \) is zero, the value of \( R_L \) is 1, which shows linear adsorption. When value of \( b \) is infinity, the value of \( R_L \) becomes zero, which shows irreversible adsorption (Dong et al. 2013).

Salman et al. (2013a) employed the Langmuir adsorption isotherm model to explain the adsorption of Cr\(^{3+}\) ions on unmodified and modified sorghum biomass. The value of \( R^2 \) and Langmuir parameters show that the Langmuir adsorption isotherm model explains well the adsorption of Cr\(^{3+}\) ions onto sorghum biomass. The value of \( q_m \) was found to be 7.05 and 16.36 mg/g while the value of \( R_L \) was found to be in the range of 0.0008 to 0.0071 and 0.0003 to 0.0051 for unmodified and modified sorghum biomass, respectively. These results showed the favorable adsorption and homogeneous distribution of active sites over the surface of unmodified and modified sorghum biomass. The same group of researchers also used sorghum biomass for removal of \( \text{Pb}^{2+} \), \( \text{Cd}^{2+} \), and \( \text{Cu}^{2+} \) ions from aqueous media (Salman et al. 2013b). Choudhary et al. (2015) used sorghum root biomass for removal of \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions from aqueous media and Langmuir parameters were calculated to interpret the adsorption process. Values of Langmuir parameters for adsorption of \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions are given in Table 2. The value of the correlation coefficient (\( R^2 \)) was found to be 0.997 for both \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions which indicates that the adsorption process followed the Langmuir adsorption isotherm model well.

Freundlich adsorption isotherm model

The Freundlich isotherm model explains the multiple layer adsorption process. This isotherm also assumes a heterogeneous surface on the adsorbent and considers that the concentration of adsorbate gets adsorbed onto the surface of adsorbent (\( q_e \)) increases with increase in its concentration in solution (\( C_e \)) (Salman et al. 2013a). The linear form of the Freundlich adsorption isotherm is given as follows:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]  

(4)

Freundlich parameters such as \( n \), which represents the adsorption intensity, and \( K_F \), which indicates the relative adsorption capacity can be found from the slope and intercept of the plot of \( \log q_e \) vs \( \log C_e \), respectively. The value of \( n \) indicates the favorability of adsorption process. Values of \( n \) in the range of 1–2 shows good, 2–10 indicates better and <1 shows average adsorption of metal ions onto sorghum biomass.

Salman et al. (2013a, 2013b) investigated the adsorption capacity of unmodified and urea-modified sorghum biomass for \( \text{Pb}^{2+} \), \( \text{Cd}^{2+} \) and \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions. They employed the Freundlich adsorption isotherm model to explain the adsorption process. The values of Freundlich parameters for heavy metal ion adsorption are given in Table 2. Results shown in Table 2 indicate the applicability of the Freundlich adsorption isotherm model for adsorption of heavy metal ions onto sorghum biomass. Choudhary et al. (2015) also observed the applicability of the Freundlich adsorption isotherm model for removal of \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions using sorghum roots biomass. The value of \( n \) and \( K_F \) for adsorption of \( \text{Cu}^{2+} \) and \( \text{Cr}^{6+} \) ions...
ions are also given in Table 2. The value of $R^2$ for $\text{Cu}^{2+}$ and $\text{Cr}^{6+}$ ion adsorption onto sorghum root biomass was found to be 0.916 and 0.950, respectively, which indicates that the adsorption process does not fit the Freundlich isotherm model well.

### Temkin adsorption isotherm model

The Temkin adsorption isotherm model explains the interaction between sorghum biomass (adsorbent) and metal ions (adsorbate) during the adsorption process (Prasanthi...
et al. 2016). The linear form of Temkin adsorption isotherm model is given as follows:

\[ q_e = BT \ln K_T + BT \ln C_e \]  

(5)

In Equation (5), \( K_T \) is Temkin binding constant, which represents the maximum binding energy, while \( B_T \) represents the adsorption heat. The values of \( B_T \) and \( K_T \) can be calculated from the slope and intercept of the plot between \( q_e \) and \( \ln C_e \), respectively, according to Equation (5). Temkin parameters also show the nature of the adsorption process, which can be either physisorption or chemisorption. A value of \( B_T \) of <8 indicates physisorption while a value of >8 shows chemisorption (Salman et al. 2013a). The values of Temkin parameters calculated by Salman et al. (2013a, 2015b) for adsorption of different heavy metal ions onto unmodified and modified sorghum hull biomass are given in Table 2.

The values of \( B_T \) for \( \text{Cr}^{3+} \) ions adsorption onto unmodified and modified sorghum biomass were found to be 2.44 and 4.59 kJ/mol, respectively. These values explain the particle diffusion mechanism (Mokkapati et al. 2016). If the value of \( B_T \) of \( \text{Cr}^{3+} \) ions adsorption is lower than 16, it shows the occurrence of the ion exchange mechanism during adsorption process.

Values of \( \varepsilon \) and \( q_m \) for adsorption of different metal ions onto sorghum biomass investigated by different researchers are given in Table 2.

**Kinetic Study for Metal-Sorghum Adsorption Process**

Different models such as the pseudo first order, pseudo second order and Elovich models have been employed to study the kinetics of metal ion adsorption onto sorghum biomass. These models give explanations for the rate of the adsorption process (Mokkapati et al. 2016). Imaga & Abia (2015a, 2015b, 2015c, 2015d) employed the pseudo first order, pseudo second order and Elovich models to study the change in concentration of \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) ions being adsorbed onto the surface of sorghum hull biomass with the passage of time. The linear form of the pseudo first order kinetic equation is given as follows:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

(7)

In Equation (7), \( q_e \) and \( q_t \) represent the concentration of metal ions (mg/g) adsorbed onto the surface of sorghum biomass at equilibrium and at any time, respectively. While \( k_1 \) (min\(^{-1}\)) is the pseudo first order rate constant. The linear form of the pseudo second order kinetic equation is given as follows (Prasanthi et al. 2016):

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(8)

In Equation (8), \( q_e \) and \( q_t \) are concentrations of metal ions (mg) adsorbed per gram of sorghum biomass at equilibrium and at any time respectively. \( k_2 \) (g/mg·min) is the pseudo second order rate constant. Prasanthi et al. (2016) employed the linear form of the pseudo second order kinetic model to explain the adsorption of \( \text{Cr}^{6+} \) ions onto sorghum stem biomass. The values of \( q_e \) and \( k_2 \) were calculated from the slope and intercept of the plot between \( t/q_t \) and \( t \), respectively. The values of pseudo second order kinetic parameters for adsorption of different metal ions onto sorghum biomass are given Table 3. The linear form of the Elovich model is given as follows:

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \]  

(9)
In Equation (9) \( \alpha \) (mg/g.min) is the initial adsorption rate while \( \beta \) relates to the surface coverage of the adsorbent and activation energy (Mokkapati et al. 2016). The value of the correlation coefficient \( (R^2) \) found by employing pseudo first order, pseudo second order and Elovich models for adsorption of \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) ions onto sorghum biomass indicates that pseudo first order and Elovich models are not suitable for explaining the kinetics of adsorption of different metal ions onto sorghum biomass. The value of \( R^2 \), rate constant \( (k_d) \) and maximum adsorption capacity \( (q_e) \) using the pseudo second order kinetic model for \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) ions by carbonized and modified sorghum hull (MSb) biomass having two different pore sizes are given in Table 3. Results indicated that adsorption of metal ions onto \textit{Sorghum bicolor} biomass best followed the pseudo second order kinetic model.

Salman et al. (2013b) also studied the kinetic aspect of the adsorption process of \( \text{Pb}^{2+}, \text{Cd}^{2+} \) and \( \text{Cu}^{2+} \) ions onto \textit{Sorghum bicolor} biomass. Pseudo first order and pseudo second order kinetic models were employed to explain the kinetics of adsorption process. \( R^2 \) values representing the adsorption of metal ions onto sorghum biomass best followed pseudo second order kinetic model. The same group of researchers also observed that adsorption of \( \text{Cr}^{3+} \) ions onto unmodified and urea-modified sorghum biomass followed the pseudo second order kinetics (Salman et al. 2013a). Values of \( R^2 \) (0.99) also give the clear indication that the adsorption process best followed pseudo second order kinetics. Values of \( q_e \) for adsorption of \( \text{Cr}^{3+} \) ions onto sorghum biomass were found to be 2.74 and 4.65 mg/g for unmodified and urea-modified sorghum biomass, respectively, which were very close to experimental values (2.5 and 4.4 mg/g). Similar results were observed by other researchers when they studied the adsorption of different metal ions using sorghum biomass (Choudhary et al. 2015; Mokkapati et al. 2016). Other models, such as the liquid film diffusivity model (Imaga & Abia 2015a), the mass transfer model (Imaga & Abia 2015b), the film surface diffusion model (Garcia-Reyes & Rangel-Mendez 2010) and the intra-particle diffusivity model (Imaga & Abia 2015a) have also been reported for studying the adsorption of different metal ions onto sorghum biomass.

**THERMODYNAMIC STUDY OF METAL-SORGHUM ADSORPTION PROCESS**

The temperature of the medium also changes the adsorption of metal ions onto sorghum biomass (Prasanthi et al. 2016). Thermodynamic parameters such as standard Gibbs energy change \( (\Delta G^0) \), enthalpy change \( (\Delta H^0) \) and entropy change \( (\Delta S^0) \) provide information about the nature of the adsorption process. The following equations are used to find the values of thermodynamic parameters such as \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \):

\[
K_D = \frac{C_o - C_e}{C_o} (10)
\]

\[
\ln K_D = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} (11)
\]

\[
\Delta G^0 = -RT\ln K_D (12)
\]

In Equations (10)–(12), \( R, T \) and \( K_D \) are general gas constant (8.314 J/mol.K), the temperature of the medium and the equilibrium constant, respectively. Researchers studied the effect of temperature of the medium on adsorption of \( \text{Pb}^{2+}, \text{Cd}^{2+} \) and \( \text{Cu}^{2+} \) ions by \textit{Sorghum bicolor} biomass in the range of 10–40 °C (Salman et al. 2013b) while other reaction conditions such as metal ion concentration (50 mg/L), agitation time (30 min) and sorghum dose for \( \text{Pb}^{2+}, \text{Cd}^{2+} \) (1.0 g/50 mL) and \( \text{Cu}^{2+} \) (0.8 g/50 mL) were kept constant. It was observed that percentage removal of metal ions was increased with increase in temperature of the medium as shown in Table 4, which indicates the endothermic nature of adsorption process.

They also found the value of \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) for the adsorption of \( \text{Pb}^{2+}, \text{Cd}^{2+} \) and \( \text{Cu}^{2+} \) ions onto sorghum biomass and observed that adsorption was feasible. Negative values of \( \Delta G^0 \) indicate the spontaneity of the adsorption process. In addition, the increase in value of \( \Delta G^0 \) with increase in temperature of the medium shows the endothermic nature of adsorption process as shown in Figure 2.
Positive values of $\Delta S^\circ$ for adsorption of $\text{Pb}^{2+}$, $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$ ions onto sorghum biomass show the increase in randomness at the metal-sorghum interface during the adsorption process.

They also studied the effect of the temperature of the medium on the adsorption of $\text{Cr}^{3+}$ ions onto unmodified and urea-modified sorghum biomass (Salman et al. 2013a). Maximum adsorption capacity ($q_e$) for both type of biosorbents was found to increase with increase in temperature of the medium as shown in Figure 3. Negative values of $\Delta G^\circ$ show that adsorption was feasible and spontaneous. Positive values of $\Delta H^\circ$ supported the endothermic nature of adsorption process while positive values of $\Delta S^\circ$ showed an increase in randomness at sorghum-chromium ions interface. They also observed the same results for adsorption of $\text{Pd}^{2+}$ ions onto unmodified sorghum and thiourea-modified sorghum biomass (Salman et al. 2014). Other researchers have also investigated the thermodynamic parameters for adsorption of $\text{Cu}^{2+}$ and $\text{Cr}^{6+}$ ions by sorghum root biomass (Choudhary et al. 2015). Negative values of $\Delta G^\circ$ and $\Delta H^\circ$ showed that the adsorption process was spontaneous and exothermic in nature.

**CONCLUSION**

Recent progress in the use of *Sorghum bicolor* biomass for removal of toxic heavy metal ions from aqueous media has been highlighted as these heavy metal ions are added to water bodies from different sources. Different factors which affect the adsorption of heavy metals onto sorghum biomass such as agitation time, amount of biosorbent, concentration of metal ions, temperature and pH of the medium have also been discussed in detail. Regeneration sorghum biomass from aqueous media using different chemical reagents has also been elaborated in this review article. The applicability of different isotherm models have also been discussed. It was concluded that removal of heavy metals from aqueous media by sorghum biomass followed pseudo second order kinetics. Thermodynamic aspects elaborated the feasibility, spontaneity/non-spontaneity and endothermic/exothermic nature of the metal-sorghum adsorption process. It was also concluded that some sort of interaction is established between functional groups of sorghum biomass and heavy metal ions during adsorption processes.

**FUTURE DIRECTIONS**

Although many researchers have used sorghum biomass for the removal of $\text{Ni}^{2+}$, $\text{Cd}^{2+}$, $\text{Pb}^{2+}$, $\text{Zn}^{2+}$ ions from aqueous media, there is also a need to employ efficient sorghum biomass for removal of other toxic heavy metals which are deleterious for humans as well as
environment. The presence of toxic heavy metals in water sources causes harmful effects on human health and induces many diseases such as depression, black foot, kidney cancer, cardiovascular issues and hair problems (Boening 2000; Jarup 2003; Virtanen et al. 2005). Also, no one has yet tried to use efficient *Sorghum bicolor* biomass for removal of toxic dyes from aqueous media, so the efficiency of sorghum biomass for removal of toxic dyes from aqueous media as compared to other adsorbents should be investigated (Din et al. 2017). In future, there is also a need to detect the efficiency of low-cost, easily available, cheaper, recyclable sorghum biomass for simultaneous removal of heavy metals and dyes from aqueous media. Different functional groups can also be introduced in sorghum biomass to improve its efficiency for different pollutants. Different methods should be employed to enhance the number of active sites of sorghum biomass for removal of heavy metals from wastewater. There is a need to move these adsorption studies to plant scale and industrial level. Although it is considered that some sort of donor-acceptor interaction is established between metal ions and sorghum particles, more work should be done on this aspect to elaborate the actual mechanism which occurs between sorghum particles and metal ions. Although chemically modified sorghum biomass shows high adsorption capacity as compared to unmodified sorghum, the cost of chemicals and technologies which are used to modify the sorghum should be addressed in future and their cost should be minimized as much as possible. It can be concluded that *Sorghum bicolor* biomass is an economical and effective method of treatment of wastewater containing pollutants due to its low cost, easy availability and recyclability. Sorghum biomass should be employed to remove toxic nitro aromatic compounds from aqueous media.

**ACKNOWLEDGMENTS**

Authors are thankful to University of the Punjab, Lahore Pakistan for financial support under research Grant No. 999/EST.I for the fiscal year of 2017–2018. Ahmad Irfan is thankful to Research Centre for Advanced Materials Science, King Khalid University, Saudi Arabia for support.

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