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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 cumini* 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 mgg^{-1} where as *S. cumini* and *M. indica* showed biosorption capacity of 13 and 21 mgg^{-1} 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.

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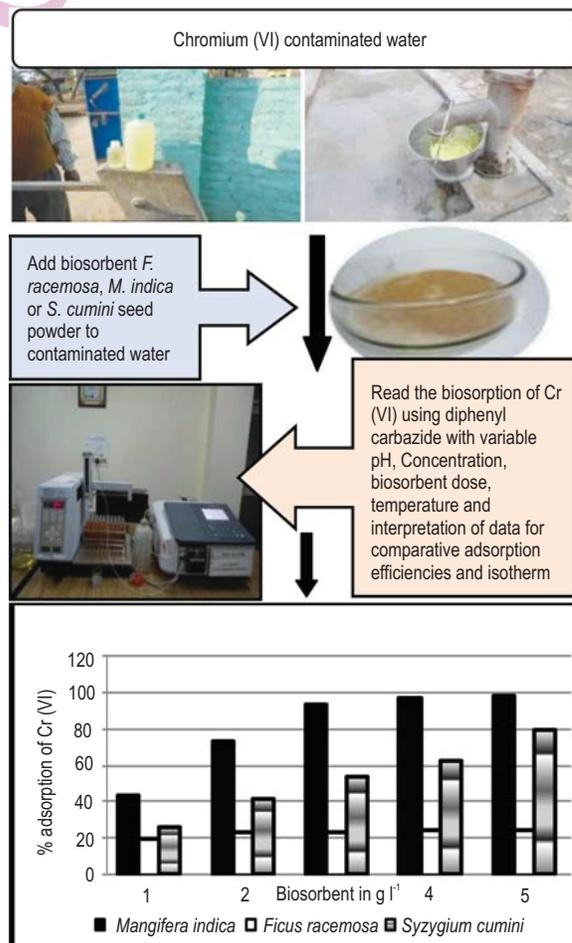
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Introduction

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 oxidization 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 like 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 glaucanol, 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 $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water and additional dilutions were made to desired concentrations for calibration. The contaminated samples were standardized against known $\text{K}_2\text{Cr}_2\text{O}_7$ solution further diluted to experimental strength of $10\text{-}50 \text{ mg l}^{-1}$ 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 ($90\text{-}110^\circ\text{C}$) and air-dried in open after grinding 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 $250 \mu\text{m}$.

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 $10\text{-}50 \text{ mg l}^{-1}$ and temperature studied was $10\text{-}40^\circ\text{C}$ 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

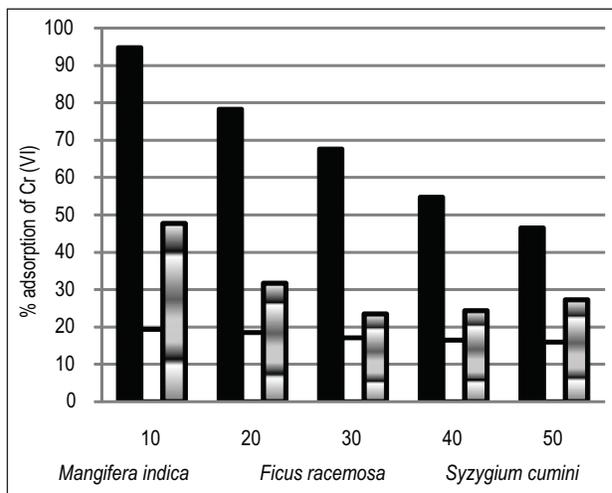
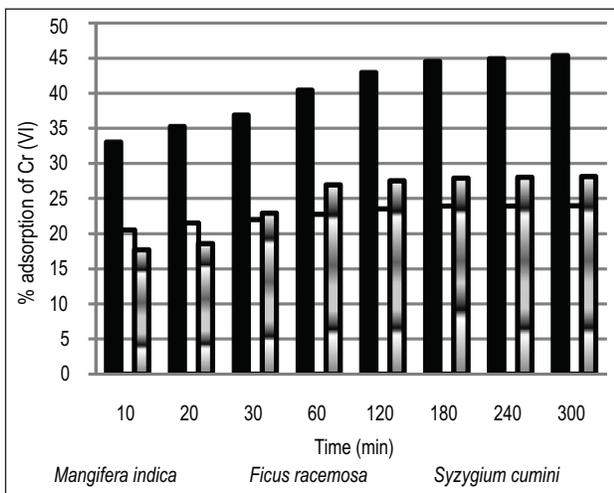


Fig. 1a : Effect of time duration on percentage adsorption of Cr (VI)

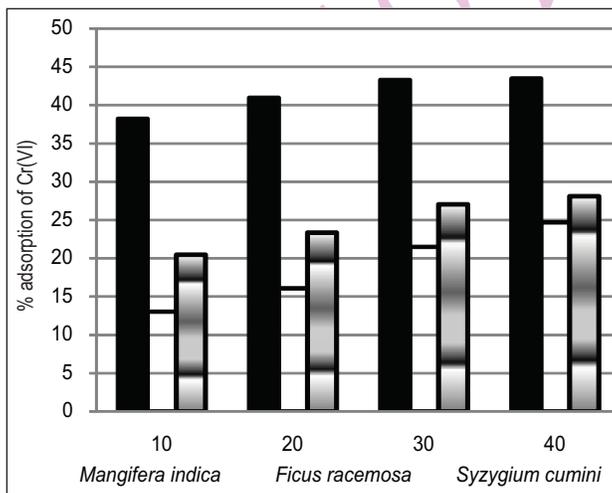


Fig. 1c : Effect of temperature (°C) on Cr assimilation

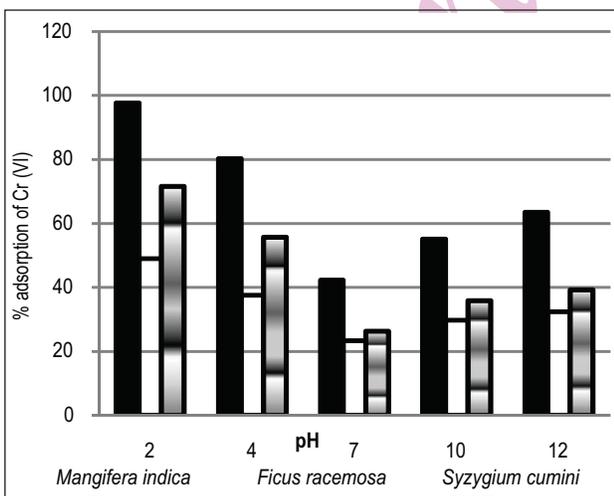


Fig. 1d : Effect of hydrogen ion activity on biosorption of Cr (VI)

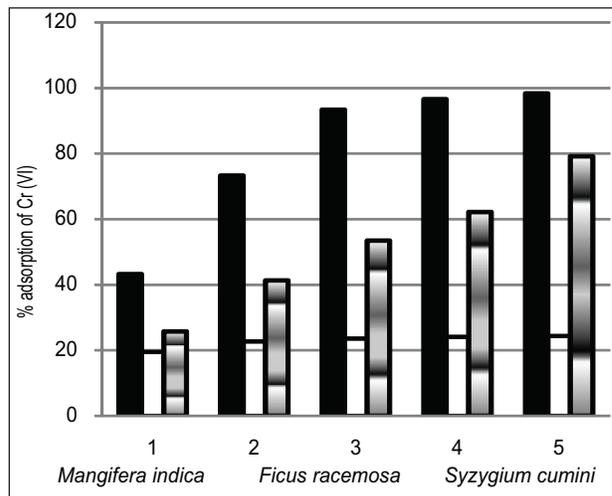


Fig. 1e : Effect of sorbent application (g^l⁻¹) on Cr (VI) biosorption

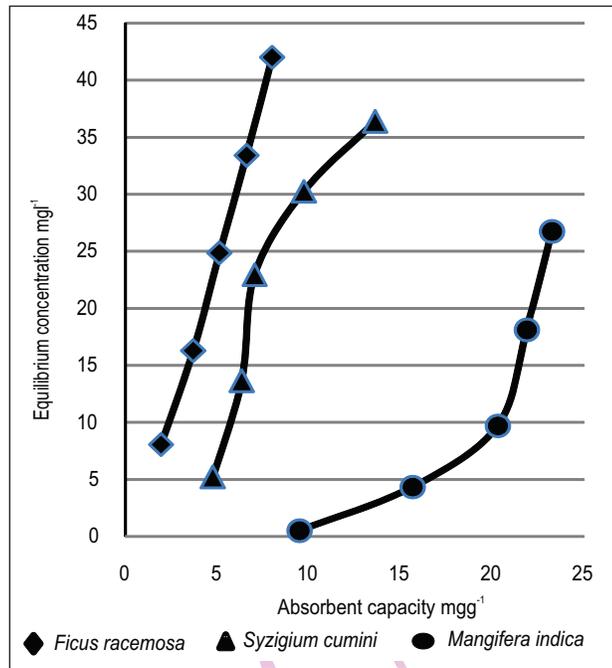


Fig. 2a : Linear sorption isotherm of Cr (VI)

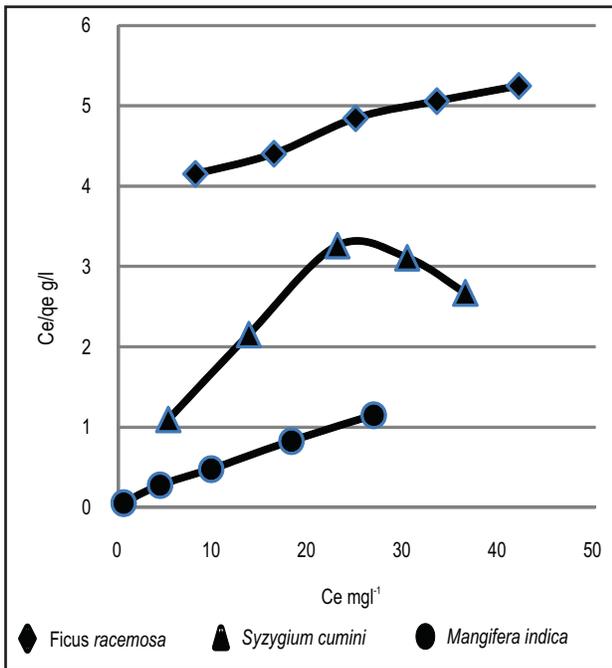


Fig. 2b : Langmuir representation for Cr (VI)

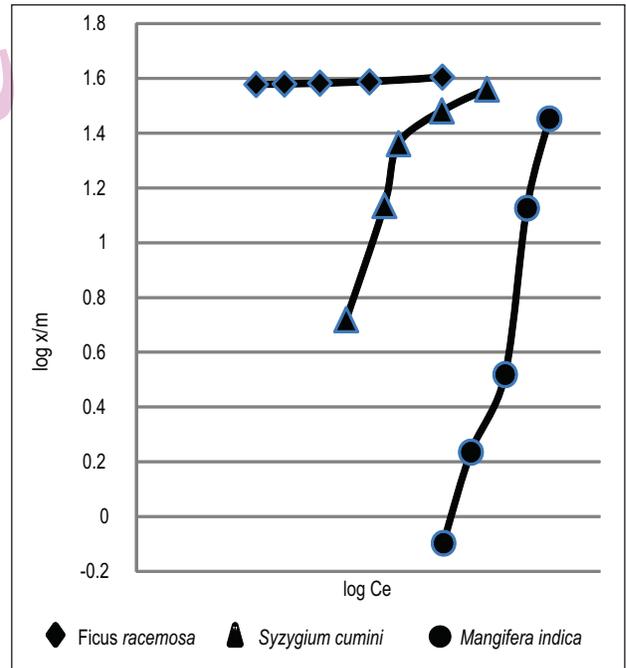


Fig. 2c : Freundlich representation for Cr (VI)

natural process with time has also been reported by Aziz (2004) for elimination of iron metal treating with CaCO₃ 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⁻¹ Cr was readily adsorbed by *M. indica*

Table 1a : Langmuir constants of seed grain powders

Sorbent powder	Constant		(R^2)
	q_m (mgg ⁻¹)	b (img ⁻¹)	
<i>F. racemosa</i>	5.13	0.033	0.976
	11.37	0.339	0.998
<i>M. indica</i>	20.29	0.041	0.996
	21.64	0.120	0.998
	21.12	0.046	0.935
	20.21	0.130	0.994
<i>S. cumini</i>	9.73	0.004	0.972
	13.53	0.345	0.993
	13.15	0.099	0.913
	13.48	0.392	0.991

Table 1 b : Freundlich constants for Cr (VI)

Sorbent material	Constant		(R^2)
	K_f	$1/n$	
<i>F. racemosa</i>	3.006	0.853	0.999
<i>M. indica</i>	1.117	0.234	0.989
	1.084	0.211	0.961
<i>S. cumini</i>	1.986	0.472	0.827
	2.518	0.421	0.821

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 Killedar 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 biosorbent 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 conjointly 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⁺, Cr³⁺ and Cr⁶⁺ 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⁻, CrO₄²⁻, Cr₂O₇²⁻ type strong electro static attraction with cationic sorbent, -COOH and -NH_x 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_x 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 chromium (VI) within the solution to its concentration on the solid exterior (mass of chromium (VI) / unit mass of sorbent) is 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 mgg⁻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 C_e/q_e (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^{-1} for *M. indica*, 13.53 mg l^{-1} for *S. cumini* and 11.37 mg l^{-1} for *F. racemosa* at neutral medium. The adsorption energy was 0.130 (*M. indica*), 0.339 (*F. racemosa*) and 0.392 (*S. cumini*) lmg^{-1} 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. Kadirvelu and Namasivayam, 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 $^{-1}$) 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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