

“Invitro reduction, kinetic modelling and Optimisation of parameters for biosorption of Cr (VI) using an ecological sorbent”

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Abstract: In this work extensive study has been carried out to understand the removal efficiency of chromium (VI) by a low cost sorbent material (lemon peel). Among the various techniques, adsorption is one of the most suitable methods which can be adopted to remove hazardous ions from water and waste water. The development of low cost adsorbent is essential for the benefit of the common people. Experiments were conducted in batch mode to know the removal efficiency of chromium (VI) as a function of size, pH, adsorbent dose, initial concentration and time. The removal efficiency of Cr(VI) was maximum at particle size of 0.46mm, pH-5, adsorbent dose of 2.5%, contact time 120 minutes from the aqueous solution having initial Cr (VI) concentration of 100 mg/L. From this study it is infer that the selected adsorbent is having high potential to remove Cr(VI) and other toxic metal which require further study.

Keywords: Lemon peel, Chromium, Sorption, Isotherm, %removal.

I. Introduction

Heavy metals are the metallic chemical element within the upper range of atomic weights and having a specific density more than 5g/cm³, this is five times greater the density of water [Hunton *et.al*, Battarbee *et.al*, Nriagu *et.al*, Garbarino *et.al*, Hawkes *et.al*]. These heavy metals are one of the most widespread origins of pollution; both in water and soil, and increasing levels of heavy metals in the environment are causing public concern [Ledin *Met.al*]. Heavy metals are toxic and have the tendency to bio-accumulate. The toxic heavy metal ions have high solubility in the aquatic environments and thus they can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested beyond the permitted concentration, they can cause serious health disorders [Dadhaniya P.V *et.al*].

Heavy metals that are often linked to human poisoning and environmental pollution are Lead, Chromium, Arsenic, Mercury, Cadmium, Nickel, Aluminium. Other metals such as Copper and Zinc are required by the body in small amounts but can be toxic in large doses. Heavy metals entered into the human system and cause serious defects such as cancer, Immune dysfunction, Allergies, Hormonal problems etc. [Cieslak *et.al*].

The conventional methods used for the removal of heavy metals are lime precipitation, adsorption into activated carbon, filtration and centrifugation, micro- and ultra-filtration, crystallization, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electro dialysis, electrolysis [Volesky *et.al*]. Adsorptions onto low cost adsorbents are used nowadays for the treatment of contaminated waste water and effluents.

1.2 Hexavalent Chromium

The salts of chromium are widely used in industry in a variety of chemical processes. It is used in the metallurgical industries to alloy with iron, nickel and cobalt to impart resistance to corrosion, in electroplating industry to provide clean finishes and in leather industry as a tanning agent. Chromium is also used in paints, pigments, inks, fungicides, wood preservatives, rubber ceramics, photography and textiles [Beszedits, 1988]. Cr(VI) species is mobile, its oxidizing character is regarded as potentially carcinogenic [Y.C. Sarma *et.al*]. The Cr(VI) is of particular concern because of its toxicity, the recommended limit of Cr(VI) in potable water is only 0.05 mg/ lit [K. Selvaraj *et.al*]. Thus, treatment of the effluent to reduce or remove the pollutant before discharging into the environment becomes important.

1.3 Biosorption

Biosorption is the removal of metal or metalloid species, compounds and particulates from solution by biological material. Biosorption is a metabolically passive process, it does not require energy, and the amount of contaminants a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbent surface. The major advantages of biosorption over conventional treatment methods include [Volesky *et.al*]

- Low cost
- High efficiency at low metal concentration
- Minimization of chemical
- No additional nutrient requirement
- Regeneration of biosorbent
- Possibility of metal recovery

Many sorbents have been used for the sorption of heavy metals. The sorption on heavy metals using agricultural products and by products such as peanut skin, mango nut powder, wool, rice straw, peanut hulls, sugarcane bagasse, tea leaves, coffee powder, saw dust, pomegranate peel etc.

There is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fiber, coal, sugarcane bagasse, straw, tea waste, wool fiber and by products of rice mill, soybean and cottonseed hulls. Ion exchange resins are totally effective but expensive. Coal and straw, are inexpensive but ineffective.

Fruits are valuable sources of natural phenolic compounds, which are known to have beneficial health promoting properties. The peels of fruits are rich in valuable compounds but not widely used anywhere. It consist of a variety of components, including pectin, hemicellulose, cellulose, lignin, flavanoids, condensed tannins, and hydrolyzable tannins [Asp.N.G. *et.al*]. Dietary components differ not only in chemical structure or physiology activity from one vegetable material to another, but also in their capacity for microelement binding [Gil *et.al*]. Hemicellulose and pectins have a remarkable capability to bind heavy metal compounds. The sorbtion capacity of dietary fiber depends on its chemical structure and proportion of particular elements [Sangmarket.*al*]. Hence fruit peels are waste material and are readily available low cost sorbent they are used in biosorption for removal of heavy metals.

II. Materials And Methods

2.1 Biosorbent preparation

Citrus limonium shell was collected from the local market. The biomass was dried in sun for ten days. Then the dried shell was washed with distilled water to remove the external dirt and impurities. The washed shells were kept in hot air oven at 50°C for 12 hrs and ground to powder with kitchen grinder. Grinded biomass was further thoroughly washed with distilled water till the color of washing water clear. The powdered biomass was dried in oven at 50°C to a constant weight. The biosorbent was again ground to powder and was graded into different sized particle using sieve shaker. Five different grade particle sizes (figure 1) were obtained.

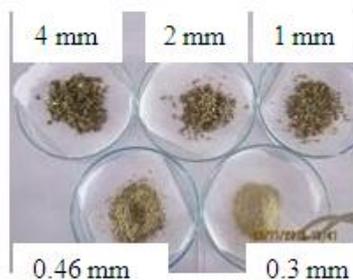


Figure 1: Sorbent graded on size

2.2 Chemicals

2.2.1 Metal solution: $K_2Cr_2O_7$ is dissolved in distilled water at a stock concentration of 1 mg/ml.

2.2.2 Di phenyl carbazide solution: 0.25g of Di phenyl carbazide was dissolved in 50% acetone.

2.2.3 3N Sulphuric acid

2.3 Equipment and apparatus: The adjustment of pH were made using digital pH meter and the Cr(VI) concentration in each experiment were determined spectrophotometrically by using Di phenyl Carbazide method [Arthur I. Vogle].

2.4 Study of process parameters

Effect of five parameters: particle size, adsorbent dose; pH; contact time; initial metal concentration were studied. To study the effect of certain parameter, that parameter has been changed progressively keeping the other three constant. After adsorption, contents of the flask were filtered and filtrate were subjected to Spectrophotometric determination.

2.5 Study of adsorption isotherms: Six solutions with concentrations 25, 50, 75, 100 and 125 mg/L were made by proper dilution of stock solutions of Chromium pH was adjusted to 5. Accurately weighed 2.5 g of sorbent was added to 50 ml of each metal solution and was agitated for an hour. At the end, suspensions were filtered and supernatants were analyzed for metal ions by spectrophotometry.

2.5 Data evaluation

Langmuir, (Equation.(1)) Freundlich, (Equation.(2)) isotherms were plotted by using standard straight-line equations and corresponding two parameters for Chromium were calculated from the graph.

Langmuir model:
$$\frac{C}{q} = \frac{1}{K_L \cdot q_m} + \frac{1}{q_m} \cdot C \quad \text{----- (1)}$$

Freundlich equation:
$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad \text{----- (2)}$$

q_e (mg/g) is the amount of metal adsorbed, and C_e (mg/L) is concentration at equilibrium. q_m (mg/g) and K_L are Langmuir isotherm parameters. K and n are Freundlich isotherm parameters

III. Results And Discussion

3.1 Effect of particle size The experimental values shows that the adsorption rate is higher for adsorbent of particle size (figure 2 (a-e)) 0.46 mm. There will be no effective adsorption for larger particle; this is because the adsorption may be obstructed by impurities and also no exposure of active compounds on the surface. For smaller particle there will be only monolayer adsorption and no intra particle diffusion of metal ion. Therefore, the influence of biosorbent size on metal uptake seems to be function of both the type of biomass and the metal ion. When the sorbent dosage is maximum the samples of different sized particle shows higher rate of adsorption because of shorter equilibrium range for minimum dosage.

3.2 Effect of pH

As can be seen in figure 3, this material can be applied easily in adsorption experiments in acidic medium, because it shows nearly 80% removal in pH 5. At pH below 5, the main group responsible for metal adsorption, carboxylic acid is protonated due to the high concentration of H^+ species. Metal solutions with pH above 5, due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. When the pH was increased beyond 6.0, a gradual decrease in the percentage adsorption was observed. This might be due to the competition between (OH^-) and chromate ions (CrO_4^{2-}). The net positive surface potential of the sorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity.

3.3 Effect of biosorbent dosage

The influence of biomass on the removal capacity of Cr (VI) was depicted in figure 4. If we increase the amount of biomass the removal of Cr(VI) in solution increases (91% of removal, with 2.5 g of biomass, 120 minutes), with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption.

3.4 Effect of initial metal concentration

At low metal concentrations (25 and 50 mg/L) biomass studies shows the best results for removal, adsorbing 100% at 90 minutes, while for higher concentration removal of Cr(VI) needs up to 120 minutes of incubation (figure 5).

3.5 Effect of contact time

A plot of percentage adsorption versus adsorption time is shown figure for sorbent, adsorption increases linearly with time. At the end of 1 hr, percentage Cr(VI) removal is 57, then there is again decrease in the Chromium removal due to continuous adsorption (figure 6). At the end of 2hrs there is no significance reduction in chromium concentration.

3.6 Adsorption isotherm studies

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption. Langmuir isotherm assumes monolayer biosorption. Freundlich model is an empirical equation

used to estimate the adsorption intensity of the sorbent towards the adsorbate. The other parameters are different isotherm constants, which can be determined by regression of the experimental data

In the Langmuir equation, θ (mg/g) is the measure of adsorption capacity under the experimental conditions and K_N is a constant related to the energy of adsorption. Freundlich treatment gives the parameters, n , indicative of bond energies between metal ion and the adsorbent and K , related to bond strength. The linearized Langmuir and Freundlich isotherm of Chromium are shown in figure 7 (a,b). The estimated model parameters with correlation coefficient (R^2) for the different Models are shown in Table 1. The values of R^2 are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's models.

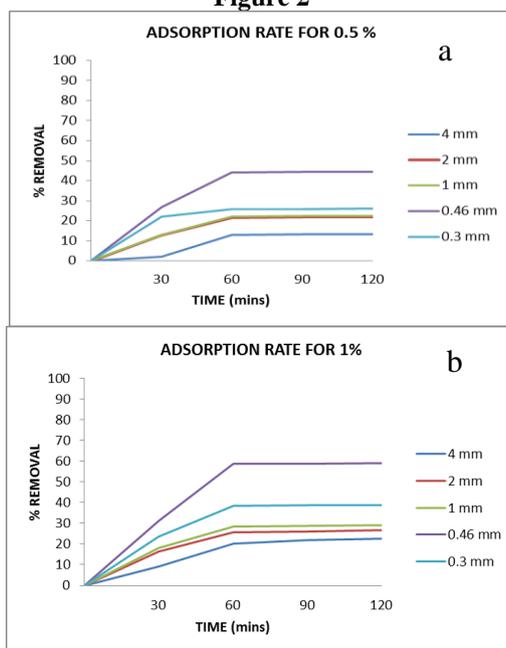
3.7 Kinetic studies

In order to analyze the adsorption kinetics of heavy metal ions, the first and second order kinetic models were applied to data. During the present study, the two different kinetic models were applied and showed in figure 8 for Cr(VI). The estimated model and the related statistic parameters are reported in Table (.). Based on linear regression ($R^2 > 0.99$) values, the kinetics of Cr(VI) adsorption on to the adsorbent can be described well by first-order equation

IV. Conclusion

The use of lemon peel in this study will be environmental friendly and can adsorb Cr(VI) ion from aqueous solution. The lemon peel material is a potential candidate for biosorption and further studies will help to evaluate economical use of this biosorbent. The biosorption was dependent on particle size, solution pH, initial Cr(VI) ion concentration, sorbent dosage, contact time. The sample of particle size around 0.46 mm shows maximum removal of Cr(VI) around 94.6% than the other particles. As the pH of around 5, the Cr(VI) ion removal leveled off at a maximum value. Equilibrium was achieved practically in 2hrs. The Langmuir, Freundlich and Tempkin isotherm fits into the experimental data and the maximum capacity of the adsorbent was found to be 25 mg/g. Adsorption follows first order kinetic model. Kinetic results showed that both bulk and intra-particle diffusion are effective adsorption mechanisms.

Figure 2



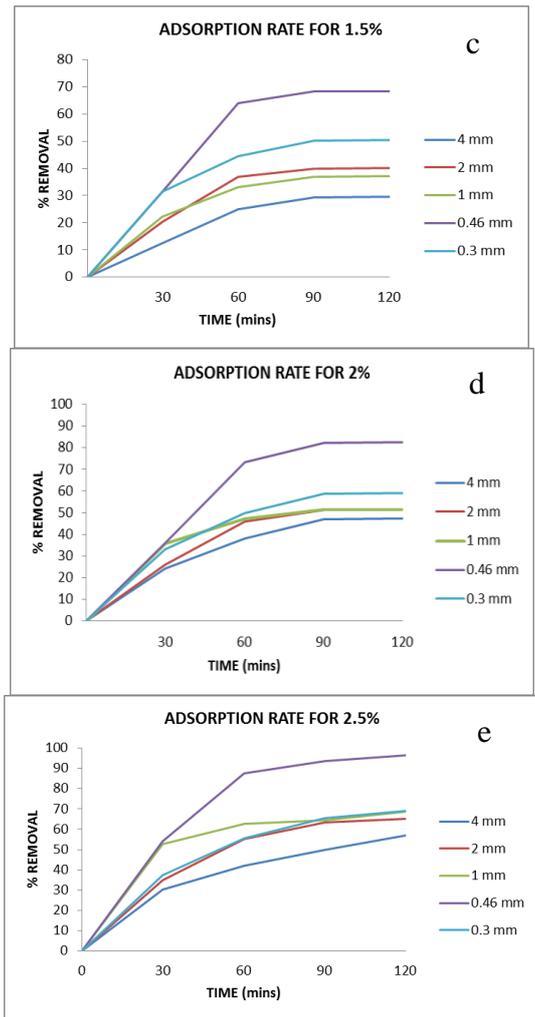


Figure 3

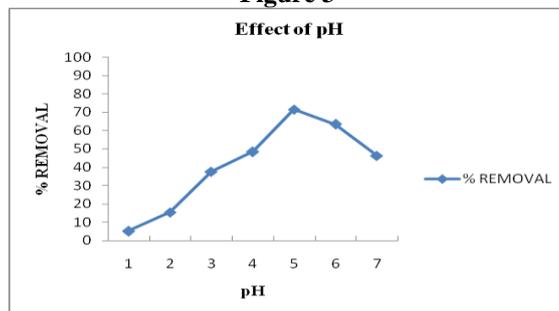


Figure 4

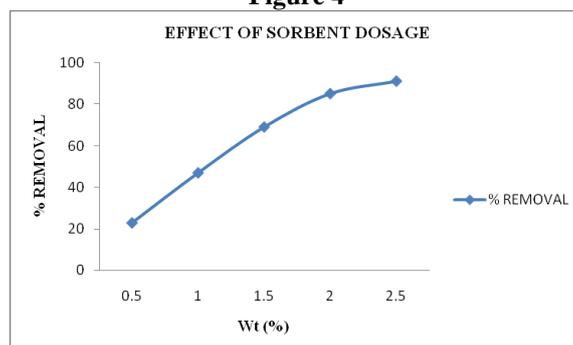


Figure 5

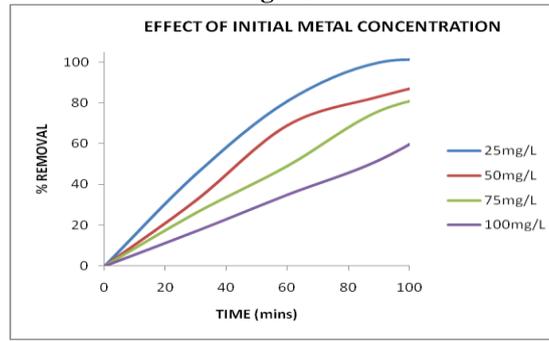


Figure 6

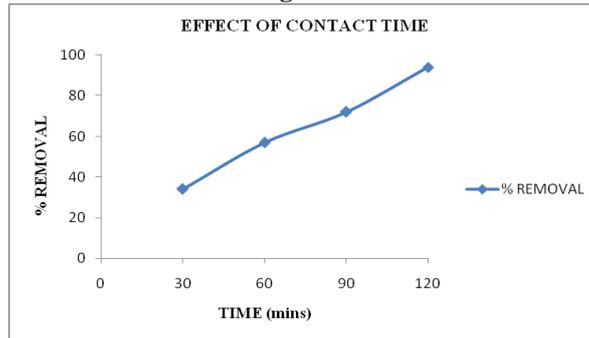


Figure 7

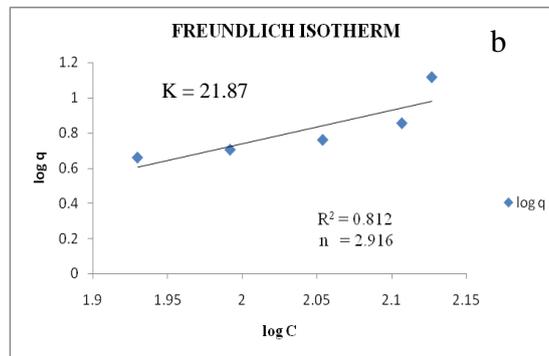
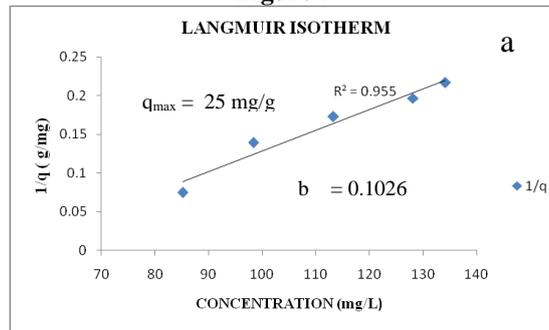
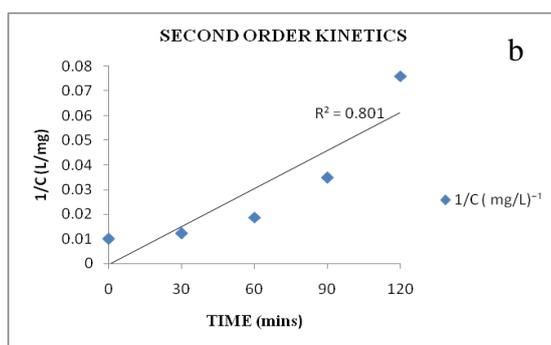
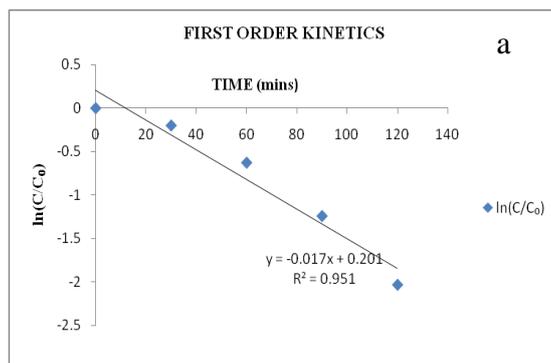


Figure 8



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