

Kinetics and Equilibrium Studies on the Biosorption of Cr(VI) by *Vigna Subterranean* (L.) *Verdc Hull*

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ABSTRACT: The *Vigna Subterranean* (L.) *Verdc hull*'s (*VSVH*) potential to remove Cr(VI) ions from aqueous solutions was investigated. The biosorbent was characterised by FTIR, SEM-EDX and XRF before and after exposure to Cr(VI). The surface comprised of phenolic, carboxylate, sulphonate, carboxyl, ammines, silica, silanol, phosphite esters, alkyl and hydroxyl functional groups responsible for Cr(VI) removal. Batch experiments were carried out in erlenmeyer flasks to optimize pH, contact time, biosorbent dosage and initial concentration of Cr(VI) ions. Reutilization of biosorbent was investigated using predetermined and optimized 0.14 M H₂SO₄. The initial and residual total chromium concentrations were estimated by FAAS. The optimum pH, contact time and biosorbent dosage were found to be 2, 180 minutes and 3 g/L respectively. The data generated from the effect of contact time and initial Cr(VI) concentration was subjected to kinetics and isotherm modelling respectively. The kinetic data fitted the pseudo first order model ($R^2 = 0.9334$) and the sorption mechanism was diffusion controlled with both film and intra particle diffusion involved in the rate limiting step. The isotherm study confirmed favourable monolayer sorption best described by Langmuir model ($R^2 = 0.9986$) with a very high monolayer sorption capacity of 232.5581 ± 0.9 mg/g. The Temkin model confirmed the endothermicity and weak ion-exchange nature of the Cr(VI)-biosorbent interactions that are important for biosorbent reuse. The biosorbent was recycled three times without significant loss of sorption-desorption capability. *VSVH* powder provides a renewable and reusable alternative for simple and effective Cr(VI) removal from wastewaters worth exploring for commercial-industrial application.

Key words: Bio-reduction, Cr(VI), Intra-particle diffusion, Kinetics, Reutilization

INTRODUCTION

Rapid industrialization has significantly increased the rate at which metal bearing wastewaters are released into the air, soil and aquatic environments (Gupta 2012). The proliferation of undercapitalized indigenous small scale enterprises, farmers, and miners together with population explosion has aggravated the situation in developing countries due to compromise or complete disregard of environmental laws. Chromium is amongst the heavy metals that are of major concern to human life. It has a wide range of industrial uses namely: as an oxidising agent in chemical industry, chrome plating in metallurgical industry, paint and pigments industry, ceramic or glass manufacture, dye production, textile industry, iron and steel industries, cement production, photography and in leather tanning (Sunil *et al.*, 2014). Apart from these beneficial uses, chromium (VI) is a highly toxic pollutant whose remediation has received much attention in recent years. The leather tanning

industries, pulp and paper, paint and pigments and Cr electroplating industries are among the worst producers of Cr(VI) rich effluents.

Cr(VI) finds its way into the environment through its release from industrial wastewaters and particulates, landfills, sewage sludge and improper discharge of Cr(VI) containing sludge among others (Gupta 2012). It has been reported to be carcinogenic and can modify the DNA transcription process. Babu and Gupta (2008) pointed out that Cr(VI) causes kidney and liver damage, stomach upset and ulcers, lung cancer, weakened immune system, respiratory problems, damages the circulatory system and nerve tissues. Hence its removal from the environment is a priority.

The conventional methods for heavy metal depollution include but not limited to: phytoremediation, precipitation, ion-exchange,

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electrolysis, reverse osmosis, solvent extraction, electrochemical precipitation, chemical reduction, nano-filtration, ultra filtration, evaporation and adsorption on silica, alumina, zeolite composites and activated carbon (Krishna *et al.*, 2013). The drawbacks of some of these techniques include: high initial and operation costs, production of post sludge that requires careful disposal and partial waste water cleaning especially of concentrations less than 100 mg/L (Abdel-Ghani and El-Chaghaby, 2014), hence the need for the search of cheaper, efficient and effective method.

Biosorption, a process of substance removal from aqueous solution by biological means has become an attractive alternative technique in wastewater treatment. Its advantages include: simple design, high abundance of biomaterial, generation of less sludge, high efficiency, environment friendly and is of low cost (Sunil *et al.*, 2014). These attributes have seen the exploration of a variety of biomaterials in the depollution of wastewaters containing both organic and inorganic hazardous substances. Amongst the most studied biosorbents, agricultural wastes have received much attention: A waste clean waste technique. The range of agricultural wastes that have been tested for Cr(VI) removal include: raw rice bran, rice straw, rice husk (Singha *et al.*, 2011), groundnut hull, sugarcane bagasse, sugar beet pulp, maize cob, coconut husk fibre (Qaiser *et al.*, 2009), neem sawdust, mango sawdust, wheat shell, orange peel (Vinodhini and Das 2009), apricot shell and almond shell (Khazaei *et al.*, 2011). Most of the biosorbents have very low uptake capacities implying that large amount of biomass is required for application purposes that would result in the generation of large amount of toxic sludge. There is need therefore, to search for better, economical and easily available biosorbents for the effective and efficient removal of Cr(VI) ions from aqueous solutions.

Vigna Subterranea (L.) *Verdc* hull (*VSVH*) is an agricultural waste that is produced in most Southern Africa countries and has no known commercial application. Large amount of the hulls are produced during harvesting time (March to April) and they pose disposal problems for they cannot be used as mulch or green manure due to their hygroscopic ability. In Zimbabwe, the hulls are burnt during land preparation (August to September) for the next farming season. Utilization of this abundant natural resource for Cr(VI) removal will significantly decrease the cost of chromium remediation by small scale industries and if found viable will minimize waste management labour on the part of the farmers.

The study focused on exploring the removal of Cr(VI) ions from aqueous solution by *VSVH* powder, an abundant agricultural waste that currently has no

known application or use. The biosorbent has not been investigated for pollutant removal except for the biosorption of Cu(II) ions where a maximum sorption capacity of 50.25 mg/g was achieved (Nharingo *et al.*, 2013). For the first time, the biosorbent was characterised by Fourier Transform Infrared spectrophotometer (FTIR), Scanning Electron Microscopy equipped with Energy Dispersive X-Ray (SEM-EDX) and X-Ray Fluorescence (XRF) before and after removal of Cr(VI) ions prior to the optimization of the critical sorption parameters, pH, contact time and dosage. The kinetic models and equilibrium sorption isotherms were applied in describing the sorbent-sorbate interactions. Finally, the study sought to establish the recyclability of the biomass through sorption-desorption cycles.

MATERIALS & METHODS

Vigna Subterranea (L.) *Verdc* (50 kg) was purchased from Kudzanai market place, Gweru, Zimbabwe, from four suppliers. The composite mixture of the nuts was hand shelled and 2 kg of the hulls was collected and washed four times with tap water, thrice with distilled water and finally rinsed with deionised water. The hulls were sun dried for 6 hours and then further dried in a laboratory oven (DHG-9070, India) set at 105 °C to constant mass (Nharingo *et al.*, 2013). The dry *VSVH* was ground into powder using pestle and mortar and sieved through a polythene 250 µm aperture sieve. The powder was sealed in polythene containers and was used as such with no further pre-treatment. Thermo Fisher FTIR was used to identify the functional groups associated with the biosorbent and those that were involved in the sorption process. SEM-EDX and XRF were employed to establish the morphology and elementary compositions of the biosorbent. The stock, 1000 mg/L, Cr(VI) solution was prepared by dissolving 2.827 g of $K_2Cr_2O_7$ in deionised water in a 1000 mL volumetric flask. All other Cr(VI) solutions were prepared by serial dilution of this stock solution. The pH of the solutions was adjusted using freshly prepared 0.1 M HCl and/ or 0.1 M NaOH solutions. Batch sorption studies were performed to optimize pH, contact time, biosorbent dosage and initial Cr(VI) concentration in triplicates.

The effect of pH was explored over the pH range from 1 to 7, where 100 mL of pH-adjusted 20 mg/L of Cr(VI) ions was agitated (200 rpm) with 0.4 g of the biosorbent for 24 hours at 25 ± 2 °C. The mixture was vacuum filtered and the initial and residual total chromium were estimated by Flame Atomic Absorption Spectrophotometry (FAAS).

Varying amounts of biosorbent masses (0.1 to 1 g) were separately added to each of 100 mL portions of 20

mg/L of Cr(VI) ions in erlenmeyer flasks. The mixtures were agitated over a shaker at 200 rpm for 24 hours at a temperature of 25 ± 2 °C and a predetermined pH of 2. The mixtures were vacuum filtered and analyzed for residual chromium by FAAS. Batch biosorption studies were also optimized for contact time in the range 1 to 300 minutes. Volumes of 100 mL of 20 mg/L of Cr(VI) ions were contacted with optimum dosage of 3 g/L at the optimum pH of 2, flask shaking rate of 200 rpm at 25 ± 2 °C in triplicates.

The effect of initial concentration of Cr(VI) ions was examined under predetermined optimum conditions (3 g/L, pH 2 for 180 minutes) in the concentration range 50 to 550 mg/L at flask shaking rate of 200 rpm at 25 ± 2 °C. The mixtures were vacuum-filtered and appropriately diluted before analysis by FAAS. Batch adsorption-desorption studies were conducted in triplicate in erlenmeyer flasks using 0.14 M H₂SO₄ as the desorbing agent. Cr loaded biomass (0.5 g) was conducted with 100 mL of 0.14 M H₂SO₄ on a rotary shaker at 200 rpm for two hours (Goyal *et al.*, 2008). The mixture was vacuum filtered and the filtrate was analysed for residual chromium using FAAS. The residue (VSVH biomass) was washed several times with deionised water followed by oven drying to constant mass. The biosorbent was used again to remove Cr(VI) ions from a freshly prepared solution of concentration 20 mg/L under previously optimized conditions. The adsorption-desorption procedures, using the same biosorbent, were repeated four times cautiously guarding against biomass loss during the washing and filtration stages.

The correlation of determination (R²) of 0.9 was used as the lower limit to accept the fitness of both kinetics and equilibrium adsorption models in describing the experimental data. The amount of Cr(VI) adsorbed was estimated from the mass balance equation (1):

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

Where q_t (mg/g) is the amount of Cr(VI) adsorbed after time t in minutes, V (L) is the volume of the solution, m is the biosorbent mass in grams and C_0 and C_t are the initial and concentration at time t respectively in mg/L. Percentage removal was computed as shown in equation (2):

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

C_e is the concentration of the sorbate (mg/L) in solution at equilibrium.

Equation (3) shows how the rate of biosorption of Cr(VI) ions was calculated.

$$\text{Biosorption rate (mg/gmin)} = \frac{q_{t_2} - q_{t_1}}{\Delta t} \quad (3)$$

where t is time in minutes and $t_2 > t_1$. The biosorption rate was used to interpret the results obtained from the relationship between q_t and contact time.

RESULTS & DISCUSSION

The VSVH biomass was characterised for surface functional groups before and after biosorption of Cr(VI) ions. The FTIR spectra showed peaks whose assignments are presented in Table 1.

Table 1 reveals slight shifting of the absorption bands either to lower or higher frequencies with some completely disappearing (3930.04 and 2031.30 cm⁻¹). These changes gave rise to the non-superimposability of the two spectra indicating the involvement of the biosorbent in the removal of Cr(VI) ions from the aqueous solution (Singha *et al.*, 2011). There is existence of hydroxyl, phenolic, carboxyl, carboxylate, amines, silica, silanes, silanol, phosphite esters, sulphonate and alkyl functional groups on the surface of the biosorbent that were directly or indirectly involved in the sorption of Cr(VI) ions. The biosorbent, VSVH, possesses a multifunctional-group surface that

Table 1. FTIR bands of VSVH powder before and after biosorption of Cr (VI) ions

Before	After	Inferences	Reference/s
3930.04	-	O-H stretching	Suyamboo and Perumal, (2012).
3372.94	3417.36	O-H, N-H, Si-OH stretching	Singha <i>et al.</i> , (2011).
2920.19	2920.96	C-H stretch in aliphatic	Suyamboo and Perumal, (2012).
2031.30	-	Phosphite ester group-P(OR) ₃	Singha <i>et al.</i> , (2011).
1737.40	1737.69	C=O of carboxylic and esters	Vinodhini and Das (2009b).
1617.95	1618.37	C=C ring, carboxylate anions	Abdel-Halim and Al-Deyab, (2011).
1512.24	1512.55	C=C ring, carboxylate anions	Abdel-Halim and Al-Deyab, (2011).
1374.96	1373.72	C-O stretching, CH ₂ wagging	Sharma and Kaur (2011).
1243.56	1263.58	C-N stretching, C-O carboxylic acid	Loukidou <i>et al.</i> , (2004).
1071.21	1033.04	OCH ₃ C-O; Si-O, P-O-C stretching	Khazaei <i>et al.</i> , (2011).
623.30	618.11	S-O sulphonate stretching	Singha <i>et al.</i> , (2011).

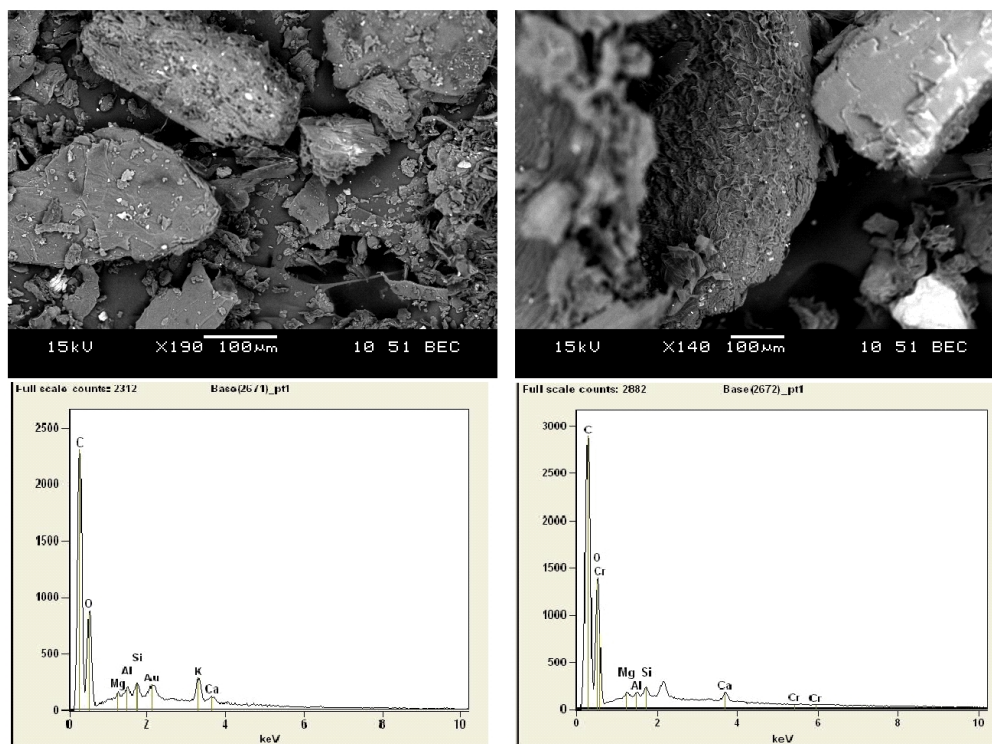


Fig. 1. SEM-EDX photographs of the *VSVH* (left) before and (right) after biosorption of Cr (VI) ions

is ideal for the efficient removal of Cr(VI) ions from aqueous environments.

The surface morphology and elemental analysis of *VSVH* powder, before and after biosorption, were studied by SEM-EDX technique. The powdered samples were mounted on the standard specimen stubs using an adhesive tape and were coated with a thin layer of gold to prevent the sample from charging. The results are shown in Fig. 1.

The external surface of the biosorbent before the removal of Cr(VI) ions had pores of different sizes and shapes. The minimization of pore number and space, surface porosity and area and roughness on the biomass after the sorption process, confirmed the adsorption of Cr(VI) onto the sorbent surface (Sharma and Kaur, 2011). Elemental analysis of the biosorbent before biosorption, indicated the presence and percentage compositions of the following elements: C (60.93%), O (35.64%), Mg (0.04%), Al (0.22%), Si (0.39%), K (2.17%) and Ca (0.62%), while that of the biomass after biosorption of Cr(VI) had the following compositions: C (67.05%), O (31.13%), Mg (0.02%), Al (0.01%), Si (0.25%), Ca (1.35%) and Cr (0.18%). The new chromium peak appeared with the surface bearing O groups suggesting the involvement of the silanol, silica, phenolic, carboxyl, carboxylate, sulphonate, phosphite and hydroxyl in removing Cr(VI) from aqueous solution (Krishna *et al.*, 2013). XRF analysis

of the raw biosorbent confirmed the presence and % composition of the elements: Mg (0.202 %), Si (0.453 %), P (0.058 %), Cl⁻¹ (0.033 %), K (0.693 %), Ca (0.302 %), Cr (0.003 %) and CHO (98.185 %). After the biosorption of Cr(VI), XRF gave the following results: Mg (0.053 %), Al (0.138 %), Si (0.265 %), P (0.002 %), Cl⁻¹ (0.003 %), K (0.048 %), Ca (0.246 %), Cr (0.162 %) and CHO (99.083 %). The results confirmed the biosorption of chromium by *VSVH* biomass by the increase in its % composition from 0.003 % to 0.162 %.

The effect of selected critical parameters was investigated in order to establish the optimum conditions for the efficient removal of Cr(VI) from aqueous solutions. The effect of initial pH of solution, biosorbent dosage, contact time and initial Cr(VI) solution were established while temperature and flask shaking rate were kept constant. The initial pH of the solution significantly influences the surface charge, the state of chemically active sites on the sorbent and the speciation of the sorbate in aqueous solution. This renders pH the most important parameter to investigate in biosorption processes (Qaiser *et al.*, 2009). The solution pH was varied from 1 to 7 while all other factors were kept constant. The results are shown in Fig. 2. The biosorption of Cr(VI) ions (q_e) increased from pH 1 to 2, followed by a gradual decrease to pH 4. There was, however, a sudden decrease of Cr(VI) ions' removal from pH 4 to 7. At low solution pH, the biosorbent surface was protonated giving rise to

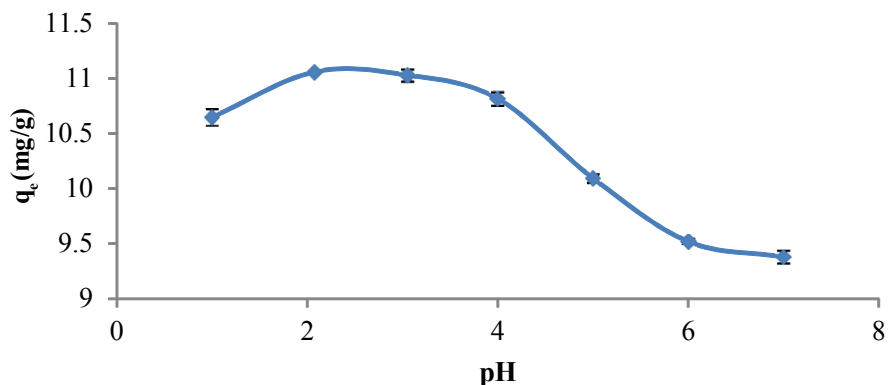


Fig. 2. Variation of q_e with pH for Cr (VI)-VSVH biosorption system

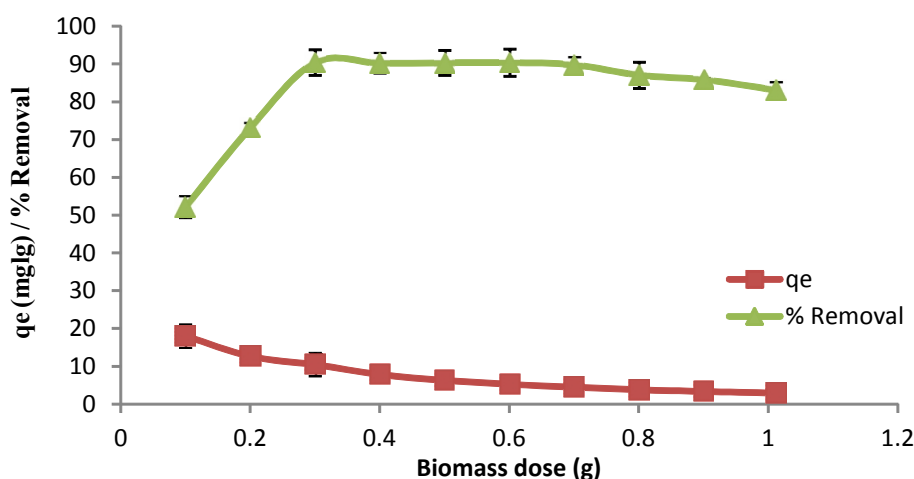
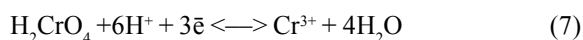
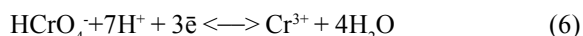
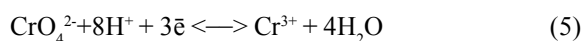
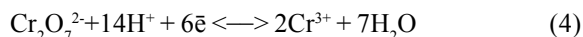


Fig. 3. Biosorption of Cr (VI) ions as function of biosorbent dosage

strong electrostatic interaction between the positive surface and the anionic species of chromium present in solution. The Cr anionic species include HCrO_4^- , CrO_4^{2-} , $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ amongst which HCrO_4^- is the predominant species (Mulani *et al.*, 2013). As the solution pH increased, the sorption of Cr(VI) decreased significantly due to the competition among ionic species, $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} and OH^- , in solution of which OH^- predominates (Malkoc and Nuhoglu, 2007). Deprotonation of the biosorbent surface occurred at higher pH, resulting in electrostatic repulsion of the anionic Cr species and hence the decrease in the biosorption of Cr(VI) ions.

Silva *et al.*, (2009) argued that electron rich species in strongly acidic conditions give rise to the reduction of Cr(VI) to Cr(III) as shown by equations 4-7.



At pH 2, there is reduction of Cr(VI) to Cr(III) by the electron rich functional groups (carboxylate, phosphite, amino, carboxyl, silanol, sulphonates, and hydroxyl) on the surface of the biosorbent, bio-reduction, followed by the biosorption of the Cr(III) ions through ion-exchange and electrostatic attraction (Vinodhini and Das, 2009). As the pH increased, the bio-reduction of Cr(VI) decreased due to the progressively diminishing amount of H^+ ions in solution. The equilibrium position then shifted to the left in equations 4-7 and hence reduced the bio-reduction and sorption of Cr(VI) ions. The optimum pH for efficient removal of Cr(VI) by VSVH was found to be 2 and was subsequently used in the biosorption experiments. Prasad and Abdullah (2010) presented several researchers who found pH 2 as the ideal for the removal of Cr(VI) from wastewaters.

The study of the effect of VSVH dosage on the removal of Cr(VI) from aqueous solution was investigated on dosages ranging from 0.1 to 1 g in 100 mL of 20 mg/L of Cr(VI) solution in erlenmeyer flasks. The variation between biosorbent dosage and q_e and % removal are shown in Fig. 3.

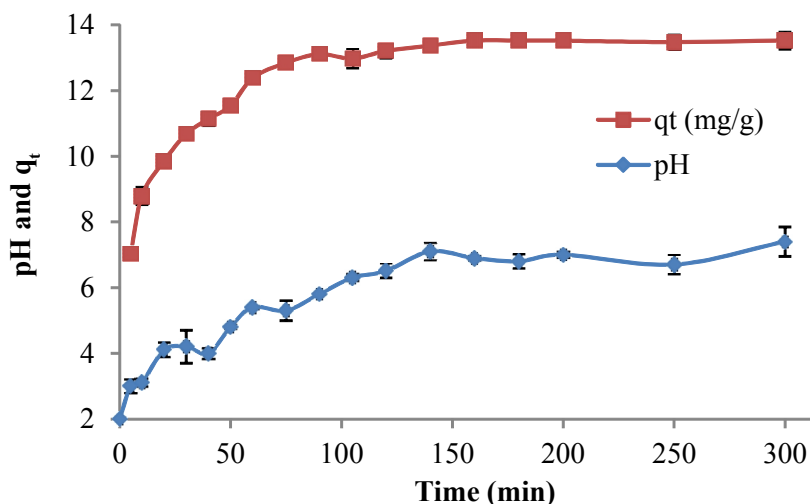


Fig. 4. Variation of q_t and pH against contact time during Cr (VI) sorption on to VSVH

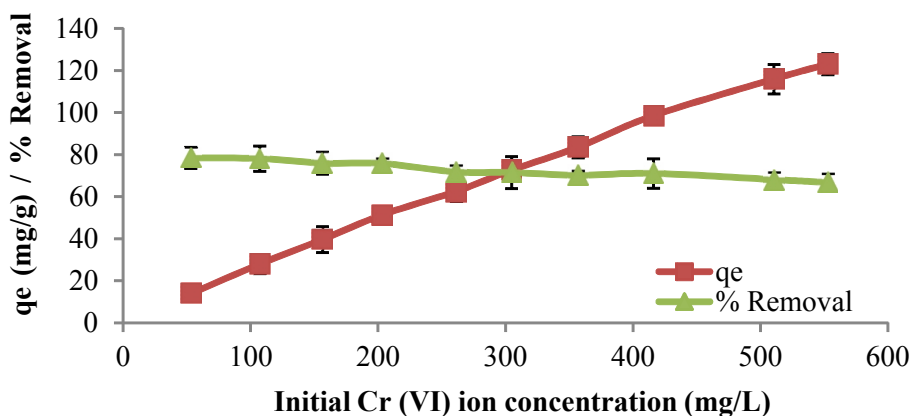


Fig. 5. Biosorption of Cr (VI) as a function of its initial concentration

The amount of Cr(VI) sorbed at equilibrium, q_e , decreased with VSVH dosage while the % removal increased up to a maximum of 90.37%. Thereafter the % removal decreased slightly with increase in dosage. This was the same trend observed in our earlier work when VSVH powder was used to remove Cu(II) ions from aqueous solution (Nharingo *et al.*, 2013). The use of activated neen leaves to remove Cr(VI) generated a similar trend in both % removal and q_e as a function of dosage (Babu and Gupta, 2008). The decrease in q_e with dosage maybe attributed to the splitting effect of concentration gradient between sorbate and sorbent causing a decrease in the amount of sorbate adsorbed onto unit weight of biomass. Suyamboo and Perumal (2012) attributed the decrease in q_e to the aggregation of particles that reduces the total surface area resulting in an increase in the diffusion path length. The increase in removal percentages of Cr(VI) ions with increase in dosage was attributed to the increased availability of

more active biosorption sites up to the optimum dosage of 3 g/L (0.3 g). Further increase in biosorbent dosage resulted in biomass unsaturation as the initial concentration of Cr(VI) ions became limiting (Asgari *et al.*, 2013).

The determination of the contact time required for the biosorption system to equilibrate is very important since it determines the efficiency of the system and hence the selection of the waste water treatment strategy. Fig. 4 shows the variation of q_t against time for the biosorption of Cr(VI) ions by VSVH powder.

There was rapid biosorption of Cr(VI) ions in the first 30 minutes and the rate of its removal decreased until it became almost constant after 160 minutes. The biosorption behaviour was attributed to the availability of biosorption sites on the surface of the biosorbent which subsequently got occupied (Gupta 2012). The Cr species on the surface electrostatically hinder the

Table 2. Kinetics and isotherm models for biosorption of Cr (VI) onto VSVH powder

Kinetic/isotherm models	General	Linearized	Reference
Pseudo 1 st order	$\frac{dq_t}{dt} = k_1 (q_e - q_t)$	$l \ln (q_e - q_t) = -k_1 t + l \ln q_e$	Demirbas <i>et al.</i> , (2004).
Pseudo 2 nd order	$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	(Qaiser <i>et al.</i> , (2009).
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_t = \frac{1}{\beta} \ln(\alpha) + \frac{1}{\beta} \ln(t)$	(Demirbas <i>et al.</i> , (2004).
Intra particle Diffusion	$q_t = k_{id} t^{1/2} + C$	$q_t = k_{id} t^{1/2} + C$	Das <i>et al.</i> , (2013)
Langmuir*	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e}$	Malkoc and Nuhoglu (2007)
Temkin*	$q_e = \frac{R}{b_T} l \ln K_T C_e$	$q_e = \frac{R}{b_T} l \ln K_T + \frac{R}{b_T} l \ln C_e$	Nharingo <i>et al.</i> , (2013)
Halsey*	$q_e = \frac{K_H^{1/n_H}}{C_e^{1/n_H}}$	$l \ln q_e = \frac{1}{n_H} l \ln K_H - \frac{1}{n_H} l \ln C_e$	Oladoja <i>et al.</i> , (2008)

* Equilibrium adsorption isotherm

Table 3. Kinetic model parameters for the biosorption of Cr (VI) onto VSVH powder

Kinetic/isotherm model	Model parameters			
Pseudo first order	q_{exp}	K₁ (min⁻¹)	q_{theory}	R²
	2.0483	0.0405	2.0596	0.9334
Pseudo second order	q_{exp}	K₂ (g/mgmin)	q_{theory}	R²
	2.0483	0.0113	2.8744	0.8667
Elovich equation	-	A	β	R²
		0.2836	2.0846	0.8864
Intra-particle diffusion	-	K_{id} (mg/g min^{1/2})	C	R²
		0.2862	-0.2233	0.9804
Langmuir*	-	q_m (mg/g)	b (L/mg)	R²
		232.6 ± 0.9	0.006 ± 0.002	0.9986
Temkin*	-	k_T (L/g)	b_T	R²
		0.087 ± 0.003	0.08 ± 0.01	0.9330
Halsey*	-	K_H	n_H	R²
		0.337 ± 0.002	-1.3 ± 0.1	0.9937

* Equilibrium adsorption isotherm

sorption of more chromium (VI) ions hence the biosorption rate decreased with increasing q_i. Further investigations were performed using contact time of 180 minutes to ensure that equilibrium was achieved/reached. Fig 4 also shows the variation of pH with contact time during the biosorption of Cr(VI) by VSVH. A similar trend to that of q_i against contact time was observed and the pH became constant at around 7 after 150 minutes. The result was in line with the reduction of Cr(VI) to Cr(III) proposed by Silva *et al.*,

(2009) that proceeds in acidic environments (equations 4 to 7).

The concentration of metal ions in solution provides the driving force to overcome the mass transfer resistance between the aqueous and solid phases. Fig. 5 shows the variation of q_e (mg/g) and % removal of Cr(VI) against initial concentration of Cr(VI) that was varied from 50 to 550 mg/L under optimized conditions. The biosorption capacity increased almost linearly with initial Cr(VI) ion concentration due to the

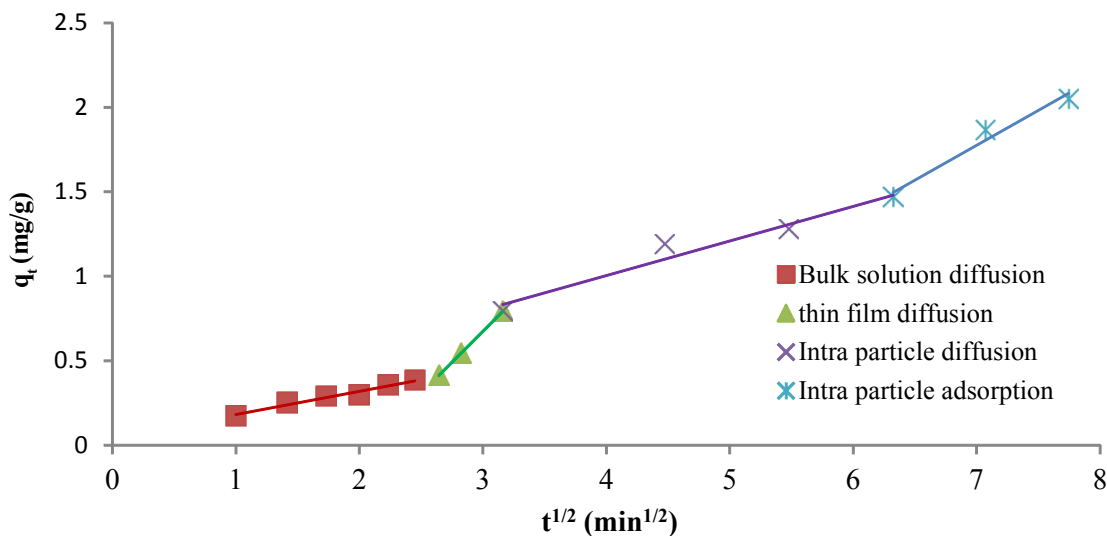


Fig. 6. Intra particle diffusion plot for Cr (VI) sorption onto VSVH

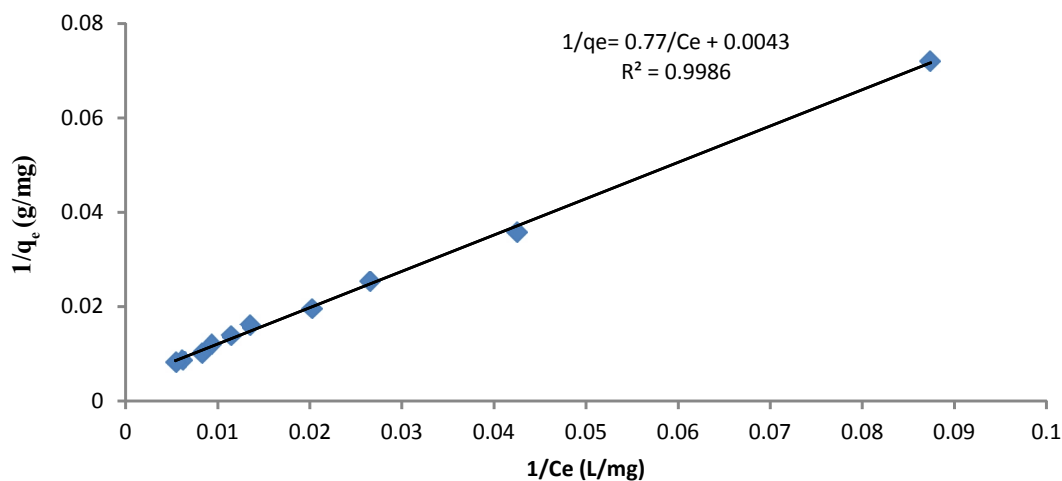


Fig. 7. Langmuir plot for the biosorption of Cr (VI) ions onto VSVH powder

increased concentration gradient of Cr(VI) between the rest of the solution and the surface of the biosorbent. The increase in initial concentration increased the driving force needed to overcome mass transfer resistance of metal ions resulting in greater probability of collision between sorbet and the biosorbent (Demirbas *et al.*, 2004).

The percentage removal of Cr(VI) decreased with increasing initial Cr(VI) concentrations due to the saturation of adsorption sites on the biosorbent and hence adsorption sites became the limiting factor (Das *et al.*, 2013). It was observed that the VSVH has a favourable biosorption capacity even at very high concentrations of Cr(VI) ions in solution as shown by the graph which is almost linear. Fitting data to kinetic models is important for the evaluation of the biosorption mechanisms and the performance of the

biosorbent for metal ion removal (Asgari *et al.*, 2013). The data generated from the investigation of the effect of contact time was fitted to four kinetic models namely; pseudo first order, pseudo second order, Elovich equation and intra-particle diffusion models in the time range of 1 to 60 minutes. The general and linearized kinetic models are presented in Table 2 and Table 3 shows the kinetic model parameters.

The magnitude of correlation of determination ($R^2 > 0.9$), shows that the pseudo first order and the intra-particle diffusion models, described the kinetic data better than the pseudo second order and the Elovich equation whose R^2 values were less than 0.9. According to Thilagavathy and Santhi (2013) the appropriateness of pseudo first order model to describe the kinetic data implied that the sorption of Cr(VI) ions from aqueous solution was dependent on

Table 4. Comparison of biosorption capacities of Cr(VI) removal by plant derivatives

Biomass	Optimum pH	q_m (mg/g)	Reference
Raw rice bran	2.0	12.34	Singha <i>et al.</i> , (2011).
Rice straw	2.0	12.17	Singha <i>et al.</i> , (2011).
Rice husk	1.5	11.39	Singha <i>et al.</i> , (2011).
Coconut shell	2.0	18.69	Singha <i>et al.</i> , (2011).
Hyacinth roots	2.0	15.28	Singha <i>et al.</i> , (2011).
<i>Pistia Stratiotes</i>	2.0	7.24	Das <i>et al.</i> , (2013).
Groundnut hull	2.0	30.21	Qaiser <i>et al.</i> , (2009).
Sugarcane bagasse	2.0	13.40	Qaiser <i>et al.</i> , (2009).
Sugar beet pulp	2.0	17.20	Qaiser <i>et al.</i> , (2009).
Maize cob	1.5	13.80	Qaiser <i>et al.</i> , (2009).
Coconut husk fibre	2.0	29.00	Qaiser <i>et al.</i> , (2009).
Apricot shell	2.0	0.05	Khazaei <i>et al.</i> , (2011).
Almond shell	2.0	0.21	Khazaei <i>et al.</i> , (2011).
Activated neem leaves	2.0	62.97	Babu and Gupta (2009)
Pine needles	2.0	21.50	Babu and Gupta (2009)
Mango sawdust	2.0	37.73	Vinodhini and Das (2009).
Wheat shell	2.0	28.08	Vinodhini and Das (2009).
Orange peel	2.0	19.80	Vinodhini and Das (2009).
VSVH	2.0	232.6	This study

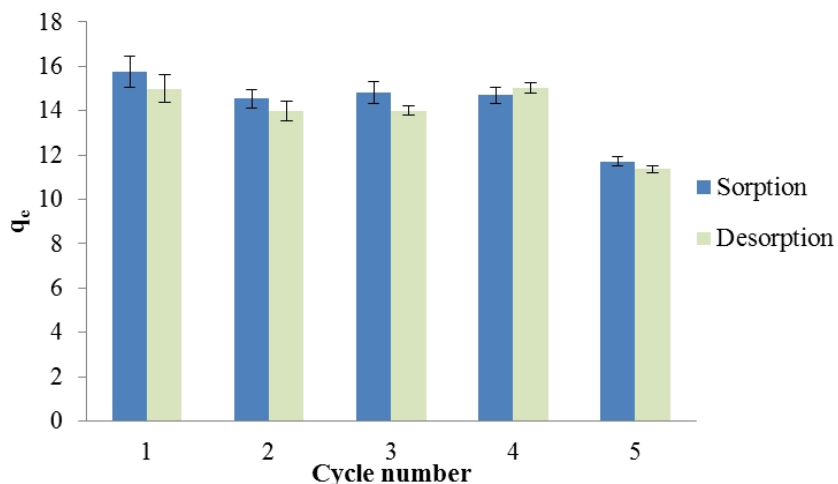


Fig. 8. Amount of Cr removed from solution (sorption) and from VSVH biomass (desorption) as a function of number of cycles

the concentration gradient and hence it was a diffusion-controlled phenomenon.

Where K_1 is the pseudo first order rate constant (min^{-1}), q_e is the equilibrium capacity (mg/g), q_t is the amount of metal ion removed (mg/g) after time t (min), K_2 is the pseudo second order rate constant (g/mgmin), α is the initial adsorption rate (mg/gmin), β is the desorption constant (g/mg), K_{id} is the intra-particle diffusion rate constant (mg/gmin^{1/2}), C gives information about the boundary layer, q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium metal ion concentration in solution (mg/L), b is the

equilibrium adsorption constant (L/mg), K_T is the Temkin equilibrium binding constant (L/g), b_T is related to the heat of sorption, R is the universal gas constant equal to 8.314 J/molK, T is the absolute temperature (K), K_H and n_H are the Halsey adsorption constant and adsorption exponent respectively. The validity of the kinetic models was further tested by comparing the similarity in magnitude between the experimental equilibrium capacity (q_{exp}) and the theoretical equilibrium capacity (q_{theory}). As shown in Table 3, there was a close agreement between q_{exp} and q_{theory} for the pseudo first order kinetic model further suggesting the appropriateness of the model in describing the kinetic

data as was the case with the correlation of determination (R^2). The apparent dynamic behaviour of a sorption system can be explored by investigating the mechanism involved. Fig. 6 shows the plot of q_t against $t^{1/2}$ for the intra-particle diffusion model showing the four transport steps in the biosorption of Cr(VI) ions by *VSVH* powder.

The adsorption dynamics consisted of four consecutive transport steps namely: diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and finally adsorption within the particles (Krishna *et al.*, 2013).

The magnitudes of parameters of the model are shown in Table 3. The gradient (K_{id}) and the intercept (C) were very low indicating the low external resistance favourable for efficient sorption process and the existence of a thin boundary layer respectively. Das *et al.*, (2013) attributed the low, non-zero magnitude of the intercept C, to the involvement of both film and pore diffusion in the rate limiting step. Similar results were obtained by Thilagavathy and Santhi (2013) during the sorption of Cr(VI) by treated *Acacia nicotica* leaf. The data generated from the effect of initial Cr(VI) ion concentration was fitted to equilibrium adsorption isotherms. This was important for identifying an equation that could be used for design purposes. The general and linearized equilibrium isotherms; Langmuir, Temkin and Halsey were employed and are presented in Table 2. Fig. 7 and Table 3 show that the equilibrium data of the sorption of Cr(VI) onto *VSVH* powder fitted the Langmuir adsorption isotherm.

The appropriateness of the Langmuir isotherm to describe the equilibrium data suggests a monolayer sorption and assumes the following nature of interaction (Kumar and Gayathri, 2009): adsorption occurs on a homogenous surface; the adsorption sites are identical, equally available and are energetically equivalent; each site carries an equal number of adsorbed molecules; there is no interaction amongst adsorbed molecules and that there is no migration of adsorbate molecules on the surface plane. *Vigna Subterranea* (L.) *Verdc* hull powder had a high potential of removing Cr(VI) from aqueous solution as indicated by the high biosorption capacity of 232.6 ± 0.9 mg/g. Most of the agricultural wastes that have been tested so far for the removal of Cr(VI) ions have maximum biosorption capacities that are less than 100 mg/g. Table 4 compares the maximum biosorption capacities of various agricultural wastes. The comparatively high sorption capacity of the abundant *VSVH* biosorbent calls for its application in removing Cr(VI) ions from real effluent water. The exceptional

biosorption capacity of *VSVH* for Cr(VI) removal can be compared to that of bacterial biomasses, *Aeromonas caviae* (284.4 mg/g) and *Staphylococcus xylosus* (143 mg/g) reported by Wang and Chen (2009) for the sorption of Cr(VI).

The separation factor, R_L , was calculated using equation (8):

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where b is the Langmuir equilibrium adsorption constant (L/mg) and C_0 is the initial adsorbate concentration in mg/L. R_L had magnitudes $0 < R_L < 1$ (0.2441 to 0.7708) indicating the favourability of the biosorption process under study (Mahamadi and Nharingo, 2007).

The Temkin adsorption isotherm assumes that the heat of adsorption of all the molecules in a layer would decrease linearly with coverage due to indirect adsorbate/biosorbent interactions. It also postulates biosorption as characterized by a uniform distribution of binding energies, up to some maximum binding energy (Kumar and Gayathri, 2009). Basing on the correlation of determination, R^2 (0.933), the model could be used to describe the equilibrium data. The Temkin equilibrium binding constant K_T , and the constant, b_T , related to heat of sorption, were determined to be 0.087 ± 0.003 and 0.08 ± 0.01 kJ/mol. The extremely small values of K_T and positive b_T pointed to a low *VSVH* to Cr(VI) potential and that a weak interaction between sorbate and biosorbent existed in the sorption mixture (Thilagavathy and Santhi, 2013). It was concluded that an endothermic, ion-exchange mechanism was responsible for the sorption of Cr(VI) ions by *Vigna Subterranea* (L.) *Verdc* hull powder.

The Halsey adsorption isotherm predicts multilayer adsorption and fitting of equilibrium data to the model suggests the hetero-porosity of the adsorbent surface. The general and linear forms of the isotherm are presented in Table 2. The parameters of the Halsey adsorption isotherm are shown in Table 3. The correlation of determination, $R^2 = 0.9937$, proved that the Halsey isotherm was ideal in describing the equilibrium data. According to Oladoja *et al.*, (2008), the result implied the multilayer sorption of Cr(VI) onto the heterogeneous surface of the *VSVH* comprising of both macropores and micropores as confirmed by the SEM-EDX images.

Preliminary batch desorption studies on previously Cr loaded biomass were performed using HCl, HNO_3 , H_2SO_4 and NaOH in the concentration range 0.04 to 0.36 M. Very low concentration of HNO_3 (0.1 M) oxidized the biomass while 0.28 M NaOH (56.23 %) and 0.2 M

HCl (80.19 %) produced lower Cr desorption percentages compared to 0.14 M H₂SO₄ (94.56 %). This was attributed to the diprotic nature of H₂SO₄ and was employed in the sorption-desorption cycles. Fig 8 shows the sorption-desorption results generated from 0.5 g of *VSVH*, 20 mg/L of Cr(VI) ions and 100 mL of 0.14 M H₂SO₄.

Fig. 8. Amount of Cr removed from solution (sorption) and from *VSVH* biomass (desorption) as a function of number of cycles. The results show that 0.14 M H₂SO₄ was effective as Cr eluting agent for all the cycles investigated (% desorption > 93.5 %) with the *VSVH* biosorbent showing effective uptake of Cr(VI) ions and their desorption in four sorption-desorption cycles. Goyal *et al*, (2008) obtained similar results (3 cycles) when *Saraca Indica* leaf powder was used for the removal of Pb ions. It was concluded that *VSVH* immersed as one of candidate biosorbents for Cr(VI) ions that showed promising recycling behaviour when sulphuric acid was used as the eluting agent.

CONCLUSIONS

Vigna Subterranean (L.) *Verdc* hull powder was effectively used for the removal of Cr(VI) ions from aqueous solutions. The biosorbent comprised of pores of different sizes and shapes and a biosorption surface having multiple functional groups that include: hydroxyl, phenolic, carboxyl, amines, carboxylate, halides, silica, silanes, silanol, phosphite esters and alkyl functional groups that were directly or indirectly involved in the sorption of Cr(VI) ions.

The pH, contact time, biosorbent dosage and initial Cr(VI) ion concentration were found to significantly affect the biosorption process and were optimized at pH 2, a dosage of 3 g/L and a contact time of 180 minutes. The pseudo first order kinetic model ($R^2 = 0.9334$) and the intra-particle diffusion model ($R^2 = 0.9804$) described the kinetic data better than the Elovich equation ($R^2 = 0.8864$) and the pseudo second order kinetic model ($R^2 = 0.8667$). It was observed that the sorption kinetics was diffusion controlled with both film and pore diffusion involved in the rate limiting step. The kinetic data did not fit to the pseudo second order model pointing to the non involvement of chemisorption in the sorption process.

The equilibrium data generated from the investigation of the effect of initial concentration of Cr(VI) ions was fitted to the Langmuir, Halsey and Temkin adsorption isotherms and the models could describe the sorption system in the following order of good of fitness based on the correlation of determination (R^2): Langmuir (0.9986) > Halsey (0.9937) > Temkin (0.933). The Langmuir was best fitted to describe the equilibrium data. The biosorption process

was favourable with a high biosorption capacity of 232.56 ± 0.9 mg/g. The heat of sorption pointed to the involvement of an endothermic, weak ion-exchange mechanism that suggested easier regeneration/recycling of the biosorbent in the sorption-desorption cycles.

Chromium desorption and biosorbent reutilization studies identified H₂SO₄ as the ideal candidate acid for Cr elution from the biosorbent surface. The *Vigna Subterranea* (L.) *Verdc* hull powder got involved in four sorption-desorption cycles without significant loss of Cr sorption-desorption ability. The reutilization ability of *VSVH* powder, coupled to its being a cheap agricultural waste having a high biosorption capacity, place it among the first choice sorbents for the removal of Cr(VI) ions from aqueous solutions. Pilot studies should be carried out to test the applicability of the sorbent to real effluent water.

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