

Biosorption of chromium (VI⁺) using tamarind fruit shells in continuously mixed batch reactor

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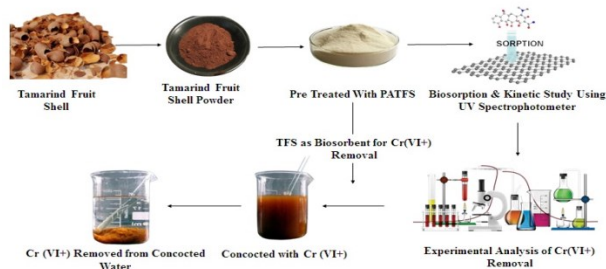
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Graphical abstract



Abstract

The locally available tamarind fruit shells (TFS) pre-treated with 1N H₃PO₄ was used to remove the hexavalent chromium (Cr⁶⁺) from aqueous phase. The investigation was done by using continuously mixed batch reactor (CMBR) under room temperature. Few preliminary investigations were undertaken to optimize the system parameters of the Cr⁶⁺ PATFS system. The batch studies cover the important experiments such as biosorption kinetics, biosorption equilibrium isotherm, effect of pH, effect of ionic strength, and effects of the presence of other anions in the system on biosorption of Cr⁶⁺. From preliminary investigation, the PATFS revealed a highest efficacy (99.1%) in removing Cr⁶⁺ from aqueous phase, apart from other pre-treated TFS. It was revealed that the density and mechanical properties of the treated and untreated composites increased with the decrease in the particle size; whereas, the water absorption percentage and void content decreased for the same. (a) Effect of heavy metal concentration on the sorption capacity. (b) Effect of solution pH on the sorption capacity. (c) Effect of sorption temperature on the sorption capacity. (d) Effect of sorption time on the sorption capacity. At a concentration of 50 mg/l of Cr⁶⁺, more than 95% was appeared to be removed by 12 g/l of 0.13 mm (geometric mean size) of PATFS. The biosorption kinetics of Cr⁶⁺ was modeled by using integrated rate expression and second order rate constants were determined for different

Cr⁶⁺ concentrations. Uptake of Cr⁶⁺ on PATFS was well described by Freundlich isotherm for different biosorbent sizes. UV-VIS spectrophotometer was used to measure the concentration of Hexavalent chromium in water. The desorption study was also carried out and it's significant by 0.5H₂SO₄.

Keywords: TFS, PATFS, PNTFS, hexavalent chromium, CMBR, biosorption, desorption

1. Introduction

The sustainability of India is continuously being dependent on agricultural development and industrial growth. After its independence, it encouraged several major industries like mining, iron and steel, cement, fertilizers and chemicals, petroleum refinery, energy, petrochemicals, pesticides, leather tanning, textiles, and others, for its self-sustenance and economic stability (Gokulan, R, *et al.*, 2022). Among several industries, the automotive and leather tanning industries are most important sectors using large amounts of chromium. Hexavalent chromium compounds are used widely in metal finishing and chrome plating, stainless steel production, leather tanning, and wood preservatives. In the automotive sector, Cr⁶⁺ is used in surface treatment or surface plating chiefly to ensure anti-corrosion protection of metallic components in steel or aluminium. The annual production of automobiles in India is about 7.3 million. Although substitution of Cr⁶⁺ by the less toxic Cr³⁺ (trivalent form) in the automobile sector is being tried globally, the Cr³⁺ cannot provide efficient corrosion protection and water resistance; and it yields very high process costs (Sharma Mona *et al.*, 2011). On the other sector, leather tanning consumes about 30% of the total World trade in chromium compounds (ChangLiu *et al.*, 2016). Chromium may be present in liquid in various chemical species. Electroplating and metal finishing wastes primarily contain Cr⁶⁺ species, whereas textile and tanning wastes contain either Cr⁶⁺ or Cr³⁺ species. Owing to its high toxicity, the United States Environmental Protection Agency (USEPA) and (Zhike Wang Cunling *et al.*, 2013) Drinking Water Standards of India (IS: 10500, 1992) have

set maximum limits of 0.05 mg/l respectively in industrial effluent and potable water. Therefore, it is essential to reduce Cr⁶⁺ concentration in effluents and encourage its recycling and reuse. Sorbent dosage, initial concentration, contact time, pH, and temperature are all variables that affect adsorption capacity. The adsorption capacity will often increase to a certain degree before becoming constant with an increase in dosage, contact time, and beginning concentration.

Among the several conventional (chemical reduction, precipitation, evaporation, ion exchange, and others) means of Cr⁶⁺ removal, chemical reduction-cum-precipitation is being adopted popularly in electroplating and leather tanning industries in many under developed and developing countries; Numerous conventional methods, including membrane filtration, reverse osmosis, ion exchange, chemical precipitation, electro dialysis, electrochemical treatment, and adsorption, have been used to remove heavy metal ions from wastewater, due to their simplicity in operation and economy in overall process cost (Gokulan R *et al.*, 2021). But, due to stringent environmental regulations in India and abroad, this technology is to be completely phased out because of its specific demerits like i) use of expensive reductive chemicals, ii) cannot sufficiently remove Cr⁶⁺ from wastewater to meet various standards, iii) generation of huge amounts of toxic sludge which requires special care towards storage-cum-further treatment, and iv) chromium cannot be recovered in Cr⁶⁺ form for effective recycle (Gokulan Ravindiran *et al.*, 2021). So, adsorption or sorption is long been recognized as one convincing alternative to tackle the demerits of chemical precipitation technique. The role of activated carbons APHA, 1985 Standard Methods for the Examination of Waste and Wastewater, 16th ed., American Public Health Association, Washington, DC (both commercially sold and prepared using several biomaterials) and synthetic resins in sorption and recovery of Cr⁶⁺ (as it is) have been documented (Blanco C *et al.*, 2021). The aim of researchers dealing with sorption was to explore new and low-cost sorbents for metal ions sorption. Cr(VI) removal by sorption onto different types of biomass has been investigated. However, owing to their exorbitant overall process costs, the use of locally available and low-cost biomaterials like agricultural products and by products are noticed from past two decades; in spite of utilization of several inorganic and inert materials and industrial wastes in removing Cr⁶⁺ from aqueous phase (Vivek Sivakumar *et al.*, 2022). But, so far, no single biomaterial could evolve as a universal material for biosorption of Cr⁶⁺, due to their specific limitations like localized availability and varied physicochemical characteristics. The US EPA's regulatory limit of Cr in treated effluent is 5 ppb or 0.005 parts per million (ppm). Heavy metals have been taken out of wastewater using nanomaterials such as zeolite, carbonaceous chitosan, magnetic, bimetallic, metal oxide, metallic, etc. Although Tamarind Fruit Shell (TFS) has already been used in Cr⁶⁺ removal, with relatively expensive oxalic acid treatment (Bailey, S.E *et al.*) in this work; TFS treated with phosphoric acid was used to treat the concocted dilute concentration

of Cr⁶⁺. The selectivity ratio, competition, and interactions of various sorbates in the system in order to appropriately estimate isotherms for multi-pollutant systems. In order to add selectivity to the extended forms of the isotherm, need to work extended Langmuir, extended Freundlich isotherms.

2. Materials and techniques

2.1. Tamarind fruit shell

TFS was obtained from a village close to Perundurai Town in the Tamilnadu, India, region of Erode. Activated carbon, classified stones, polymers, and other sorbers were developed in the last few years for the treatment of wastewater. In this field, activated carbon has been altered in a variety of ways, including by imprinting polymers to better bind heavy metals like chromium and cadmium (as demonstrated by my thesis project), but the most crucial aspect for utilisation is its economics. It was powdered and sieved using Indian Standard (IS) sieves to achieve three different sizes: i) passing through a 0.7 mm sieve and retaining on a 0.5 mm sieve with a geometric mean size of 0.6 mm; (ii) passing through a 0.5 mm sieve and retaining on a 0.211 mm sieve with a geometric mean size of 0.33 mm; and (iii) passing through a 0.211 mm sieve. It was completely cleaned with distilled water to get rid of any foreign objects, then dried in an oven for 10 hours at a temperature no higher than 110° C, cooled in a desiccator, and kept in an airtight plastic container. The physicochemical characteristics of TFS are shown in Table 1. Yes, eco-friendly grinding method available. In the first case rollers or mechanical shafts directly act on the particles and transfer the kinetic energy. The detailed characteristics along with functional groups present on crude TFS are reported elsewhere (Cabatingan LK *et al.*, 2001).

2.2. Chemicals

All of the chemicals and reagents were purchased from S.D. Fine chemicals Ltd. in Mumbai, India, and were of LR grade. Chromium stock solution (1000 mg/L) was created by dissolving 2.8g of K₂Cr₂O₇ in doubly-distilled water free of pyrogens. The stock solution was then diluted in accordance with the experimental requirements. The average pH of the distilled water was 6.6, and its electrical conductivity was less than 9.8 µS/cm.

2.3. Biosorption studies

The biosorption studies (either preliminary or any other study as specified later) were conducted in CMBR system, using either distilled water or tap water, at room temperature. The sorption method is popular for removing heavy metals from wastewater due to its accessibility, affordability, and eco-friendliness. High removal capacity commercial adsorbents and biosorbents are both utilised to remove heavy metals from wastewater. Normally the removal % increases with the increase in adsorbent dosage. Using a 0.05 HP motor with an induced speed range of 10 to 400 rpm, a jar test apparatus (Secor Laboratory Instruments, India) with six flat blade stirrers (each 7.6 x 2.5 cm²) was used (Figure 1). The model equation in the paper is one form of a non-linear logistic equation. All of the

studies used BorosilR glass beakers with a 1L capacity, 300 mL of prepared Cr⁶⁺ solution, equal to a liquid depth of 3.5 cm, and a specified dose of biosorbent. BET isotherm may show better results as there is possibility of multi layers. Langmuir and Freundlich will follow if BET follows.



Figure 1. Photograph Showing the Removal of Cr⁶⁺ using Jar Test Apparatus

Table 1. Physicochemical Characteristics of TFS before pretreatment

S. No.	Parameter	Value*
1.	pH value	3.98
2.	Specific gravity	1.28
3.	Bulk density, kg/m ³	0.55 – 0.57
4.	Porosity	0.24 – 0.31
5.	Loss of weight after washing with 4 l (200 ml x 20) of distilled water, %	4
6.	Dissolved organic matter from TFS, %	1.5
7.	Ash content, %	6.9

(* - average of triplicate results).

2.4. Analysis of Cr⁶⁺

The Cr⁶⁺ was analysed by diphenylcarbazide method, using single beam UV-VIS Spectrophotometer (Systronics-117, India) with a 10 mm path length high quality quartz cuvette at a maximum wavelength of 540 nm. The concentration of Cr⁶⁺ in the aqueous phase was calculated by using the standard graph (linear plot of absorbance versus concentration of Cr⁶⁺) as shown in Figure 1. (Chanda M. *et al.*, 1993). The experimental error was observed to be between n 2 and 3 %, for all the experiments.

2.5. Pre-treatment of Biosorbent

The Pre-treatment of 0.13 mm size TFS was carried out under three separate process like i) phosphoric acid treatment followed by neutralization with 1N NaOH (PNTFS), ii) phosphoric acid treatment alone (PTFS), and iii) phosphoric acid treatment followed by washing with distilled water (PATFS). In process i. 10 g of TFS was treated with 100 ml of 1N H₃PO₄ for 24hr and retained in the water bath (75°C) for 30 min. It is cooled and is neutralized with 50 ml of 1N sodium hydroxide. The filtrate was separated and dried in oven for 4 hrs at 60°C. (Papouri *et al.*, 2007), In process ii, only H₃PO₄ treatment was given without neutralization and, In process iii, TFS was treated with H₃PO₄ and then thoroughly washed with distilled water until there was no traces of acid residue. Pre-treating a sorbent with phosphoric acid can increase its selectivity to chromium iron. In all the above schemes, the treated TFS were stored in air-tight plastic container.

2.6. Desorption Studies

Desorption studies were conducted in CMBR system utilizing tap water for preparation of acid medium (0.5N H₂SO₄ and 0.5N HCl), under room temperature: Prior to desorption, 3.6 g of 0.13 mm size PATFS was initially loaded with appropriate Cr⁶⁺ ions onto its surface, using 300 ml of

tap water containing 50 mg/l of Cr⁶⁺ concentration with a contact time of 2 h (Dakiky, M *et al.*, 2002). The tannery industry contains pollutants that are difficult to remove from the wastewater. Regeneration after sorption is also difficult. However, an electrochemical regeneration is performed well. After biosorption Cr⁶⁺ onto PATFS, the spent PATFS was dried at room temperature overnight and then, used in the desorption experiments. However, separate desorption studies were undertaken in the two acids media like 0.5N H₂SO₄ and 0.5N HCl. (R Gokulan *et al.*, 2022).

3. Result and discussion

3.1. Preliminary biosorption studies

Few preliminary studies were undertaken to appropriately select the pre-treatment process for TFS, to fix the optimum pre-treated biosorbent dosage, effect of pre-treated biosorbent size. Identification the source of chromium is important, then we need to look for the oxidation stages. The aeration method can be applied as a pretreatment. However, in this work, phosphoric acid treatment, under different process was adopted (Gokulan R *et al.*, 2022). Figure 2 shows the efficacies of various pre-treated TFS in removing Cr⁶⁺ from aqueous phase. From Figure 2, it is seen that PTFS and PATFS performed well in sorbing Cr⁶⁺, when compared to crude TFS; but PNTFS exhibited very poor performance. Also, a maximum removal of 99.1% was seen with PATFS when compared to the other types of TFS's. A similar behavior of Cr⁶⁺ sorption was also reported by [5], on phosphoric acid treated spent coffee waste. The average range of that heavy metal concentration in the waste is identified and to alter different concentrations and apply Langmuir or Freundlich to match the results after the kinetic experiment.

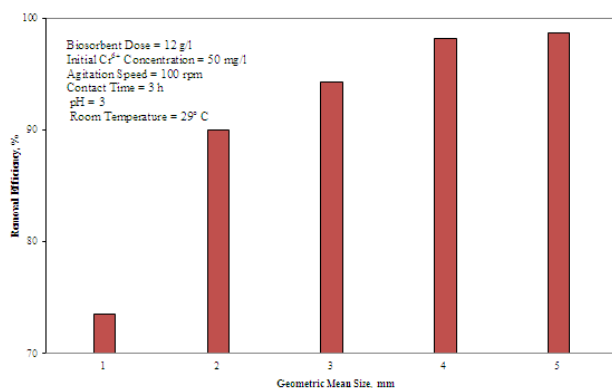


Figure 2. Outcome of PATFS size on Cr6+ removal

From Figure 2, it is seen that PATFS and PATFS performed well in sorbing Cr⁶⁺, when compared to crude TFS; but PNTFS exhibited very poor performance. Also, a maximum removal of 99.1% was seen with PATFS when compared to the other types of TFS's. A similar behavior of Cr⁶⁺ sorption was also reported by (Volesky, Bohumil *et al.*, 1994) on phosphoric acid treated spent coffee waste.

3.2. Effect of pH on biosorption of Cr⁶⁺

In order to appropriately explain the effect of pH on biosorption of Cr⁶⁺ onto the surface of PATFS, the pH of zero point charge (pH_{zpc}) (at which the surface charge on the potential sites will be zero, Huang and Ostovic, 1978) is very essential; but not available in this work. The surface charge can be related to 'zeta-potential', not 'zero point charge'. If the zeta-potential is negative, surface charge is positive and vice versa. However, the knowledge of probable protonation and deprotonation of various functional groups present in PATFS, due to the repetitive decrease or increase of solution pH is essential, if pH_{zpc} value is not available. Therefore, based on the detailed discussion on effect of pH on biosorption of Cr⁶⁺ by treated TFS (Popuri *et al.*, 2007) is made use of in this work. As the TFS is reported to contain chiefly proteins and amino acids (Maratheet *al.*, 2002), amines play a major role in attaining either positive or negative charge in TFS. Apart from above, the speciation of Cr⁶⁺ in aqueous phase, at different pH is also essential to clearly enunciate the interaction between PATFS and Cr⁶⁺. The hydrolysis of Cr⁶⁺ produces HCrO₄⁻ and CrO₄²⁻ and their equilibrium is given by:



Equation.1, depends on pH of the solution and the concentration of total Cr⁶⁺. In order to assess the Cr⁶⁺ species at different pH values. Above neutral pH conditions CrO₄²⁻ is the only anionic species present in the solution and its concentration varies from 50% at pH 7 to 100% at pH > 8.5. Therefore, in acidic media, HCrO₄⁻ and Cr₂O₇²⁻ are the two predominant species of Cr⁶⁺; whereas in alkaline media, CrO₄²⁻ is the lone species of Cr⁶⁺. Based on the above information, between pH 2 and 3 (Figure 2) (approximately at pH 3), the maximum removal of Cr⁶⁺ was due to positive charges are attracted strongly by electrostatic forces functional groups on PATFS and the negatively charged species like HCrO₄⁻ and CrO₄²⁻ (mostly

HCrO₄⁻ species). On the other hand, beyond pH 7, significant reduction in removal of Cr⁶⁺ was owing to strong negatively charged between electrostatic repulsion functional groups on PATFS and negatively charged species like CrO₄²⁻. Further, at pH 2 or 3, Cr⁶⁺ was reported to be reduced to Cr³⁺, respectively about 1 and 3 mg/L (Popuri *et al.*, 2007). Also, significant variation between the initial and final pH of the solution (about 1 to 2 units of pH) was noticed in sample adjusted with pH 2 to 6. However, no changes in variations of pH were noticed in those samples having an initial pH greater than 6. In consice, maximum biosorption of Cr⁶⁺ is expected to takes place at a pH around 3 (Cabatingaon *et al.*, 2000).

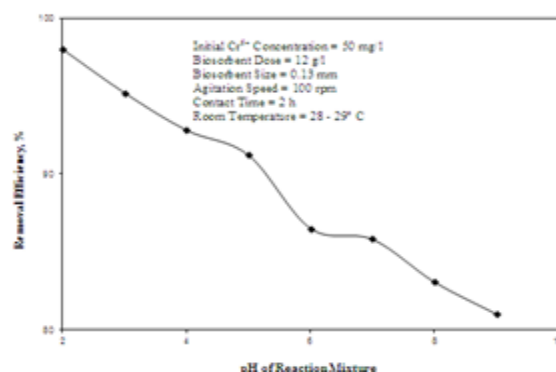


Figure 3. Effect of pH on Biosorption of Cr⁶⁺ by PATFS

From Figure 3, it is understood that the overall effect of pH is only marginal (about 18% between pH 2 and 9), and a continuous decrease in removal efficiency was noticed between pH 2 and 9. Although similar results of biosorption of Cr⁶⁺ on TFS, (Pankaj Kumar M. S *et al.*, 2019)

3.3. Sorption kinetics

The biosorption kinetics of Cr⁶⁺ onto PATFS, for different initial concentrations, is shown in Figure 4. The longer the contact time and the more changes to different vessels the higher the contamination risk. Within 30 minutes of contact time, PATFS was able to remove more than 90% of the original Cr⁶⁺ concentration (for 50 and 25 mg/l of Cr⁶⁺), and two different zones, such as quick biosorption (0 to 1h) and slow biosorption (1 to 4h), were found. All of the kinetics curves were asymptotic to the time axis after 2 hours of contact time. Therefore, a 3 hour equilibrium time was set for the remaining tests.

Additionally, significant decreases in the removal of Cr⁶⁺ for starting concentrations of 25, 50, and 100 mg/l were caused by increased concentration gradients between the solution and surface of PATFS. Similar behaviour of Cr⁶⁺ uptake within 30min of contact time onto different sorbents was reported and available in Volesky (1990). The longer the contact time and the more changes to different vessels the higher the contamination risk. A rise in the metal content of the solid isolate must coincide with a reduction in the metal content of the supernatant liquid. The removal kinetics of Cr⁶⁺ by PATFS was measured by the biosorption kinetics of Cr⁶⁺ onto PATFS and modeled by integrated rate expression, which represents a second order kinetics in equation 1. By plotting the sorption

kinetics. The connection representing the change in the amount of sorbed substance over time expresses the attained sorption equilibrium. The kinetic models into pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetics must fit the experimental results. Where, C_t and C_0 are the respective absorptions of the sorbate in solution at time t and zero

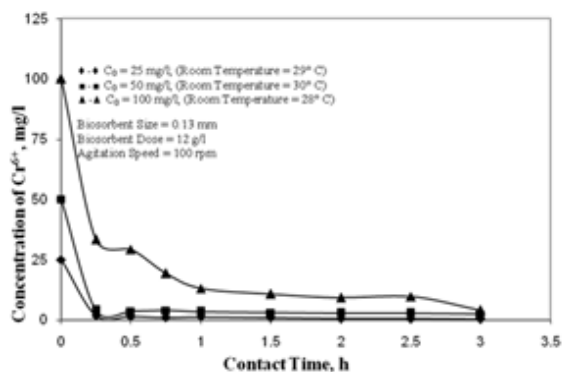


Figure 4. Sorption Kinetics Profiles of Cr^{6+} by PATFS

$$1/C_t - 1/C_0 = k_{ad} t \quad (2)$$

The second order rate constants (k_{ad}) were determined

from the slope of plot of $1/C_t$ versus t (Figure 5) and shown in Table 2. From Table 2, the biosorption kinetics of Cr^{6+} on PATFS could very well follow the second order kinetics with correlation coefficients greater than 0.95. By modifying the sorbent dose and set the time for sorption to be varied lengths of time, such as 15, 30, 45, or 60 minutes. And by checking the final $Cr(VI)$ concentration in them. The contact time can then be extended to get the equilibrium contact time. A particular amount of trash is collected, handled chemically, physically, or biologically, and then released in a batch treatment system. Bulk has to do with vast numbers. Bulk waste treatment's main objective is to treat trash on a scale that keeps costs as low as possible.

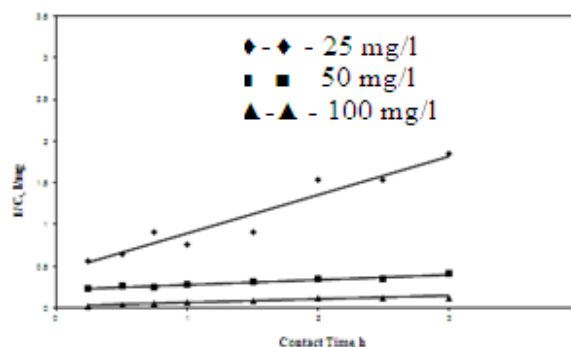


Figure 5. Integrated-rate model for Biosorption Kinetics of Cr^{6+} by PATFS.

Table 2. Second-order Rate Constants for the Biosorption of Cr^{6+} on PATFS.

Sl. No.	Concentration of Cr^{6+} , mg/l	k_{ad} , l/mg.h	R
1	25	0.577	0.947
2	50	0.060	0.970
3	100	0.038	0.954

3.4. Equilibria Study

The solutes are removed from the solution by porous sorbents in essentially three successive mass transport processes. These involve three steps: Because of mixing and convective movement, the first step, bulk transport of the solute in the solution phase, is frequently quick. The diffusion of a solute across a fictitious "film" or hydrodynamic boundary layer is the second phase, film transport. Thus, the primary variables affecting the rates of sorption from solution by porous sorbents are film and pore diffusions. The slower of the two stages will be rate limiting because they happen in succession.

Table 3. Regenerants for Cr^{6+} Recovery from Spent Sorbents.

Sorbent Loaded with Cr^{6+}	Regenerant (s) Used	Percentage Recovery, %	Reference
Commercial activated carbon	H_2SO_4 and NaOH (sequential)	36.6	Srinivasan <i>et al</i> (1988)
Rice husk carbon	H_2SO_4 and NaOH (sequential)	22.5	Bailey <i>et al</i> (1999)
Waste tea leaves carbons	NH_4OH	85	Singh <i>et al</i> (2001)
Saw dust ^a	0.1M NaOH	95.5	Unnathan and Annirudhan (2001)
<i>Streptomyces noursei</i>	Conc. HCl, $NaHCO_3$, NaOH, EDTA	10 to 99.99	Mattuschka <i>et al</i> (1993)
<i>Saccarmyces cerevisiae</i>	0.1M NaOH	5.2	Zhao and Duncan (1998)
<i>Sargasam siliquosum</i>	0.2M H_2SO_4	10	Cabatingan <i>et al</i> (2000)
Phosphoric acid treated spent coffee waste	0.1 and 0.5M H_2SO_4	99	Keerthnarayana (2009)
PATFS	0.5N H_2SO_4 and 0.5N HCl	48.9 and 20.3	Present work

Variation of removal rate K and sorbate concentration, is presented in (Figure 6) for Cr^{6+} , for two different stages of sorption. While film diffusion is rate limiting step (since the slope of the linear curve was taken from 1 h^{1/2}; otherwise, the process would have been pore diffusion controlled); whereas, pore diffusion is rate limiting for slow biosorption zone.

3.5. Desorption of Cr^{6+}

In view of recovering the Cr^{6+} ions biosorbed onto the surface of PATFS, solvent mode desorption was undertaken, separately using 0.5N HCl and 0.5N H_2SO_4 . The desorption kinetics curves are shown in Figure 7

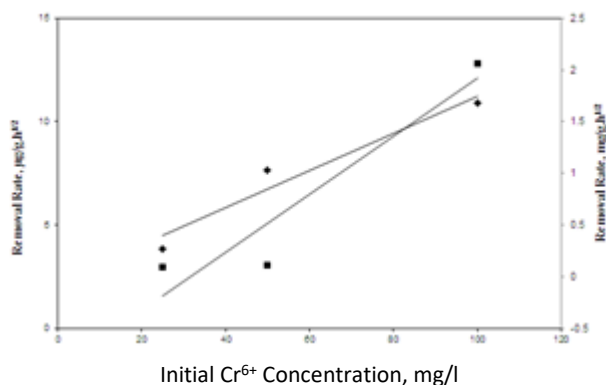


Figure 6. Plot of Removal Rate versus Initial Cr⁶⁺ Concentration

From Table 3, it is understood that acids and alkalis could effectively regenerate the various spent sorbents such that more than 85% of Cr⁶⁺ sorbed can be recovered; except from few biosorbents. This was due to i) either ineffectiveness of the acids or alkalis to completely desorb the Cr⁶⁺, or ii) probable reduction of Cr⁶⁺ and Cr³⁺ on the sorbents Cr⁶⁺

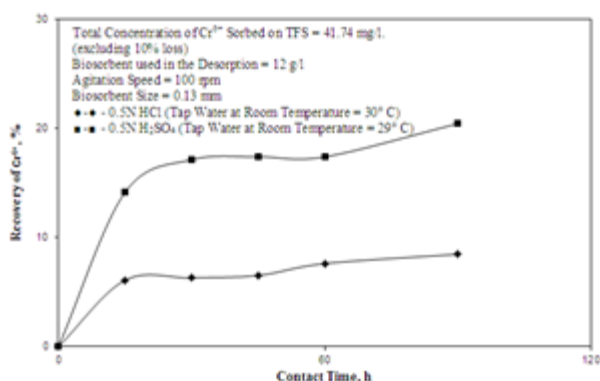


Figure 7. Desorption Kinetics of Cr⁶⁺ in Acid Media.

From Figure 7, it is observed that the desorption rate of Cr⁶⁺ was significantly higher in 0.5N H₂SO₄ than in 0.5N HCl; and also, at the end of 1.5 h, the respective recoveries of Cr⁶⁺ were around 48.9% and 20.3%. Also, Table 3, shows various regenerants used for Cr⁶⁺ recovery in spent sorbents.

4. Conclusions

Based on the investigation pertaining to the biosorption of Cr⁶⁺ by PATFS, in CMBR systems, the following conclusions are drawn. The PATFS is a good biosorbent in eliminating Cr⁶⁺ from aqueous phase and it is highly suitable in CMBR system. The biosorption of Cr⁶⁺ by PATFS is very fast in low concentration and follows second order kinetics. In the rapid biosorption zone, film diffusion is rate limiting, and in the slow biosorption zone it is pore diffusion. Metal removal and recovery from industrial wastewater by using batch adsorption technique. The equilibrium distribution of Cr⁶⁺ onto the surface of PATFS can be well explained by Freundlich isotherm. The system pH fairly affects the biosorption process and maximum removal in acidic range

especially between pH 2 and 3. The effect of ionic strength is negligible on biosorption of Cr⁶⁺ by PATFS. The presence of Cl⁻ does not significantly affect the biosorption of Cr⁶⁺ and the presence of SO₄²⁻ does significantly impede the biosorption of Cr⁶⁺. The combined effect of both SO₄²⁻ and Cl⁻ is antagonistic and very negligible on biosorption of Cr⁶⁺. The sorbed Cr⁶⁺ can be partially recovered easily by using 0.5N H₂SO₄ within short periods.

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