Comparative biosorption competencies of *Ficus*, *Syzygium* and *Mangifera* seeds for hexavalent chromium mitigation from polluted water

**Abstract**

**Aim**: The dumped subsurface industrial wastes containing toxic metals have contaminated water resources because of their natural process leading to severe threat to flora, fauna and ecosystem in UPSIDC, Unnao area. The waste water contaminated chromium compounds can be purified through surface assimilation. The aim of the present study was to match sorption competencies of *Ficus racemosa* with *Syzygium cumini* and *Mangifera indica* seed for chromium (VI) removal from polluted water.

**Methodology**: Chromium (VI) contaminated water samples were collected from UPSIDC sites, Unnao, Uttar Pradesh standardized and diluted to experimental strength. The sorption of Cr (VI) was investigated with relative competencies of biosorbents (*F. racemosa*, *M. indica* and *S. cumini* seeds) with retention time, sorbent dosage, temperature, chromium concentration and hydrogen ion activity. The biosorption was tested with various isopleths (Linear, Chemist and Freundlich).

**Results**: The sorption potential of *F. racemosa* seeds was of 10 mg/g where as *S. cumini* and *M. indica* showed biosorption capacity of 13 and 21 mg/g Cr at neutral hydrogen ion activity scale. The surface assimilation was found highest at low pH scale range of two, rising with sorbent application quantity, temperature and decreased with higher Cr (VI) content.

**Interpretation**: The study reveals that biosorption efficiency decreased in the following order: *M. indica* > *S. cumini* > *F. racemosa* seed for hexavalent chromium from waste water.
Introduction

The bioaccumulation tendency and toxic nature of water soluble metals like chromium, mercury, lead, arsenic and cadmium has caused significant menace to the environment (Chen et al., 2015). Currently, Cr (VI) is one of the significant hazardous metals in wastewater that are not degradable and highly immune to oxidation even at high temperatures. Physiologically, Cr compounds have been found as respiratory tract irritants and may cause pulmonic sensitization resulting in increased risk of respiratory organ, nasal and sinus cancer (Eastmond et al., 2008). Industrial out come of chromium (VI) compounds depends on factory and related to accrued threat of systema respiratorium. Ingestion of lethal dose of chromate can result in cardiovascular collapse. Oral exposure to chromium (VI) compounds may result in hematological toxicity. Cr(VI) compounds impact deoxyribonucleic acid damage, gene mutation, sister fibril exchange, body aberrations during a number of targets, including animal cells in vivo and animal and human cells in vitro (Eastmond et al., 2008). The reported management procedures for replacing Cr (VI) ions from wastewater have been replaced with new techniques such as solidification, sorption on the charcoal (Lotfi et al., 2002), reduction, elution (Mauri et al., 2001), opposed osmosis, cation replacement (Rengaraj et al., 2003), separation at low temperature and electrolysis deposition strategies. The initial and subsequent running costs in afore said methods is very high as compared to sorption (Sharma et al., 2004), which is easy and appropriate technique (Dakiky et al., 2002; Gupta et al., 2006, 2008) for removing Cr from waste water to make it potable (BIS, 2012). Enormous plant resources / thrown away commodities are usually available in rural (Kumar et al., 2016) from factories or unindustrialized byproducts (Palanisamy et al., 2015) that have competency to bind metal Cr (VI) through sorption (Nirmal Kumar et al., 2012). In most of the sorbent substances, the sorption capacity is low and creates a problem of their secure disposal on land / water. Consequently, the search for economical sorbent having high Cr (VI) sorption competency is the necessity of current time from available plant materials (Nourbakhsh et al., 1994; Bai et al., 2003) and unindustrialized waste products (Bailey et al., 1999).

Mangifera (Mango), Ficus (Fig) and Syzygium (Jamun) are economically important trees. It’s fully grown-up primarily for its edible fruits and timber merchandise. The fruits of Ficus contain glauanol, sitosterol, aldohexose and alternative phytosterols (Padma, 2009). The phytochemical studies of Mangifera seeds have reported the presence of alkaloids, steroids, tannins, phenol, resins, organic compound and essential oil (Anjaneyulu et al., 1994). Similarly, composition of S. cumini seed contain organic compound jambosine and glycoside jambolin or antimellin (Muniappan, 2012). The bark of F. racemosa has been deliberated (Singh et al., 2013) and found to have outstanding sorption (25.9 mgg\(^{-1}\)) capacity of Cr (VI), however studies on the biosorption capacity of seed of F. racemosa is meager. In view of the above, the present paper aimed to analyze the biosorption efficiencies of F. racemosa, M. indica and S. cumini seeds for the removal of hexavalent chromium from surface and ground waters. The experimental impact of pH scale range, length of time, heat, chromium concentration, sorbent doses and equilibriums on surface assimilation were also investigated.

Materials and Methods

Preparation of standard Cr (VI) solution : The chromium (VI) contaminated surface and ground waters were collected from Unnao industrial areas of Uttar Pradesh (UPSIDC). The experimental reagents were of NIST grade K\(_2\)Cr\(_2\)O\(_7\) in deionized water and additional dilutions were made to desired concentrations for calibration. The contaminated samples were standardized against known K\(_2\)Cr\(_2\)O\(_7\) solution further diluted to experimental strength of 10-50 mgL\(^{-1}\) with deionised water.

Preparation of biosorbent powder : The pulverized seeds of F. racemosa, M. indica and S. cumini obtained from local villages were used as biosorbent. The deionised water was used for washing and cleaning of seeds, dried in oven (90-110°C) and airdried in open after gridding and sieving. The sorbent powder was preserved in air tight amber colored bottles in dark for experimental use. The sorbent grain size was of geometric mean 250 \(\mu\)m.

Screening of adsorbent : One hundred mg of each seed powder was tested as adsorbents during various experiments with identified Cr standard. The experiments were done by provocative the medium for a definite duration, temperature, dosage, medium hydrogen ion activity scale and concentration. The seed powder quantity was changeable one to five gram per liter for a range of experiments. The concentration of chromium solution experimented was 10- 50 mgL\(^{-1}\) and temperature studied was 10-40°C maintained in ice bath / thermoregulatory oven. The hydrogen ion activity scale of pH 2,4,7,10 and 12 was maintained by 0.01N HCl and 0.01N NaOH solution and monitored. The quantity of unreacted Cr (VI) in different experimental conditions (time, doses, metal concentration, medium, temperature) was calculated by reacting with 1, 5-diphenyl carbazide in pH scale 4-5 (1:1 HCl) by forming purple complex at 540 nm (APHA, 2012). The experiments were dispensed in triplicate and mean values were used for illustration and interpretation of figures. The Chemist (Langmuir, 1918), Freundlich (1928) isopleths model for sorption of fine seed particles of Syzygium cumini, Ficus racemosa and Mangifera indica for Cr (VI) has additionally been investigated.

Results and Discussion

The surface assimilation of Cr (VI) on absolutely different sorbents with time is specified in Fig. 1a. Sorption of chromium (VI) ions showed a linear function with time on F. racemosa seed up to 2 hrs then slowed down.

Similar trend was also observed by M. indica (33% to 43%) and S. cumini seeds (17% to 27%). A decrease in the rate of
Fig. 1a: Effect of time duration on percentage adsorption of Cr (VI)

Fig. 1c: Effect of temperature (°C) on Cr assimilation

Fig. 1d: Effect of hydrogen ion activity on biosorption of Cr (VI)

Fig. 1e: Effect of sorbent application (gl⁻¹) on Cr (VI) biosorption
natural process with time has also been reported by Aziz (2004) for elimination of iron metal treating with CaCO$_3$ and Samdani et al. (2008) for chromium (VI) removal by Hydrilla. The positive sorption is additionally due to free sorption sites on the adsorbent surface as large numbers of vacant adsorbent sites were available for initial stage of sorption, thenceforth with lapse of time the remaining vacant surface sites were occupied and because of repulsive forces between the Cr molecules at the sorbent exterior, the speed of adsorption was decreased (Ucun et al., 2002). It was observed that 50 mg/l Cr was readily adsorbed by $M. indica$. 

**Fig. 2a**: Linear sorption isotherm of Cr (VI)

**Fig. 2b**: Langmuir representation for Cr (VI)

**Fig. 2c**: Freundlich representation for Cr (VI)
Table 1a: Freundlich constants for Cr (VI)

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Constant</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>F. racemosa</td>
<td>3.006</td>
<td>0.853</td>
</tr>
<tr>
<td>M. indica</td>
<td>1.177</td>
<td>0.234</td>
</tr>
<tr>
<td>S. cumini</td>
<td>1.084</td>
<td>0.211</td>
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Table 1b: Langmuir constants of seed grain powders

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Constant</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>F. racemosa</td>
<td>5.13</td>
<td>0.033</td>
</tr>
<tr>
<td>M. indica</td>
<td>0.339</td>
<td>0.998</td>
</tr>
<tr>
<td>S. cumini</td>
<td>0.041</td>
<td>0.996</td>
</tr>
<tr>
<td>M. indica</td>
<td>0.046</td>
<td>0.935</td>
</tr>
<tr>
<td>S. cumini</td>
<td>0.130</td>
<td>0.994</td>
</tr>
<tr>
<td>M. indica</td>
<td>0.004</td>
<td>0.972</td>
</tr>
<tr>
<td>S. cumini</td>
<td>0.345</td>
<td>0.993</td>
</tr>
<tr>
<td>M. indica</td>
<td>0.099</td>
<td>0.913</td>
</tr>
<tr>
<td>S. cumini</td>
<td>0.392</td>
<td>0.991</td>
</tr>
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followed by S. cumini and F. racemosa seeds, and there after the rate of biosorption was found to decrease with contact time (Fig. 1a)

Charcoal prepared from fish bone was used as sorbent material for halide ion by Kiledar and Bhargava (1990). The sorption rate on fig seed powder increased to 19.4% and subsequently it decreased (Fig. 1b), where as in M. indica and S. cumini seed it was determined 94.8 and 47.7 % at contact time of 120 min. The percentage removal was found to decrease exponentially at high Cr concentrations due to unavailability of active sites on adsorbent as a result of saturation (Gupta et al., 2006). Similar conclusions were drawn by Samdani et al., (2008) using aquatic plant as biosorbornt and Sasikala et al., (2015) for chromium (VI) surface assimilation by Moringa oleifera.

The impact of high temperature on chromium (VI) sorption was found in linear correlation with temperature and analogous conclusions were jointly found by Sasikala et al., (2015) within which they used Moringa species for chromium. The sorbent (fig, mango and jamun seed fine particles) showed sorption efficacy directly proportional to the rising temperature, indicating an energy captivating phenomenon (Fig. 1c).

The effect of hydrogen ion activity on surface assimilation of Cr (VI) is specified in Fig. 1d. Sasikala et al., (2015) reported that surface assimilation of metal ions increase at acidic pH values and H+, CrO4- and Cr2+ ions present in solution vie for the active sites of sorption. The low proton activity range of pH over eight was found to metal hydroxide configuration turning to solidification. The highest assimilation of chromium (VI) on fig seed was discovered at higher proton activity (pH-2) that decreased slowly at neutral and further rose at lower proton activity (pH-12, Fig. 1d) similar to S. cumini and M. indica seeds, however M. indica seed in high hydrogen activity showed vital biosorption up to 97%.

At neutral pH, the sorption of Cr (VI) on S. cumini was analogous to F. racemosa seed. Analogous explanation of exceptional sorption of chromium VI in acidic medium decreased at neutral medium using Hydrilla verticillata (Samdani et al., 2008) and Aspergillus niger biomass (Chhikara and Dhankhar, 2008). Park et al. (2008) reported that at acidic medium the predominant anionic varieties of hexavalent chromium HCrO4-, CrO4-2, CrO7-2 type strong electro static attraction with cationic sorbent, -COOH and -NH, species lead to increased sorption at high hydrogen ion activity range. The hydrolysis of esters and amide linkage in sorbent material molecules in acidic / basic medium results in formation of free - COOH and -NH, species having lepton donor nitrogen and oxygen atoms sites for Cr bindings resulting to increase in sorption. The acid catalyzed hydrolysis of phyto chemicals in M. indica seed (Anjaneyulu et al., 1994) results more free amino and carbonyl electron donor moieties compared to S. cumini and F. racemosa (Padma, 2009), hence more adsorption observed in high hydrogen ion activity range.

The percentage change in surface assimilation of adsorbent S. cumini (25.7% to 79.1%), F. racemosa (19.5% to 24.4%) and M. indica (43.2% to 98.4%) seed for Cr (VI) was directly correlated with the quantity of sorbent (Fig. 1e).

The outstanding high percentage surface assimilation more than 98 was found in seeds of M. indica, which enhanced with sorbent quantity. Sasikala et al. (2015) reported the parallel results during Cr elimination by Moringa oleifera and Regina de Moreira et al. (2010) ferric mitigation applying carbon as sorbent. The boost in surface assimilation of chromium (VI) with rising biosorbent application quantity showed that further and additional active sites becomes accessible on the outer surface of biosorbent for chromium particles to adsorb (Rio et al., 2002).

Sorption isopleths: The necessary physical-chemical aspect for the analysis of the sorption is the quantity of different material phases in equilibrium media. The sorption was studied in different experimental environment of quantity and chromium application at stable temperature. The stability between the quantities of experimental environment of quantity and chromium application was represented in Fig. 2a.

The interpretation infers that sorption capability will enhance with increasing chromium (VI) concentration at equilibrium. As depicted in Fig. 2a, the surface assimilation ability of M. indica seed was higher (23 mg g⁻¹) for the equilibrium Cr quantity (Ce) of 26 mg l⁻¹, while in S. cumini it was 13 mgg⁻¹ for 36 mg l⁻¹ Ce. The adsorbent competency of Mangifera seed towards
Cr removal was greater than Syzygium and Ficus seeds at same equilibrium concentration.

The sorbent *F. racemosa*, *M. indica* and *S. cumini* seeds for Cr (VI) is represented for Langmuir (Chemist) isopleths in Fig. 2b, which shows the equilibrium quantity of Cr (VI) in soluble form and adsorbed solid phase. The low values of Eq/qe (Fig. 2b) indicate higher sorption capacity found in *Mangifera* and Syzygium as compared to *Ficus*.

The $R^2$ constant was close to one (0.998, Table -1a), which indicate a decent harmonization with the equilibrium Cr quantity and sorption competency. The sorption capability (qm) to generate a single coating on exterior was found to be maximum 21.64 mg/l for *M. indica*, 13.53 mg/l for *S. cumini* and 11.37 mg/l for *F. racemosa* at neutral medium. The adsorption energy was 0.130 ($M. indica$), 0.339 ($F. racemosa$) and 0.392 ($S. cumini$) mg/l showing active chromium (VI) sorption conditions (Hall et al., 1966).

The Freundlich isopleth (Fig. 2c) and constants (Table 1b) showed $R^2$ close to unity (0.999) conforming the Freundlich equation. Kadivelu and Namasiyavam, 2000; Qaiser et al., 2005 found that intensity of biosorption (n) between one and ten showed positive active sorption. The magnitude of Kf and n shows straight forward sorption of significant metal ion and high adsorption capacity (Ahalya et al., 2005). Distribution of metal ions on the biosorbent surface was found to over unity (n values), indicating active adsorption.

The comparative sorption competencies increased in the following order *F. racemosa* < *S. cumini* < *M. indica* seed (11, 13 and 23 mgg/ ) for chromium (VI) at neutral pH scale. The highest sorption occurred at high sorbent doses, low hydrogen ion activity, increase in temperature and low Cr (VI) concentration within two hour duration and the process also confirmed the isopleths applications.

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References


