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Removal of chromium(VI) heavy metal ions through biosorption using betel seeds from aqueous solution

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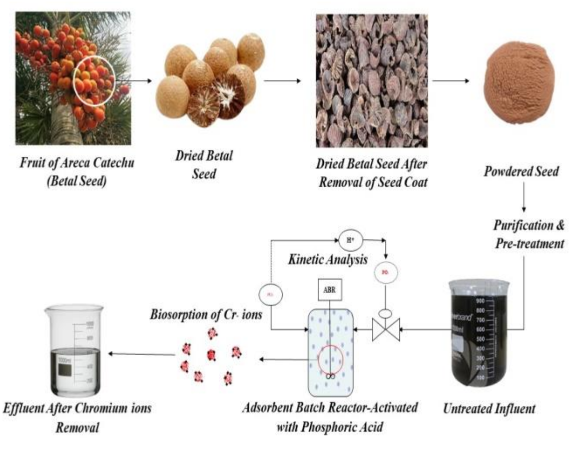
Graphical abstract



Abstract

The reduction of highly toxic Cr (VI) from industrial wastewater of low concentration by different low-cost ample sorbent materials was investigated. In order to remove Cr (VI) from aqueous solutions, the biosorption properties of natural waste (Betel Seeds) were investigated with varying several parameters like contact period, sorbent dose, sorbate sorption, and pH. The study's contact period, biosorbent dosage, sorbate concentration, and pH were all varied from 0 to 120 minutes, 12 g/l, 40 mg/l, and 2 to 7, respectively. According to the study, chromium sorption by betel seed powder reached equilibrium after 60 minutes, and a small change in chromium removal effectiveness was then noticed (Gode *et al.*, 2003). At pH 3 and doses of 12 g/l and 30 mg/l of sorbent and sorbate, the maximum removal of chromium (99.2%) was achieved. The results revealed that chromium(VI) biosorption follows the Langmuir isotherm comparison with a correlation factor of 0.998. Additionally, the biosorption process's kinetics adheres to the pseudo-second-order kinetics model, with a rate constant of 0.721 min-1 and the rate constant was evaluated at 30°C. Hexavalent chromium in water was quantified using a UV-VIS spectrophotometer. A desorption examination was also carried out, and it is vital by $0.5H_2SO_4$. Results indicate that the cheap, readily available, widely cultivated sorbent can be used to effectively remove chromium ions.

Keywords: Betel seeds powder, chromium(VI), CMBR, biosorption, desorption

1. Introduction

Due to their toxicity to many types of life, metal ions in the environment are a significant cause for concern. Metal ions do not biodegrade into inert by-products like organic contaminants, the majority of which are capable of doing so. Only 0.06% of the world's fresh water is readily accessible as lakes and rivers, and only these waters get the majority of the world's effluents, which are waste products. Water usage rises daily along with population growth and industrial development, necessitating immediate preventive action to stop pollution of the limited water supplies (Veli *et al.*, 2007). Wastes from industry, government, and agriculture are the main causes of water contamination. The water pollutants can be categorised as either organic or inorganic based on their chemical composition. As a result of their widespread distribution in the components that constitute the surface of the earth, the metals Cr, Mn, Fe, Zn, and Cd are of the greatest urgent concern. Among these heavy elements, chromium is more prevalent in the waste from the paper, paint, dye, and chrome tanning industries use severe environmental and public health problems (Tan *et al.*, 2015). Chromium levels in discharged wastewater have to be lowered or recycled if at all possible. Chromium removal from industrial effluent can be accomplished using a number of techniques. At room temperature, the investigation was carried out in a continuously mixed batch reactor (CMBR). If *k* is temperature-dependent and a large amount of heat is produced or consumed by the reaction, significant concentration inhomogeneities may develop in a batch reactor (this is much more likely in a heterogeneous/surface reactor). Regional compositional variations could also emerge from interactions with the confinement vessel. These justifications make stirring a batch reactor a popular choice (Senthil Rajan *et al.*, 2022). Several preliminary researches were conducted to improve the Cr (VI) Betel seeds powder parameters. Phytoextraction, reverse osmosis, adsorption, precipitation, ion exchange, membrane, and biological methods have all been studied for the removal of chromium (Das and Mishra, 2010). The amount of heavy metals in the soil, aside from determining the total hazard, is basically irrelevant (maximum concentration that can be mobilized). It is essential to identify the bioavailable fraction, which is the percentage that plants can access or use to mobilise water resources (Vivek *et al.*, 2022). Bioavailability is the ability of a trace element to enter the plant. Different plant species react in various ways, just like invertebrates do. Heavy metals can be fatal to some persons since they have little to no tolerance for them. Some individuals have defensive mechanisms that block absorption by secreting acids that increase pH and reduce the mobility of trace elements. There are also people that can withstand metals and even gather and concentrate them. These plants are referred to as hyperaccumulators. Usually, trace elements are absorbed by the roots and stored there. While the transit in the aerial parts (stems, leaves), which varies depending on the metals, is a sign of a rise in the concentration of metals in the soil, lead is retained in the roots. The aerial components are more easily penetrated by chromium (VI). As a stabiliser or even a healer, plants might be used. Without discounting their aesthetic value, plants can be used to vegetate polluted areas and, as long as the pollution is not severe and only affects certain metals (zinc, cadmium, for instance), they can be utilised to control the movement of dust. We are not aware of any plants that keep lead or mercury.) This sort of remediation is called "phytoremediation." (Sasil Kumar *et al.*, 2022) When metals are present in small amounts, these traditional procedures are ineffective for removing them. Consequently, an economical and effective parting technique must be created in order to lower the reduction of heavy metal ion concentration to a safe level for the environment. Prior research (Mondal and Nayek, 2019; Mondal *et al.*, 2019a) highlighted the use of a variety of readily accessible biosorbents for the removal of Cr(VI) from the aqueous medium, such as rice bran, fly ash, spent activated clay, activated rice husk carbon, sawdust, floating macrophytes, and magnolia leaf. However, none of the biosorbents form of better performance in terms of both sorption and considerable Cr(VI) removal efficiency. Considering the same molecule, the more effective the sorbent is at removing pollutants, whether it is stated as mg/g or mmol/g, for instance. For instance, knowing merely a sorbent's capacity for absorbing betel seed powder does not allow one to draw any conclusions about how effective it is in removing Cr(VI). Furthermore, even if trends exist, the sorption capacity measurement parameters (such as pH and temperature) cannot be immediately applied to other situations.(Logesh *et al.*, 2022).

The World Health Organization (WHO) recommends that surface water bodies' permitted level be less than 0.04 mg/L. Therefore, before releasing effluents into aquatic habitats, Cr (VI) must be reduced to permissible levels. When compared to chromium (III) compounds, chromium (VI) compounds will have quite different environmental consequences (Hui *et al.,* 2005). Plants, birds, and terrestrial animals may be acutely poisonous to high to moderate levels of chromium (VI) (United States Envrionmental Protection Agency, EPA). This could indicate reduced growth rates in plants or the mortality of animals, birds, or fish. The predominant colour of chromium (VI) compounds ranges from lemon yellow to orange to dark red. While most of them are solid (i.e. crystalline, granular, or powdered), one substance (chromyl chloride) is a dark red liquid that breaks down into chromate ion and hydrochloric acid in water (OSHA, 2006).

1.1. Effluent constraints

The following Table 1 lists a few harmful inorganics for which the United States Environmental Protection Agency (USEPA) has established limitations. The same Table also provides the limits established by India.

Table 1. Contaminant maximum allowable limits for drinking water

S.No	Pollutants	Limits (mg\l)	
		USEPA	**IS**
1.	Chromium (VI)	0.05	0.05
2.	Lead (II)	0.05	0.100
3.	Mercury (III)	0.02	0.010
4.	Silver (I)	0.05	0.05

2. Materials and methods

2.1. Betel seed powder

Betel Seeds Powder was acquired in the Namakkal region of Tamilnadu, India, from a village close to Tiruchengode Town. In recent years, sorbers for the treatment of wastewater have included activated carbon, categorized stones, polymers, and other absorbers. The most significant aspect of its usage is its economics. In this field, natural waste biosorbents have been enhanced in various ways, many other ways, imprinting polymers will help heavy metals like chromium and cadmium better bond. The particle diameter that corresponds to the 60% probability point is the geometric mean size. By dividing the geometric mean by the particle size with a 15.78 percent probability, can calculate the standard deviation by equation 1. It was ground into a powder; the ball milling process is economical and good for the environment (Selvakumar *et al.*, 2022). And divided into three sizes using Indian Standard (IS) sieves: passing through a 0.8 mm sieve and staying on a 0.6 mm sieve with a geometric mean size of 0.7 mm; passing through a 0.6 mm sieve and staying on a 0.213 mm sieve with a geometric mean size of 0.43 mm; and passing through a 0.213 mm sieve. Additionally, multipoint Brunauer-Emmett-Tell was used to assess the surface area of the betel seed powder (Alverez *et al.*, 2003). The ratio will drop as the structure size increases because the volume will grow faster than the surface area. The transit of molecules within the cell and with the surrounding environment is slowed down by a lower ratio (Logesh *et al.*, 2022).

$$\sigma_g = d_{50} / d_{15.78} \tag{1}$$

To eradicate any foreign particles, it was thoroughly disinfected with distilled water. It was then dried for 24 hours at a temperature no greater than 100° C, cooled in a desiccator, and stored in an airtight plastic container (Chan *et al.*, 1991). Table 1 displays the physiochemical properties of Betel. On crude Betel Seed, the functional groupings and specific features are provided elsewhere (Bhattacharya *et al.*, 2019).

S. No.	Limitation	Assessment*
1.	pH range	2.96
2.	Moisture Content	64
3.	Nitrogen	2.0 – 7.0%
4.	Phosphorous	0.04-.007%
5.	Specific gravity	1.28
6.	Bulk density, kg/m3	0.50 – 0.57
7.	Porosity	0.22 – 0.35
8.	loss of weight following use of 2l of distilled water, %	3

2.2. Reagents

All of the reagents used were of grade L. R. $K_2Cr_2O_7$ was dissolved in doubly distilled water free from endotoxins to create stock solutions of the metal ions (1000 mg/L). All aqueous solutions were created in double distilled water. The level of Cr (VI) was measured in distilled water (Dabrowski *et al.*, 2004). The distilled water had an average pH of 6.07, the electrical conductivity was found as 2.24 µS/cm, and its density was 995kg/m^3.

2.3. Study of Cr6+

The concentration of residual chromium (VI) ions in the effluent was determined spectrophotometrically using diphenyl carbazide as the complexing agent, a high-quality quartz cuvette with a 10 mm path length and a 540 nm maximum wavelength. Chromium (VI) content in water can be determined using spectrophotometry, diphenylcarbazide as the reagent, and a maximum wavelength of 540 nm at pH=1. The experiment's results showed that 0.0015% diphenylcarbazide may be used to quantify Cr(VI).(Thangavelu *et al.*, 2022) The experimental error was observed to be between 3 and 5 %, for all the experiments (Forstner *et al.*, 1979). To test the effect of organic matter on desorption, desorption tests are also carried out using soil samples that have been H2O2-treated. It has been found that lowering organic matter causes a large increase in the amount of desorption (Ravidaran *et al.*, 2022).

2.4. Biosorption studies

In the CMBR system, using either distilled water or tap water, at room temperature, the biosorption tests (whether preliminary or any other study as indicated subsequently) were carried out (Rengaraj *et al.*, 2001). A jar test apparatus (Vector Laboratory Instruments, India) with six flat blade stirrers (each 6.6 x 2.0 cm2) was employed with a 0.5 HP motor with an induced speed range of 10 to 300 rpm (Figure 1). While Removal (%) refers to the relative percentage fraction of the (Adsorbate=the substance in the solution) before and after biosorption, qe refers to the number (quantity) of sorbed substances per the sorbent mass & more sorbed *substances (Sapna et al.*, 2022). Due to its accessibility, cost, and environmental friendliness, For the purpose of removing heavy metals from wastewater, sorption is a popular technique. Cr (VI) ions are removed from wastewater using both biosorbents and commercial adsorbents with high removal capacities. Equation was used to calculate the removal % (Eq. 2). Typically, as the sorbent dosage is increased, the removal percentage decreases (Cliffor *et al.*, 1990).

$$\text{Removal}\,(\%) = \frac{c_{\text{initial}} - c_{\text{final}}}{c_{\text{initial}}} \times 100 \tag{2}$$

Aqueous metal ion solutions were used for the experiments on the effects of pH on metal ion removal, agitation time and initial metal ion concentration, adsorbent dosage, and sorbent particle size. An increase in porosity tends to increase the adsorption sites of the sorbents, which enhances their capacity for adsorption. For adsorbents with high carbon content, such as activated carbon and sawdust, this effect is more prominent (Manoj *et al.*, 2022). In order to account for metal ion biosorption on the container walls, control experiments were conducted without biosorbent *(Lin et al.*, 2000).

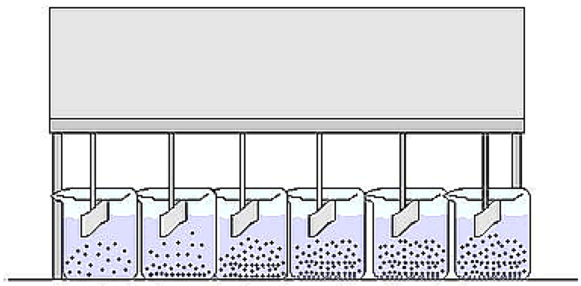


Figure 1. Image Showing the Removal of Cr6+ using CMBR

2.5. Desorption studies

The sorbent that was loaded with metal in the sorption experiment was centrifuged to separate it, and the supernatant was then drained. The sorbent was given a gentle water rinse, and any unsorbed metal ions were swiftly removed by suction filtration from the rinsed water. Apart from Cr, all metal ions are typically desorbed using acids like HCl, HNO3, and H2SO4 (VI). Along with acids, Pb2+ and Zn2+ can also be eliminated with EDTA. Since Cr(VI) is present in anionic form, bases like NaOH, Na2CO3, or NaHCO3 can be used to remove it from the loaded adsorbents (Gandhimathi *et al.*, 2022). The metal-loaded adsorbent was then given 50 mL of water, and the pH was then corrected with a solution of sodium hydroxide or diluted sulfuric acid, the desorption percentage was calculated from Equ. 3.

$$\% \ Desorption = \frac{C_{des}}{C_{abs}} x \ 100 \qquad (3)$$

3. Result and discussion

3.1. Primary biosorption studies

In order to properly account for the interference produced by the leaching of organic matter from prewashed BS (Betel Seeds), to set the optimum pH of the medium, and to determine the optimum biosorbent dosage, a few initial investigations were carried out before understanding the biosorption of Cr (VI) on BS. Since tap water was taken into account in the majority of studies, it is important to comprehend how Cr (VI) on BS biosorption in the tap water system. On the adsorption of Cr (VI), the effects of process variables including contact time, initial metal ion concentration, adsorbent dosage, pH, and temperature were investigated in batch mode. By plating metal ions on a cathode surface, electrochemical processes can recover metals in their elemental metal state. Since they need significant upfront investment and an expensive energy source, electrochemical wastewater treatments aren't commonly used (Balaji *et al.*, 2022). The results were also used for isotherm modelling and kinetic adsorption modelling (Mullen *et al.*, 1992).

4. Effect of reaction parameter on bulk sorption studies of Cr(VI) by betel seeds

4.1. Outcome of pH on Bisorption of Cr(VI)

The investigation revealed from the Figure 2, that the PZC value for the betel seeds biosorbent was 3.0, indicating that its surface is strongly adsorbed on the surface and prone to anionic chromium binding. In particular, because chromium mostly resides in the oxidation states Cr(VI) and Cr(III), the stability of these forms depends on the pH of the environment. The sorption is adversely affected by the pH of the contact solution. The experimental equilibrium capacity reduces when the solution pH drops from 4 to 1 (Sampathkumar *et al.*, 2022).

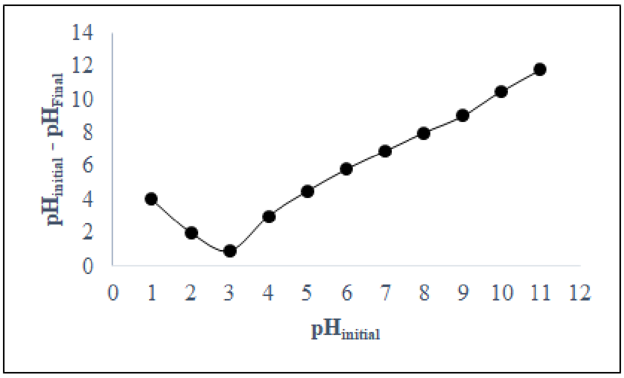


Figure 2. Result of pH on Bisorption of Cr(VI)

From the Figure 3 shows how the solution pH affects the biosorption of Cr (VI) at starting metal ion concentrations between 10 mg/L and 90 mg/L. The pH range of the solution was 2 to 7. In a low pH solution, the proportion of Cr(VI) removal for cationic ion sorption should decrease, but the percentage of Cr(VI) removal for anionic ions will increase. The apparent variability in your data is wide and fairly consistent, spanning a range of 100 to 300 ppm. The amount of metal in the liquid supernatant must decrease while the amount of metal in the solid isolate increases. Bacterial mortality may occur after the two days of treatment, which is followed by the desorption of the metal ions that had been deposited. Such a claim assumes that the metal ion concentration in the control flask remained the same (Sundaramoothy *et al.*, 2022). In contrast, cationic Cr(VI) sorption at high pH solutions will result in an increase in the percentage of Cr(VI) removal, whereas anionic Cr(VI) sorption would result in a decrease (Peters *et al.*, 1985). It was observed that the stated biosorbent biosorption properties are strongly pH dependant. Adsorption is hindered at lower pH levels by the H+ ion or proton factor, while at higher pH levels, the metallic ions start to precipitate as metallic hydroxide or metallic oxide. So far, the pH value is in the range of 4-6, and you should research the ideal pH for the removal of a certain metal like Cr. In contrast, finding the breakthrough time for a column research is more difficult than it is for a batch study. Here, you must perform numerous trials (Mani *et al.*, 2022). Since pH 3 was shown to be the ideal pH for the removal of Cr(VI), this pH was maintained throughout all subsequent research on the biosorption of Cr(VI) by the chosen biosorbent.

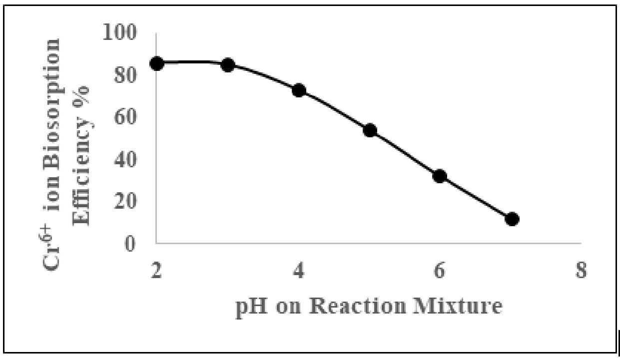


Figure 3. Effect of pH on the biosorption of Cr(VI) by the Betel Seed biosorbents (Biosorbent dose: 12 g/L, temperature: 26 C, C0: 30 mg/L and contact time: 2 h).

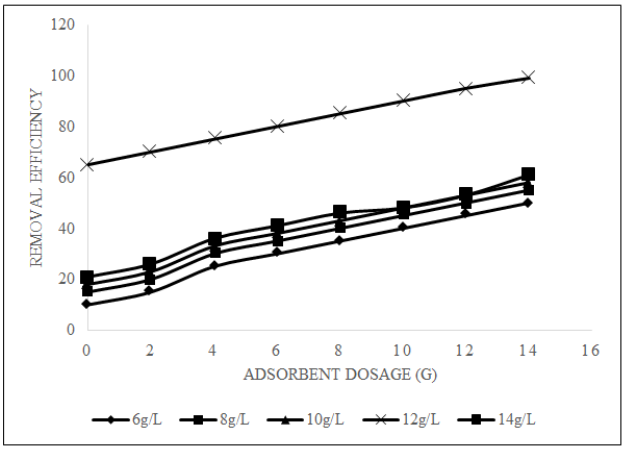


Figure 4. Effect of Biosorbent Dosage concentration.

4.2. Effect of biosorbent dosage concentration

The sorbent dosage was changed from 0 to 14 g/L for initial Cr(VI) concentrations of 10, 20, 30, 40, 60, 80, and 100 mg/L in order to evaluate the impact of sorbent dosage on the removal of Cr (VI). Following specific time intervals, such as 10, 30, 60, 90, or 120 minutes, you can monitor the remaining Cr(VI) concentrations using the sorbent dose and Cr(VI) concentrations, until you reach adsorption equilibrium (Vignesh *et al.*, 2020). According to Figure 4, for all initial Cr(VI) concentrations, an increase in sorbent dosage resulted in an enhanced elimination of Cr(VI) and a lower uptake of metal ions (Reynolds *et al.*, 1996).

5. Equilibrium studies

5.1. Langmuir isotherm model

It was studied that Langmuir Model cultures could be used with betel seed powder. The equilibrium between sorption and desorption for each reactant in contact with a surface is described by the constant K. For a specific sorbate temperature and pressure, the Langumuir adsorption isotherm represents the portion of the surface that is covered by adsorbate molecules. This constant is comparable to the K values used to characterise the distribution of components between the gas and liquid phases in equilibrium. K value can both be less than one and more than one in both scenarios (Dabrowski *et al.*, 2004). The Langmuir isotherm parameters were calculated in Table 2. For the Langmuir model, the coefficient of determination (R2) was typically higher than 0.90 and near to 0.98. This shows that the experimental data of Cr (VI) biosorption are well described by Langmuir model in Eqn. 4 Where, Ct and Co are the respective absorptions of the sorbate in solution at time t and zero (Spinti *et al.*, 1995).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (4)$$

$$R_L = \frac{1}{(1 + K_L CO)} \qquad (5)$$

Table 2. Indicates the Langmuir Model Parameter

Metal Cr(VI)	Equilibrium Models Langmuir Model	Bisorbents (Betel Seed Powder)
1	Qm (mg/g)	42.8
2	KL (L/mg)	0.0454
3	RL	0.075
4	R2	0.998

The fundamental properties of the Langmuir isotherm can be stated in terms of an equilibrium parameter, R_L, Eqn. 5, Even though $R_L > 1$ indicates unfavourable biosorption and $R_L = 1$ indicates linear biosorption, the value of R_L is between 0 and 1 for the favourable biosorption. It represents irreversible adsorption if $R_L = 0$ (Thomas *et al.*, 1948) (Figure 5).

5.2. Kinetic studies

A proper kinetic model is needed to assess the biosorption process in order to look at the mechanism, such as mass transfer and chemical reaction. Thus, the kinetic data was applied to pseudo-second-order kinetic models. By multiplying the concentration by the dilution factor for each sample after determining each sample's concentration based on its absorbance on the standard curve. The concentration in an unknown sample can be predicted using a plot of the curve, which displays the instrumental response (the so-called analytical signal) to an analyze (the substance being measured) *(Vignesh et al.,* 2020). The pseudo second order has calculated of adsorption kinetics by using given below Eqn.6, Plotting the second order equation for t/qt against t (Tobin *et al.*, 1993). The values of qe and k2 are determined by using the slope and intercept of this Figure.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

The plot of a pseudo-second-order kinetic model is shown in Figures 6 and 7 for various initial Cr(VI) concentrations between 0 and 120 mg/L. It can be approximate both exponential and exponential functions on a common kinetic curve for adsorption (qt(0)=0, qt() -> qe), without inflection points. Commonly used as an exponential function is qt=qe(1-exp(- kt)) (differential equation solution: dqt/dt=k(qe-qt), qt(0) = 0). One can utilise, but is not limited to, qt=kqe2t/(1+kqet) (the solution of the differential equation is dq/dt=k(qe-qt)2), where qt(0) = 0). The Elovich equation can also be used to approximate a single kinetic curve (Gandhimathi *et al.*, 2022). The regression values are considerably higher and the qe values obtained from the model were well associated with experimental values, showing that the elimination of Cr(VI) followed pseudo-second order kinetics.

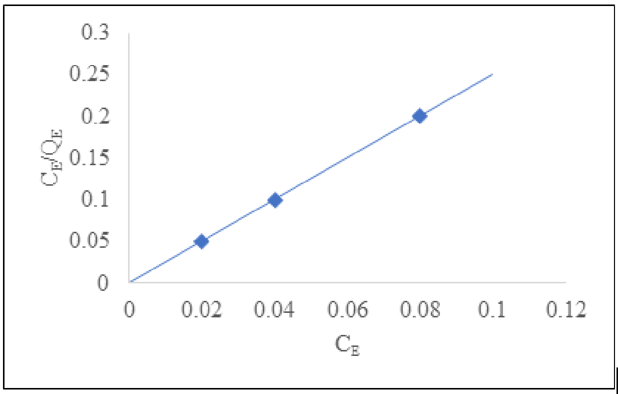


Figure 5. Adsorption Kinetics on Langmuir isotherm equation

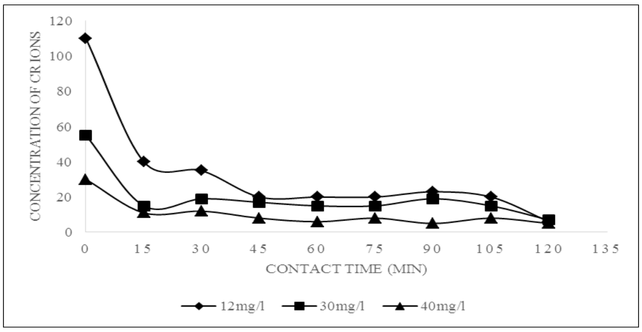


Figure 6. Sorption Kinetics Profiles Cr^{6+} ions

5.3. Desorption of Cr (VI)

After two cycles from the Figure 8 it is observed that 0.5 HCL, 0.5 H2SO4, and distilled water were able to recover 65% of the Cr (VI). As a result, compared to other biosorbents, the produced betel seed resin biosorbent represents a substantial potential biosorbent for removing Cr (VI) from aqueous solutions due to its high biosorption capacity (Wales *et al.*, 1990). The pseudo-second-order kinetic model predicts behaviour over the whole adsorption range under the presumption that chemical sorption or chemisorption is the rate-limiting phase (Hui *et al.*, 2005).

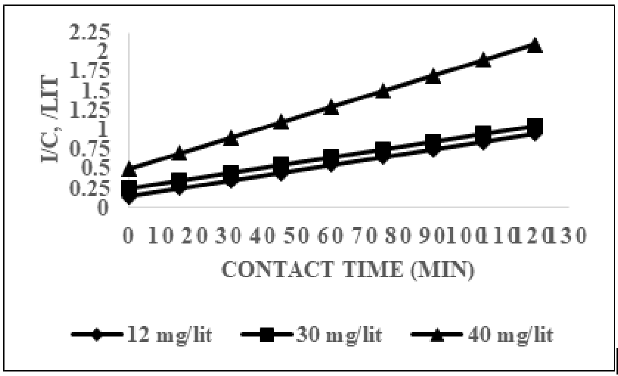


Figure 7. Integrated Rate Model Kinetics of Cr^{6+} ions

Figure 8. Desorption Kinetics Profiles Cr^{6+} ions

6. Conclusions

The current study is a novel approach that makes use of sorption technology to treat massive amounts of Cr(VI) ions. Using a lab setup, it was possible to remove 99.2% of Cr(VI) to the utmost extent. Studies on the biosorption and desorption of Cr(VI) from solutions using betel seed powder are presented in the current work. Despite the varied terminology used, there was no difference between batch and bulk removal of chemicals in the experimental sections, and none of the articles showed even a tiny difference between the two (Dabrowski *et al.*, 2004). It was found that the best conditions for removal were a pH of 3, a sorbent dosage of 12g/l, an initial concentration of 40mg/l, a contact time of 120 minutes, and maintenance at room temperature. The Langmuir isotherm and second order kinetics are effective solutions for the equilibrium distribution of Cr(VI) onto the surface of the powdered betel seed (Zhou et. al, 1991). The pH of the system has some influence on the biosorption process and maximal removal in the acidic range, particularly between pH 2 and 3.

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