Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 05, pp.51087-51093, May, 2017

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

CHARACTERSTICS AND ADSORPTION CAPACITIES OF BIOSORBENTS FOR REMOVAL OF Cr (VI) FROM AQUEOUS SOLUTION: A REVIEW

Meenakshi Singh and *Meenu Agarwal

Galgotias University, Plot No.2, Sector 17-A Yamuna Expressway, Greater Noida, Gautam Buddh Nagar, Uttar Pradesh, India

ARTICLE INFO

Article History:
Received 25th February, 2017
Received in revised form
21st March, 2017
Accepted 14th April, 2017
Published online 31st May, 2017

Key words:

Biosorbents,
Batch experiments,
Langmuir and Freundlich adsorption isotherm, Pseudo-first order and pseudo-second order kinetic model.

ABSTRACT

Low-cost biosorbents can be made from the by-products of agricultural, household and various industrial processes. It has been proved by several researches that these biosorbents provide a better solution for the removal of contaminants from wastewater. The object of the study is to find a sustainable low cost biosorbent for the removal of Cr (VI) from wastewater. In current review both adsorbent's characteristics and adsorption capacities of nine biosorbents for the removal of Cr (VI) from aqueous solution were studied. Batch experiments of various adsorbents revealed the optimum conditions required for better removal of this heavy metal. The results showed that maximum adsorption occurs at highly acidic pH. Contact time, initial conc. of adsorbent & adsorbate also affect the heavy metal removal efficiency of biosorbent material. Under optimum conditions, the removal efficiency of adsorbent prepared from mango kernel was found upto 100% out of nine adsorbents studied. The Langmuir and Freundlich adsorption isotherm gave the better explanation for the surface properties of adsorbents. Maximum Cr (VI) uptake per unit mass ($Q_{max.}$) values obtained from Langmuir adsorption isotherm for different biosorbents ranged from 6.17mg/g to 151.51mg/g. The adsorption kinetics was explained through pseudo-first order and pseudo-second order kinetic model. The results of study suggest that these biosorbents could be a better solution for the removal of Cr (VI) from the wastewater.

Citation: Meenakshi Singh and Meenu Agarwal, 2017. "Characterstics and adsorption capacities of biosorbents for removal of Cr (VI) from aqueous solution: A Review", *International Journal of Current Research*, 9, (05), 51087-51093.

INTRODUCTION

Industrial effluent contains a large amount of different heavy metals. These metals enter into the environment through different sources and contaminate it. These metals are non-biodegradable and remain in the environment for a long time. Heavy metals are highly toxic and once enter into food chain, accumulate in it. Some of the heavy metals are soluble in aqueous media and easily pollute the aquifers. Chromium is one of such kind of metal which is present in the effluent of different industries such as tanning and leather manufacturing, paints and pigments, electroplating, textile, dying, fungicides, ceramics, photography and metal processing etc. Presence of high amount of chromium in the vicinity of tannery unit was reported by several authors (Brindha, 2012; Oruko, 2014; Azom, 2012 and Ramesh, 2014). Chromium is present in aqueous media mainly in two oxidation states Cr (III) and Cr (VI). Trivalent Chromium (in small quantity) is required for biological metabolism but hexavalent Chromium is toxic and carcinogenic to humans. Cr (VI) is 500 times more toxic (Belay, 2010), than Cr (III). In solutions Cr (VI) can be present in different forms (like chromate $Cr_2O_4^{2-}$, hydrochromate $HCrO_4^-$ or dichromate $Cr_2O_7^{2-}$) depending upon the pH of the solution. The standard limit of Cr in drinking water prescribed by WHO & BIS is 0.05mg/l. The prolonged consumption of Cr contaminated water causes body weakness, kidney and liver damage, ulcers on the skin and paralysis. Several techniques have been used by different researchers to remove Cr (VI) from waste water such as chemical precipitation, membrane processes, adsorption, redox adsorption, cementation, electrodialysis and ion exchange (Hua, 2017 and Assadi, 2012). Most of the techniques except adsorption have some limitations like complexity, sludge formation and expensive too. Adsorption technique is a latest technique for the removal of metal ions as it is cost effective and easy to handle. In adsorption- reduction process, Cr (VI) is reduced to less toxic Cr (III) and then removed by using adsorbent material (Fellenz, 2017; Li, 2011 and Misaelides, 2011). Now a days a number of adsorbent materials have been developed for the removal of Cr (VI) from the waste water. Conventional adsorbent materials are expensive like activated carbon (Ghosh, 2009), but now cheap bioadsorbents like grape fruit

Corresponding author: **Meenu Agarwal,**
Galgotias University, Plot No.2, Sector 17-A Yamuna Expressway, Greater Noida, Gautam Buddh Nagar, Uttar Pradesh, India

peelings (Rosales, 2016), banana peels (Ali, 2016), teff straw (Wassie, 2016), waste news paper (Dehghani, 2016), melaleuca leaf (S. Australia) (Kuppusamy, 2016), spirulina algae (Kwak, 2015), sea food processing waste (Dima, 2015), mango kernel (Rai, 2016), wood apple shell (Doke, 2017), etc. have been examined by several authors. In the present study, the efficiency of different bioadsorbent materials to adsorb Cr (VI) from aqueous solution has been reviewed.

MATERIALS AND METHODS

Preparation of Adsorbents

The activated carbons (both fresh and waste, AC and WAC respectively) were washed with distilled water and then removed the moisture by keeping it in an oven for 10hrs. at the temp. of 110-120^0 C. Both activated carbon and waste activated carbon were treated with mineral acids (sulfuric acid and nitric acid) to prepare different grade of adsorbent material. Different methods of pretreatment were used to prepare different adsorbent materials. The grapefruit peelings (GP) were washed with distilled water and then dried in oven at 60^{0}C. The dried material was grinded to the size lesser than 0.5mm. The pretreatment of biosorbent was done by H_2O_2 (1M) (Shen, 2011). For the preparation of adsorbent from banana peels, first acid and alkaline hydrolysis of banana peels was done and then alkali hydrolyzed banana peels were bleached by sodium chlorate in the presence of acetic acid & H_2O_2. To increase the adsorption capacity of banana peels, the content was washed with distilled water. Washing of pulp remove the viscous compound like lignin and pectin (Yang, 2009). The grafting copolymerization of acrylonitrile onto the bleached peel was carried by Fenton's initiator (Fe^{2+}/ H_2O_2).

The grafted banana peel (GBPs) was thoroughly washed with 2-propanol and acetone and dried. Brown teff straw was washed, dried, milled and then sieved to the size ranged from 0.1-0.6 mm. Waste newspaper (WNP) adsorbent material was prepared by treating tiny newspaper pieces with conc. $NaHCO_3$ solution and then phosphorylation was done with 5.0% Na_2HPO_4. The specific surface area of treated newspaper (TWNP) was increased due to phosphorylation. To prepare biosorbent from Melaleuca diosmifolia (M. diosmifolia) plant, twigs of plant were washed, dried, ground and sieved (particle size 0.5mm). Spirulina platensis extract (SPE) was prepared by soaking 20gm of Spirulina platensis algae in 1lit. of distilled water and shaken continuously for 24h at 4^{0}C. After centrifugation (at 5000 rpm for 10min.), the supranatant was filtered, dried and stored. SPE beads were prepared by dissolving different amounts of SPE into 10 ml. of 1 M LiCl/DMSO* for 3hrs and the solution was dripped into coagulants. The methanol and ethanol gave better strength to SPE beads. Shrimp shells which were discarded by seafood processing industry in Argentina had a large amount of chitin material. This chitin was used to prepare chitosan (CH) and reticulated micro/nanoparticles of chitosan (MCH). MCH was synthesized by ionic gelation of chitosan using tripolyphosphate (TPP). To get adsorbent material from mango kernel, it was dried, crushed and sieved to the particle size of 710-1000µm. The powered material was activated by 40% H_3PO_4 and then activated material was carbonized at 600^{0}C for 1hr under inert atmosphere. Thus mango kernel activated carbon (MKAC) was obtained. The shells of wood apple fruit were crushed and soaked in conc. H_2SO_4 for 48 hrs. The obtained material was heated in muffle furnace for 2 hr at 600^{0}C and cooled down.

* Dimethyl sulfoxide

Preparation of adsorbate

In most of the reported papers, stock solution of chromium was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in distilled water. Stock solution was further diluted to obtain required conc. of solution. pH value of the solution was adjusted by 1.0N HCl and 1.0N NaOH. E. Rosales *et al*. used four leather dyes (Sella Solid Blue, Special Violet, Derma Burdeaux and Sella Solid Orange) to prepare pollutant solution (DM i.e. Dye mixture).

Characterization of Adsorbents

The results of characterization of different biosorbents are given in Table 1. FTIR (Fourier transform infrared spectroscopy) spectra of treated biosorbent made from grape fruit peelings showed modified peaks at 3650- 3200, 1738, 1375-1365, 1050-1010 cm^{-1}. These peaks are characteristic peaks of cellulose, hemicelluloses and lignin. Pretreatment of biosorbent increased the surface area of material for more adsorption. Adsorption capacity of treated biosorbent was found 1.1003meqg^{-1} for the different reaction sites. The surface chemistry of biosorbent is determined by point of zero charge (pH_{ZPC}). The pH_{ZPC} value of pretreated grapefruit peelings biosorbent was found 3.48 by mass titration (Noh, 1989). The SEM (scanning electron microscopy) images of grafted banana peel, before and after adsorption showed that before adsorption the surface of biomaterial has open pores and fibres but after the adsorption the pores and caves were filled by adsorbate ions. It also showed that the surface became much smoother after adsorption.

The scanning electron micrographs of teff straw surface showed that the surface of the biomaterial was porous in nature. Elemental composition of bio material was determined through EDX (Energy dispersive X-ray spectroscopy) analysis and results showed that 49%carbon, 45%oxygen and rest calcium, magnesium, iron was present. The internal structure was studied by Barrett Joyner-Helenda (BJH) analysis. The observed BJH pore diameter was 43.9Å. Thermo gravimetric analysis of the teff straw showed that during the heating the 6 - 9 % weight loss (upto 150^{0}C) due to moisture loss , 65-75% weight loss (220^{0}C-320^{0}C) due to hemi-cellulose and cellulose decomposition . Decomposition of lignin occurs at 320^{0}C - 500^{0}C. FTIR of teff straw after absorption showed that the peak strength of all functional group was reduced due to involvement of these functional groups in the absorption process. By BET (Brunauer- Emmett-Teller nitrogen adsorption technique) method, the observed S_{BET} value of WNP was ranged from 885-1020m^2 gm^{-1} & of TWNP was 1214-1652 m^2 gm^{-1} which clearly indicate that the surface area of adsorbent material increased after treatment. The calculated pore volume of the WNP & TWNP was 0.98 and 1.01 ml gm^{-1}. The FTIR spectra of treated news paper before and after Cr (VI) adsorption were found in the range from 4000cm^{-1}-400cm^{-1}. The chemical composition of the adsorbent material made from Melaleuca diosmifolia Leaf was determined by Trumac Carbon Nitrogen analyzer and gas chromatography. Surface morphology was investigated by SEM analysis and FTIR. The S_{BET} value of adsorbent material was 0.99m^2 gm^{-1}.

Surface charge of the material at different pH was ranged from +0.81 to -8.37 mV. The major constituents of the material were C (502.1 mg/g), N (9.8mg g^{-1}), Ca (8.4mg g^{-1}) and K (6.4mg g^{-1}). Other constituents were Na, P, Mn, Fe, Al, Zn, Cu, Ni, and S etc. The main component of Spirulina platensis extract (SPE) is protein and it was the 60% of the total SPE. The spherical shaped beads were obtained at the concentration of 20% and 25% (W/N). The surface of SPE was characterized through FE-SEM. The results showed that methanol and ethanol coagulant gave better strength to SPE beads. The surface of SPE beads were studied by ATR-FTIR. After the adsorption of Cr (VI) a new peak at 933cm^{-1} in the ATR-FTIR (Attenuated total reflection fourier transform infrared spectroscopy) spectrum was observed due to Cr-O stretching vibration.

The degree of deacetylation of chitosan particles (CH) obtained from seafood processing wastes (shrimp shells) was determined by FTIR and potentiometric titration. The calculated N- deacetylation percentage from the potentiometric curve was 90.2% and from the FTIR was 86.9%.The obtained molecular weight of CH from intrinsic viscosity measurement was 1.46×10^5 Da. Reticulated micro/nanoparticles (MCH) were characterized by SEM, measurement of the size distribution and Zeta potential (Photon correlation spectroscopy, PCS). Incorporation of TPP increases the particle size of MCH. At the pH > 5, the particle size of MCH also increased. The optimum conditions for MCH synthesis were volumetric proportion of TPP and CH should be 1:3, concentration of TPP and CH should be 1.5gm/lit and 1.25gm/lit at pH < 5. The chemical composition of Raw mango kernel and carbonized mango kernel activated carbon (MKAC) was done with elemental analyzer and high content of carbon (78%) was found in MKAC. The FTIR spectrum of the material before and after the adsorption of Cr (VI) showed that the intensity of the peaks became less after the Cr (VI) adsorption. The location of the peaks were also shifted due to adsorption. The SEM images of the adsorbent material before adsorption showed high porosity and homogeneity but after adsorption of Cr (VI), a layer is formed on the surface of the adsorbent material.

The FTIR spectrum of adsorbent prepared from wood apple shell (WAAC) has the peaks from 3000 cm^{-1} -800cm^{-1}. The pH_{PZC} value of the adsorbent material was 3.95. The adsorption of Cr (VI) is favourable below this pH value as the electrostatic attraction between the surface functional group and anionic $HCrO_4^-$.

Batch Adsorption Experiments

The adsorption assays were carried out in Erlenmeyer flasks (250ml) containing a known amount of the stock solution of Cr (VI) and adsorbent material at controlled temperature. The batch experiments were done at different contact times, initial conc. of Cr (VI) ions, adsorbent dose and at different pH.

The removal percentage of Cr (VI) ion was calculated as follows-

$$\% \text{ Removal of Cr (VI)} = \frac{C_0 - C_e}{C_0} \times 100$$

The amount of Cr (VI) adsorbed per gram of adsorbent material was calculated according to the following equation-

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where C_0 *and* C_e are the initial and equilibrium concentration of Cr (VI), V is the volume of the solution in litres, W is the adsorbent dose in grams and q_e is the amount of Cr (VI) ion adsorbed per gram of adsorbent material. Experiments were replicated many times to obtain the conditions required for equilibrium. The effect of pH, initial conc. of Cr (VI) ion, adsorbent dose and contact time on the efficiency of adsorbent material to remove Cr (VI) was given in Table-2.

Adsorbent activity for Cr(VI) removal under different optimum conditions

The optimum conditions for Cr (VI) removal were determined by the kinetic study of the reaction. The pH of the solution is a major factor which affected the rate of adsorption. To know the effect of pH on the rate of adsorption, experiments were carried out over a wide range of pH (2-10). At highly acidic pH Cr (VI) was present as oxyanions ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}) and the surface of biosorbents was also protonated. A strong electrostatic attraction between the oxyanions of Cr (VI) and surface functional group was present and it decreases with the increasing pH (Gupta, 2009) Fig. 1(a) showed the optimum pH for various adsorbents at which maximum removal of Cr (VI) occurs.

The effect of contact time between the biosorbent and adsorbate solution on the removal efficiency was given in Fig. 1(b). The effect of contact time on Cr (VI) removal was studied at optimum pH. The figure clearly indicates that the contact time of 60 minutes to 400 minutes was necessary for maximum removal of Cr (VI). The rate of removal of Cr (VI) initially increases with time but after equilibrium no significance change in Cr (VI) concentration was observed. Initial high rate of adsorption was due to the availability of plenty of active sites on the surface of biosorbent and high interaction between the adsorbate and absorbent surface (Gupta *et al*., 2010).

To study the effect of initial Cr (VI) conc. on the removal efficiency, the experiments were carried out with variable initial Cr (VI) conc. at optimized conditions. Initially adsorption increases with the increase in the conc. of Cr (VI) but after equilibrium remained nearly constant. Fig. 1(c) shows the effect of Cr (VI) conc. on the removal efficiency of different biosorbents. Initially the number of metal ions at the surface of adsorbent was high hence adsorption occurs at faster rate but after equilibrium most of the active sites of adsorbent became saturated (Donmez and Aksu, 2002).

The optimum biosorbent dose at which maximum removal of Cr (VI) was reached is given in Fig. 1(d). Results of several researches showed that removal of Cr (VI) was increased with the increasing amount of adsorbent. Higher Cr (VI) removal efficiency at high adsorbent dose was due to larger surface area was available for the adsorption. The 5gm/l dose of M. Diosmifolia adsorbent removed 99.9% of Cr (VI) from the solution (Jung *et al*., 2013).

Adsorption Isotherm Study

The surface properties of adsorbent material were determined through adsorption isotherms. In most of the research papers the interaction between adsorbent surface and adsorbate molecules was explained through Langmuir and Freundlich isotherms. These two common isotherm models explain the adsorption equilibrium data.

Table 1. Adsorbent Properties and Characterization

Adsorbent	Characterization Technique used	Obtained characteristics/ results
Grape fruit peelings	FTIR	Pretreatment of grape fruit peelings with H_2O_2 reduces the cellulose
	SEM	crystallinity and increase the surface area of the adsorbent.
	EDX analysis	The pH_{PZC} of biosorbent was 3.48.
	Boehm titration mass titration	
Acrylonitrile grafted banana peel	SEM	Bleaching of raw banana peel remove the lignin, pectin & other viscous compound.
Teff straw	SEM	Porous surface of biomaterial,
	EDX analysis	Elemental composition (49% C, 45% O & rest were Ca, Mg, Fe).
	BJH analysis	BET surface area was 30.5m^2/g.
	Therogravimetric analysis	Peaks were found between 3420 cm^{-1} – 1090 cm^{-1}.
	FTIR	
Waste Newspaper	BET method	S_{BET} of WNP = 885-1020 m^2g^{-1}
	SEM	S_{BET} of TWNP = 1214-1652 m^2g^{-1}.
	FTIR	Pore volume of WNP = 0.98mlg^{-1}
		Pore volume of TWNP = 1.01mlg^{-1}
		Moisture content of WNP = 7.68%
		Moisture content of TWNP = 6.82%
Melaleuca diosmifolia Leaf	Gemini V surface analyser	S_{BET} = 0.99 m^2/g
	Trumac CN analyzer (instrument)	Mineral composition of the material was
	ICP-MS	C = 502.1mg/g,
	Gas chromatography	N = 9.8
	SEM	P = 0.6
	FTIR	K = 6.4, Ca = 8.4, Mg = 1.7, Na = 2.1 etc.
Spirulina platensis extract	SEM	Yield of SPE was 30.77%
	ATR-FTIR	Suitable solvent was 1M LiCl/DMSO
Sea food processing wastes	FTIR	Deacetylation degree of CH = 86.9% (FTIR)
	Potentiometric titration	Deacetylation degree of CH = 90.2% (T. Curve)
	Intrinsic viscosity (η) measurement SEM	η = 1002.9mlg^{-1}
Mango kernel	BET analysis	S_{BET} = 490.43 m^2g^{-1}
	FTIR	Bulk density = 1.43 g/cm^3
	SEM	Porosity = 0.576
		Average particle size = 781.5µm
		Average pore size = 38.9µm
		pH_{PZC} = 6.8
Wood apple shell	Batch equilibrium method	pH_{PZC} = 3.95
	FTIR	Specific surface area = 1898 m^2g^{-1}.

Table 2. Optimum conditions for Cr (VI) adsorption

Adsorbent	pH	Contact Time(min.)	Initial Cr (VI) conc. (mg/l)	Adsorbent Dose (gm/l)	Removal Efficiency (%)
AC	2	360	10	2	83
GP	5.5	400	35	1	99.95
GBPs	3	120	400	4	96
Teff straw	2	360	400	10	97
WNP	3	60	70	3	64
M. Diosmifolia	2	120	250	5	99.9
SPE	2	-	250	1	-
MCH	2	180	50	0.8	98
MKAC	2	150	60	2.5	100
WAAC	1.8	120	75	1.25	95

Table 3. Parameters of Langmuir isotherm for adsorption of Cr (VI) onto different adsorbents

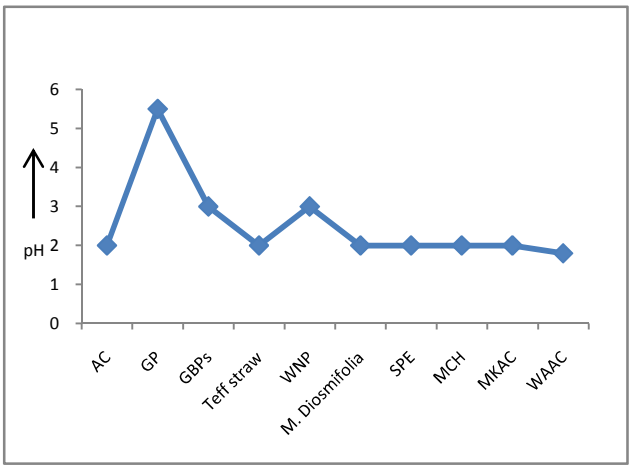
Adsorbents	Q_{max} (mg/g)	K_L(l/gm)	R_L	R^2
AC	10.9290	4.2087	0-1	0.9882
GP	39.0628	2.8631	0-1	0.9802
GBPs	6.1728	0.9884	0-1	0.9957
Teff straw	86.1	1.6597	0-1	0.999
WNP	59.88	0.371	0.058-0.303	0.98
M. Diosmifolia	62.50	0.13	0.01-0.07	0.980
SPE	50.530	0.101	0-1	0.989
MCH	124	0.086	0-1	0.990
MKAC	7.96	0.2634	0.157-0.2702	0.995
WAAC	151.51	0.1524	0.0318-0.0805	0.9883

Table 4. Parameters of Freundlich isotherm for adsorption of Cr (VI) onto different adsorbents

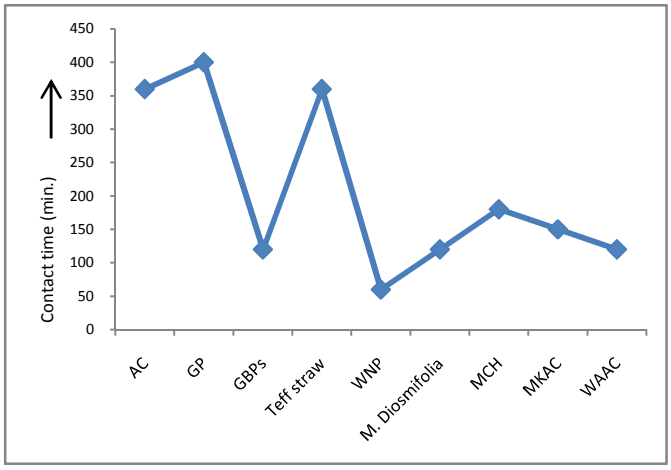
Adsorbents	K_A (mg/g)	$1/n$	R^2
AC	2.2636	0.5875	0.9876
GP	76.6809	0.9185	0.9784
GBPs	3.8308	1.2376	0.997
Teff straw	37.7	0.2778	0.646
WNP	19.02	0.691	0.96
SPE	15.755	0.2278	0.946
MCH	60.42	0.12	0.977
MKAC	1.198	1.3158	0.974
WAAC	39.07	0.3389	0.9753

Table 5. Kinetic Parameters for the adsorption of Cr (VI) on different biosorbents

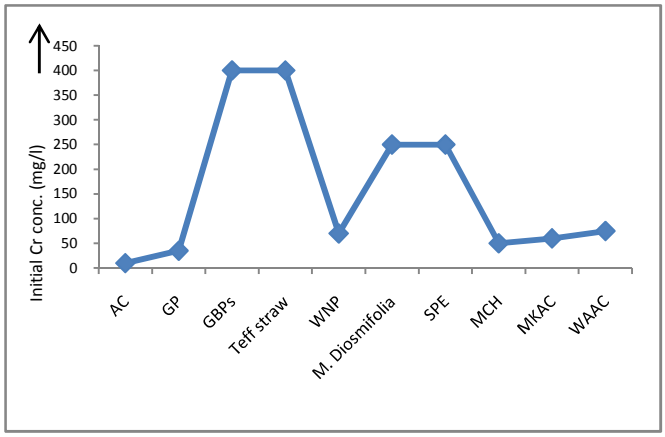
	Pseudo-first order kinetic $q_t = q_e\ [1 - \exp(-k_f\ t)]$			Pseudo-second order kinetic $q_t = \frac{tk_s\ q_e^2}{1 + tk_s\ q_e}$			
Adsorbents	q_e (Mg/g)	k_f (1/min.)	R^2	q_e (mg/g)	k_s (g/mg.min.)	h (mg/g.min.)	R^2
GP	1.8280	1.0820	0.9996	1.8587	1.4655	-	0.9795
GBP_S	64.21	0.0594	-0.9957	135.75	0.0417	-	0.9954
Teff straw	7.13	0.028	0.9020	9.09	0.005	0.413	0.990
WNP	1.63	0.007	0.9700	8.79	0.002	-	0.99
M. Diosmifolia	-	-	-	49.38	0.15	378.8	1
MCH	-	0.032	0.9320	-	0.0013		0.946
MKAC	5.60	0.017	0.9650	8.54	0.0022	-	0.981
WAAC	19.01	0.0231	0.9590	27.03	0.00177	1.292	0.982



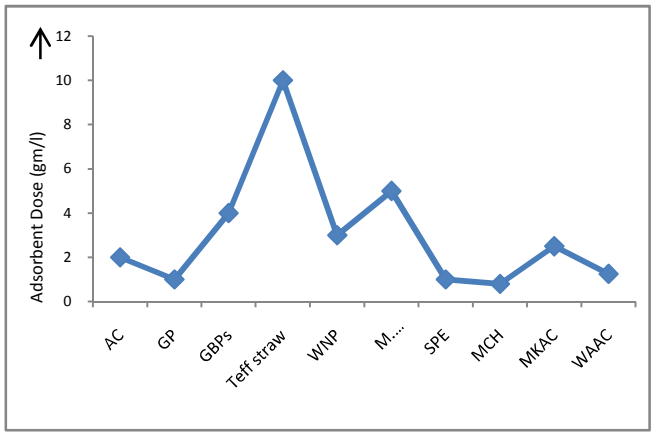
(a)



(b)



(c)



(d)

Fig.1. Removal efficiency of adsorbents at different (a) pH range, (b) contact time, (c) initial Cr (VI) conc., and (d) adsorbent dose

Langmuir adsorption isotherm

Langmuir model suggest the monolayer adsorption of adsorbate molecules on the homogenous surface of adsorbent having finite number of adsorption sites. The adsorbate molecules have no interaction to the adjacent molecules.

The linear form of Langmuir adsorption isotherm is given as-

$$\frac{C_e}{q_e} = \frac{1}{Q_{max.}\ K_L} + \frac{C_e}{Q_{max}}$$

Where C_e is the equilibrium conc. of adsorbate in mg/l, q_e is the amount of the adsorbate, adsorbed at equilibrium in mg/g, Q_{max} is the maximum monolayer adsorption capacity in mg/g and K_L is the Langmuir equation constant.

Linear plot was obtained by plotting C_e / q_e against C_e with intercepts $\frac{1}{Q_{max.}\ K_L}$ and slope 1/ Q_{max}.

The essential characteristics of Langmuir isotherm is dimensionless separation factor R_L (Iglesias *et al*., 2013), which is calculated by the following equation –

$$R_L = \frac{1}{1 + K_L\, C_0}$$

Where C_0 is the initial conc. of Cr (VI) in mg/l. The value of R_L indicates whether the adsorption isotherm to be unfavourable ($R_L > 1$), favourable ($0 < R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). In the reported research papers the calculated value of R_L was between 0 to 1 which indicates the favourable adsorption of Cr (VI) on the biosorbent material. Different parameters of Langmuir isotherms for the adsorption of Cr (VI) on different adsorbents are given in the Table 3. The maximum Langmuir monolayer adsorption capacity of Cr (VI) adsorption is for activated carbon obtained from wood apple shell. The adsorption capacity of different biosorbents for the removal of Cr (VI) in terms of $Q_{max.}$ was studied by many researchers (29-38). The results indicate the higher adsorption capacity at low pH value.

Freundlich adsorption isotherm

Freundlich adsorption isotherm gives empirical relation between conc. of adsorbate on the surface of adsorbent to the conc. of adsorbate in the solution. It is used to describe the data for multilayer adsorption on heterogenous surface of adsorbents. Freundlich adsorption isotherm is given by the following equation-

$$q_e = K_A\ C_e^{\,1/n}$$

Where K_A is the Freundlich adsorption capacity parameter in mg/g and $1/n$ is the Freundlich adsorption intensity parameter. The plot of $\ln q_e$ against $\ln C_e$ gives a straight line with slope $1/n$. The values of different parameters of Freundlich isotherm were given in Table 4. The values of $1/n$ show that adsorbents are effective for the adsorption of Cr (VI).

Adsorption Kinetics

In the present review study, several kinetic models were used to study the rate of adsorption of Cr (VI) on the adsorbents but most of the adsorption kinetics studies were well fitted in Lagergren pseudo-first order kinetic and Ho and Mckay pseudo-second order kinetic models. The adsorption kinetics shows the relation of contact time with the rate of adsorption. The equation of pseudo-first order and pseudo-second order with the parameters value for different adsorbent are given in Table 5. Where q_t is the quantity of Cr (VI) (in mg/g) adsorbed at time t , q_e is the quantity of Cr (VI) adsorbed at equilibrium, k_f is the pseudo-first order rate constant (1/min.) and k_s is the kinetic rate constant (g/mg.min.) for pseudo-second order kinetic model. $h = k_s\ {q_e}^2$ (mg/g.min.) is the initial adsorption rate which is used for the determination of adsorption rate. The values of correlation coefficient (R^2) from the Table-5 shows that adsorption of Cr (VI) on grapefruit peelings is well fitted into pseudo- first order model and adsorption kinetics of Cr (VI) on rest of the reported biosorbents follow pseudo-second order model.

Conclusion

Based on the literature reviewed, it was concluded that different low cost biosorbents are available which can remove Cr (VI) from the waste water effectively. At the acidic pH, biosorbents show high adsorption capacity. The adsorption capacity decreases with increasing pH. Rate of adsorption of Cr (VI) on the surface of adsorbent decreases with time. Rate of adsorption also depends on the initial conc. of adsorbate and adsorbent. Langmuir and Freundlich isotherms were used to explain the adsorption equilibrium data. The adsorption kinetics was studied using pseudo-first order and pseudo-second order model. Kinetic analysis of all the studied biosorbents (except grapefruit peelings) was well fitted into pseudo-second order model. Study of reported papers reveals that low cost adsorbents present a promising solution for the removal of Cr (VI) from the waste water. However majority of the adsorption process was tested at lab-scale.

Acknowledgement

The authors express their gratitude and thanks to Galgotias University, Greater Noida to publish this review paper.

REFERENCES

Ali, A., Saeed, K., Mabood, F. 2016. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent, *Alex. Eng. J*., 55 2933-2942.

Altundogan, H. S., Bahar, N., Mujde, B., Tumen, F. 2007. The use of sulphuric acid-carbonization products of sugar beet pulp in Cr (VI) removal, *J. Haza. Mat*., 144 255-264.

Argun, M. E., Dursun, S., Ozdemir, C., Karatas, M. 2007. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, *J. Haza. Mat*., 141 77-85.

Assadi, M. H. Dehghani, N. Rastkari, S. Nasseri, A. H. Mahvi, 2012. Photocatalytic reduction of hexavalent chromium in aqueous solution with zinc oxide nanoparticles and hydrogen peroxide, *Environ. Prot. Eng*., 38 5-16.

Azom, M. R., Mahmud, K., Yahya, S. M., Sontu, A., Himon, S. B. 2012. Environmental Impact Assessment of Tanneries: A Case Study of Hazaribag in Bangladesh, *Inter. J. Environ. Sc. Develop*., 3 152-156.

Belay, A. A. 2010. Impacts of Chromium from Tannery Effluent and Evaluation of Alternative Treatment Options, *J. Environ. Prot*., 1 53-58.

Brindha, K., Elango, L. 2012. Impact of Tanning Industries on Groundwater Quality near a Metropolitan City in India, *Water Resour. Manage*., 26 1747–1761.

Dakiky, M., Khamis, M., Manassra, A., Mer'eb, M. 2002. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents , *Advan. Environ. Res*., 6 533-540.

Dehghani, M. H., Sanaei, D., Ali, I., Bhatnagar, A. 2016. Removal of chromium(VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: Kinetic modelling and isotherm studies, *J. Mol. Liq*., 215 671-679.

Dima, J. B., Sequeiros, C., Zaritzky, N. E. 2015. Hexavalent chromium removal in contaminated water using reticulated chitosan micro/nanoparticles from seafood processing wastes, *Chemosphere*, 141 100-111.

Doke, K. M., Khan, E. M. 2017. Equilibrium, kinetic and diffusion mechanism of Cr (VI) adsorption onto activated carbon derived from wood apple shell, *Arab. J. Chem*., 10 S252-S260.

Donmez, G., Aksu, Z. 2002. Removal of chromium (VI) from saline wastewaters by Dunaliella species, *Pro. Bioche*., 38 751-762.

Fellenz, N., Alonso, F. J. P., Martin, P. P., Fierro, J. L. G., Bengoa, J. F., Marchetti, S. G., Rojas, S. 2017. Chromium(VI) removal from water by means of adsorption-reduction at the surface of amino-functionalized MCM-41 sorbents, *Micropo. Mesopo. Mat*., 239 138-146.

Gao, H., Liu, Y., Zeng, G., Xu, W., Li, T., Xia, W. 2008. Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste—Rice straw, *J. Haza. Mat*., 150, 446-452.

Ghosh, P. K. 2009. Hexavalent chromium [Cr(VI)] removal by acid modified waste activated carbons, *J. Haz. Mat*., 171 116-122.

Gupta, V. K. A. 2009. Rastogi, Biosorption of hexavalent chromium by raw and acid-treated alga Oedogonium hatei from aqueous solutions, *J. Haza. Mat*., 163 396-402.

Gupta, V. K., Pathania, D., Sharma, S., Agarwal, S., Singh, P. 2013. Remediation of noxious chromium (VI) untilizing acrylic acid grafted lignocellulosic adsorbent , *J. Mol. Liq*., 177 343-352.

Gupta, V. K., Rastogi, A., Nayak, A. 2010. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material,, *J. Coll. Inter. Sci*., 342, 135-141.

Hua, M., Yang, B., Shan, C., Zhang, W., He, S., Lv, L. Pan, B. 2017. Simultaneous removal of As(V) and Cr(VI) from water by macroporous anion exchanger supported nanoscale hydrous ferric oxide composite, *chemosphere*, 171 126-133.

Iglesias, O., Fernandez de Dios, M. A., Pazos, M., Sanroman, M. A. 2013. Using iron-loaded sepiolite obtained by adsorption as a catalyst in the electro-Fenton oxidation of Reactive Black 5, *Environ. Sci. Poll. Res*., 20 5983-5993.

Jung, C., Heo, J., Han, J., Her, N., Lee, S. J., Oh, J., Ryu, J., Yoon, Y. 2013. Hexavalent chromium removal by various adsorbents: powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, Sep. Purif. Techno., 106 63-71.

Kobya, M. 2004. Adsorption, Kinetics and equilibrium studies of Cr(VI) by Hazelnut Shell Activated Carbon, *Adsorp. Sci. Techno*., 22 51-64.

Kuppusamy, S., Thavamani, P., Megharaj, M., Venkateswarlu, K. Lee, Y. B., Naidu, R. 2016. Potential of Melaleuca diosmifolia leaf as a low-cost adsorbent for hexavalent chromium removal from contaminated water bodies, *Proc. Saf. Environ. Prot* 100 173-182.

Kwak, H. W., Kim, M. K., Lee, J. Y., Yun, H., Kim, M. H., Park, Y. H., Lee, K. H. 2015. Preparation of bead-type biosorbent from water soluble Spirulina platensis extracts for chromium (VI) removal, *Algal Res*., 7 92-99.

Li, Y., Zhu, S., Liu, Q., Chen, Z., Gu, J., Zhu, C., Lu, T. D. Zhang, *J. Ma,* N- doped porous carbon with magnetic particles formed in situ for enhanced Cr(VI) removal, *Water Res*., 47 (2013) 4188-4197.

Misaelides, P. 2011. Application of natural zeolites in environmental remediation: a short review, *Micropo. mesopo*. Mat., 144 15-18.

Noh, J. S., Schwarz, J. A. 1989. Estimation of the point of zero charge of simple oxides by mass titration, *J. Coll. Inter. Sci*., 130 157-164.

Oruko, R. O., Moturi, W. N., Mironga, J. M. 2014. Assessment of tannery based solid wastes management in Asili, Nairobi Kenya, *Inter. J. Qual. Res*., 8 227–238.

Pehlivan, E., Altun, T. 2008. Biosorption of Cr (VI) ion from aqueous solutions using walnut,hazelnut and almond shell, *J. Haza. Mat*., 155 378-384.

Prasad, A. G. D., Abdullah, M. A. 2010. Biosorption of Cr (VI) from synthetic wastewater using the fruit shell of gulmohar (*Delonix regia*): application to electroplating wastewater, *Bioresources*, 5 838-853.

Rai, M. K., Shahi, G., Meena, V., Meena, R., Chakraborty, S., Singh, R. S., Rai, B. N. 2016. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4, *Resou. Effi. Tech*., 2 S63-S70.

Ramesh, K., Thirumangai, V. 2014. Impacts of Tanneries on Quality of Groundwater in Pallavaram, Chennai Metropolitan City, *Int. J. Eng. Res. Appli*., 4 63-70.

Rosales, E., Meijide, J., Tavares, T., Pazos, M., Sanroman, M. A. 2016. Grapefruit peelings as a promising biosorbent for the removal of leather dyes and hexavalent chromium, *Proc. Saf. Environ. Prot*., 101 61-71.

Sarin, V., Pant, K. K. 2006. Removal of chromium from industrial waste by using eucalyptus bark, *Bioresource Techno*., 97, 15-20.

Sharma, D., Forster, C. 1994. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, *Bioresource Techno*., 47 257-264.

Shen, C., Wen, Y., Kang, X., Liu, W. 2011. H_2O_2-induced surface modification: A facile, effective and environmentally friendly pretreatment of chitosan for dyes removal, *Chem. Eng. J*., 166 474-482.

Wassie, A. B., Srivastava, V. C. 2016. Teff straw characterization and utilization for chromium removal from wastewater: Kinetics, isotherm and thermodynamic modelling, *J. Environ. Chem. Eng*., 4 1117-1125.

Yang, F., Li, G., He, Y. G., Ren, F. X., Wang, J. X. 2009. Synthesis, chracteriation, and applied properties of carboxymethyl cellulose and polyacrylamide graft copolymer, *Carbohydrate Poly.*, 78 95-99.

****