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Research Article

Converting Banana Peels from Agricultural residues to Advantageous Substances

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Abstract: Constantly, increase and vary the human needs and its requirements that don't expire as a result of witnessed development of the life in all fields. Whenever the technology is advance in any area, increased human welfare and rebound his life, whenever it is at the expense of earth planet environment where human live in it along with other organisms. The most important of these problems is the problem of environmental pollution with various and different types of toxic and harmful contaminants. This paper is related to the ability of Banana Peel (BP) to remove hexavalent chromium Cr (VI) ions from simulated synthetic aqueous solutions (SSAS) by adsorption process, after extraction of Polyphenol Oxidase (PPO) enzyme from BP. The results show that best ability of BP to produce PPO enzyme by extraction process and the maximum yield of enzyme produced was 14.75% and also show that high capability of BP waste residue to remove Cr (VI) from SSAS with removal efficiency reach to 93.75%. Statistical model is achieved to find mathematical expression combined all operating parameters used in adsorption process in one equation.The synthesis of cheap liquid varnish and rodenticide from BP waste remaining was investigated. The results obtained illustrate that the synthesis liquid varnish give a high luster on the lather tested and the prepared rodenticide give good ability as used. By this way it can possess different benefits which are: produced an important type of enzyme which is PPO, remove hexavalent chromium Cr (VI) contaminated the water and get rid of agricultural waste BP, i.e. it can discard more than type of pollutants in aneconomic and eco-friendly method.

Keywords: banana peel, PPO, extraction, Cr (VI),adsorption, varnish, and rodenticide

INTRODUCTION

The problem of water pollution is no longer a simple thing or limited matter, but has become a major challenge exacerbated by the day because the scarcity of drinking water source, increasing population and the diversity of pollutant substances that poses to rivers, lakes and other water resources [1]. The wastes of industrial, agricultural, health and municipal activities from heavy metals, various dyestuffs, agricultural pesticides, organic and inorganic pollutants, radioactive materials and other types of contaminants often find their way to the surface or ground water sometimes without any pretreatment and therein lies the tragedy [2-7]. One of the most important of these hazardous pollutants that poses to water are remnants of the lather industries precisely hexavalent chromium metal Cr (VI) which is used in tanning to provide lather the desired softness and luster and considered as carcinogenic agent[1].

The permitted concentration of chromium in drinking water is 0.05 mg/l according to World Health Organization [1]. On the other hand, agricultural residue constitutes another source of pollution in the environment due to their poses quantities resulting from growing consumption as a result of increasing population numbers which requires an increase in food production to meet the rising demand for food and can exploitative these residues in synthesis benefit substances, producing new materials and removing of various types of pollutants [6-10]. The best example of agricultural residues is banana peels (BP) [11-12]. The environment in which we live with all its basic elements water, soil and air must be kept clean and non-polluting – at least with required limits – to be valid for the life of living organisms whether they human or animals or plants [6,7, 13,14]. Without it and with constantly accumulation of contaminants in its without real and rapid treatment, the properties of environment basic elements will change and cannot satisfy the needs of humans and other living organisms required for life, leading to spared of hazardous and fetal pollutant pathogens and thus, threat all forms of life on the earth [6].

In this search, the problem of water pollution with hexavalent chromium ions Cr (VI) produced as a tannery waste has been addressing and try to find a way to get rid of this toxic and carcinogenic contaminant using banana peels which considered one of the most important and largest agricultural wastes with economical manner based on adsorption of this contaminant from polluted water. Before starting the adsorption process and to get the highest leverage from banana peels – which are the adsorbent material in this study – the extraction of polyphenol oxidase (PPO) enzyme which considered as one of important enzyme used in remove the cyclic compounds like phenol and dyes was carried out. After that the banana peels waste remaining – after PPO enzyme extraction – are used in the process of removing of hexavalent chromium Cr (VI) from simulated synthetic aqueous solutions (SSAS) prepared for this purpose.

Then the use of BP waste remaining loaded with low concentration of Cr (VI) in synthesis of cheap type of liquid varnish and the use of BP waste remaining loaded with high concentration of Cr (VI) in preparing of active rodenticide have been studied. So, the production of benefit substance which is PPO enzyme, treated the wastewater of tanneries and disposal of hexavalent chromium Cr (VI) carcinogenic have been achieved. In the same time synthesis of cheap and good type of liquid varnish and prepare an active rodenticide, all these using non-valuable material which is banana peels (BP) with simple, economic and eco-friendly methods.

EXPRIMENTAL WORK

Adsorption Media Banana peel (BP)

Banana peel (BP), mature banana with yellow peel, was collected from local market in Baghdad. The BP was washed three times with excess double distilled water and boiled to remove dust, impurities and other fine dirt particles that may be attachedto the BP. The washed BP was cut into small pieces (0.5-1 cm) after that and then dried at 50°C for 24 hours.

Preparation of Crude Poly Phenol Oxidase (PPO) Enzyme Extract from BP

BP (100g) was cut into small pieces and homogenized by using (200 ml) of prechilled (4°C) containing 0.1M sodium phosphate buffer extraction buffer (pH 6.5), Poly vinyl pyrolidone (PVP) and Triton X-100 using blender for 1 minute at maximum speed. The slurry was centrifuged at 9000 rpm at 4°C for 15 minutes. The supernatant obtained was filtered under vacuum from a buncher funnel containing Whitmann® No. 1 filter paper and the filtrate was collected in a conical flask. Then, 100ml of the filtrate was pipette drop by drop into 200mlof cold acetone (– 20°C) for the formation of the precipitates. The crude PPO precipitates separated by centrifugation at 10,000 rpm at 4°C for 15 minutes. The resultant light brown coloured acetone precipitates was dried overnight at room temperature. The acetone powder that obtained was stored at (– 20°C). The enzyme extraction from acetone powder was conducted by mixing 0.1g acetone powder, 15 ml of prechilled 0.1M sodium phosphate buffer, pH 6.5 and stirring for 1 hour at 4°C with a magnetic stirrer. The temperature was maintained by covering the beaker with aluminium foil and was enclosed with ice surrounding the beaker. The obtained crude extract was filtered through cheese cloth and the filtrate was centrifuged at 10,000 rpm for 30 min. The supernatant was discarded and used as crude PPO [10].

Enzyme Assay

The assay solution was prepared by mixing 1 ml of 20 mM substrate (L-DOPA), 1 ml 0.2M sodium phosphate buffer, 0.9 ml H_2O and 0.1 ml of enzyme solution. Enzyme activity was measured spectrophotometrically at 475 nm against a blank containing no enzyme. One unit of enzyme activity is defined as the amount of enzyme that transforms 1 µmole of substrate **Levodopa** (L-DOPA) (**L-3,4-dihydroxyphenyl-alanine**) per minute under assay conditions [10].

Stock solution

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different Cr (VI) ion concentrations. 1000 mg/l stock solution of Cr (VI) ionwas prepared by dissolving 2.282 g of potassium dichromate ($K_2Cr_2O_7$) inoneliterofdoubledistilledwater, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The Cr (VI) ion concentrations were measured using spectrophotometer thermo – genesys 10 UV, USA.

Sorption unit

Fixed bed column of continuous mode experiments were conducted in order to test nine types of dyes removal by treated SSAS of above Cr (VI) ion at desired concentration with the various bed heights of the adsorbent media (*BP waste remaining after extraction of PPO enzyme in section 2.2 above*) using different flow rates of SSAS of Cr (VI) ion solutionat various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. The sorption unit consists of two glass container of SSAS of dyesone for inlet and another for outlet each of (1 liter) capacity. Glass column has 2.54 cm ID and 150 cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5 cm ID, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column.

The BP is packed in the column to the desired depth, and fed to it as slurry by mixing the media BP with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the dyes SSAS of required concentration and pH down flow through the sorption column from inlet container by gravity at a precise flow rate in experiment which is adjusted by the valve. To determination the best operational conditions, the experiments were carried out at a temperature between (25-45°C), various pH values which are (1–8) and initial feed concentrations of SSAS of different dyeswhich are between (1-100) mg/l each one alone and at different flow rates which are between (5–100) ml/min for Cr (VI) ion initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unadsorbed concentration of Cr (VI) ion in SSAS was analyzed by spectrophotometer.

UTILIZATION OF BPWASTE REMANINGAFTER USES IN Cr (VI) ADSORPTION

Huge amount of BP waste remaining was lingered after using it in removal of Cr (VI) fromSSAS as explained aforementioned. Utilization from above BP uses can be achieved in synthesis of cheap and active varnish and rodenticide. The samples of used BP waste remaining which were adsorbed Cr (VI) from SSAS at different operating conditions were segregated and classified according to it’s contain of Cr (VI),the samples give different ratios of Cr (VI)to BP. The ratios were between (0.05 to 1.0 wt %) the low ratio of***Cr (VI) to BP***(0.05 – 0.1 wt%) were used to synthesis of a cheap type of varnish and the high ratio of***Cr (VI) to BP***(0.1 – 1.0 wt%) were utilize in preparingof rodenticide without any treatment.

Employment of BP waste remaining in synthesis of lather varnish

The BP waste remaining after used in adsorption of Cr (VI) were collected and washed carefully with water and prepare for synthesis of liquid varnish. 22% of traditional wax was mixed in 55% turpentine oil at 50°C with continuous stirring until dissolved in stainless steel container. After that 18% of banana peels residues were added to above mixture also with continuous stirring. Then added a solution of 4% turpentine oil and 1% of 4092 acid black (leather dyes) and leave the final mixture until cool.

Employment of BP waste remaining in preparation of rodenticide

Before BP waste remaining after used in adsorption of Cr (VI) used as rodenticide, the laboratory rats were left for ten days and nurtured with normal feed to make sure that it’s were not suffer from anything leading to death. After that the rats nurtured with treated BP wastes with Cr (VI)

RESULTS AND DISCUSSION

The ability of BP to remove dyes from SSASin fixed bed column of continuous mode at various parameters which are pH’s of SSAS of Cr (VI) ion (*pH*), height bed of adsorbent media BP (*l*), flow rates of SSAS (*F*), SSAS temperature (T_f) and time of treatment (*t*) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (C_o) of SSAS of Cr (VI) ion. Thus, the results obtained are explained below.

Effect of Initial Concentration

The results showed that using adsorbent material, the percent removal of Cr (VI) ion was decreased when the initial concentration (C_o) of SSAS of nine types of Cr (VI) ion was increased at constant other variables as shown in Figure 1. This can be explained by the fact that the initial concentration of Cr (VI) had a restricted effect on Cr (VI) removal capacity; simultaneously the adsorbent media(BP) had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of Cr (VI) molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of Cr (VI) than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of Cr (VI). For adsorbent media(BP), higher percent removal were 93.75% forCr (VI)at initial dye concentration of 1 mg/l, so adsorbent material was found to be efficient to Cr (VI) ions removal from SSAS and wastewater.

Effect of pH

The results showed that using adsorbent material, the percent removal of Cr (VI) ions was decreased when the pH of SSAS was increased at constant other variablesas shown in Figure 2. It is well recognized that the pH of the aqueous solution is an important parameter in affecting adsorption of Cr (VI). High adsorption of Cr (VI) at low pH can be explained in both terms; the species of these dyes and the adsorbent surface.The pH of the solution is an important factor that controls the uptake of Cr (VI) ions, pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution.High adsorption ofCr (VI) ions at low pH can be explained by the species of the Cr and the adsorbent surface. At acidic pH, the predominant species of Cr are $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ ions and above pH 6, only CrO_4^{2-} ion is stable and as the pH decreases into the region 2-6, the equilibrium shifts to dichromate according to the overall equilibrium: $\mathbf{2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O}$.

At still lower pH values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed. Thus, decreasing pH results in the formation of more polymerized chromium oxide species. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favours adsorb of Cr (VI) ions in the anionic form. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased. Furthermore, as pH increases there is competition between (OH^-) and (CrO_4^{2-}), the former being the dominant species at higher pH values. The net positive surface potential of sorbent decreases, resulting in a reduction in the electrostatic attraction between the (*sorbent*) Cr (VI) ions species and the (*sorbate*) adsorbent material surface (BP), with a consequent reduced sorption capacity which ultimately leads to decrease in percentage adsorption of Cr (VI) ions [15].

Effect of Adsorbent Media Bed Height

The results elucidated that when the adsorbent media bed height was increased, the percent removal of Cr (VI) ions was increased too at constant other variables as shown in Figure 3. The increased of bed height (l) meaning increased in the amount of adsorbent media BP, thus increasing the surface area of adsorbent material, hence increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase Cr (VI) ions removal capacity on BP. This lead to increase the ability of adsorbent media to adsorb greater amount of Cr (VI) ions from SSAS at different initial concentrations and ultimately the percent removal of Cr (VI) ions increased.

Effect of Flow Rate

The results illustrated that when the flow rate of SSAS was increased, the percent removal of Cr (VI) ions was decreased at constant other variables as shown in Figure 4. This may be due to the fact that when the flow of SSAS of Cr (VI) ions increasing, the velocity of solution in the column packed with the adsorbent media BP was increasing too, so the solution spend shorter time than that spend in the column while at low flow rate, the SSAS of Cr (VI) ions resides in the column for a longer time, and therefore undergoes more treatment with the adsorbent media, thus the adsorbent media uptake low amount of Cr (VI) ions from SSAS for high flow rate, therefore the percent removal of Cr (VI) ions was decreased when the flow rate was increased.

Effect of Feed Temperature

The results demonstrated that when the temperature of feed which was SSAS of Cr (VI) ions was increased, the percent removal of Cr (VI) ionswas increased too at constant other variables as shown in Figure 5.The effect of temperature is fairly common and increasing the mobility of the ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling Cr (VI) ions to penetrate further. It was indicated that Cr (VI) ions adsorption capacity increased with increasing feed temperature from 20 to 45°C. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

Effect of Treatment Time

The results demonstrated that when the treatment time of SSAS of Cr (VI) ions increased the percent removal of Cr (VI) ions increased at constant other variables as shown in Figure 6. This may be due to the fact that when the time of treatment of SSAS of Cr (VI) ions increasing and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of Cr (VI) ions from SSAS, therefore the percent removal of Cr (VI) ions from SSAS was increased.

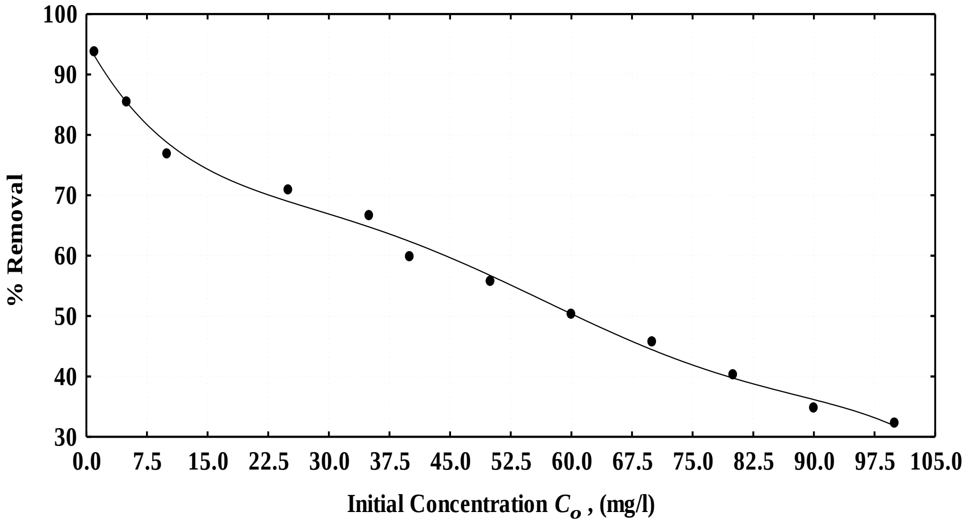

Fig-1: Effect of initial concentration ($C_\circ$) on the percent removal of Cr (VI)
@ T_f = 45°C, l = 1 m, pH=1, t=60 min and F=5 ml/min.

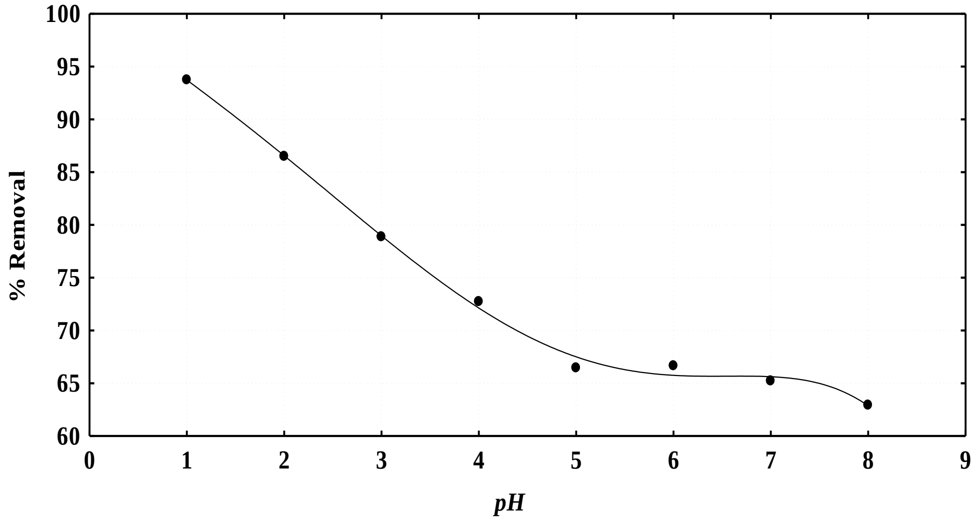

Fig-2: Effect of *pH* on the percent removal of Cr (VI)
@ $C_\circ$= 1 mg/l, T_f = 45°C, l = 1 m, t=60 minand F=5 ml/min

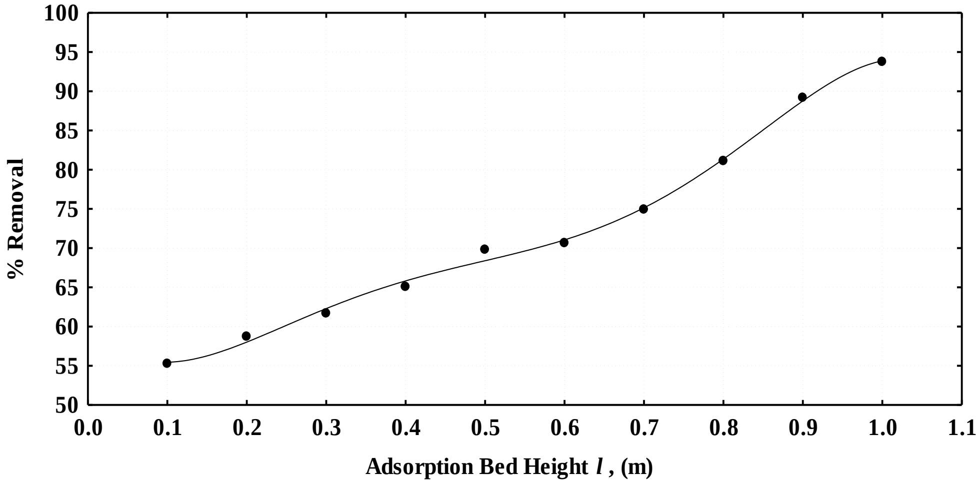

Fig-3: Effect of adsorbent media bed height (*l*) on the percent removal of Cr (VI)
@ $C_\circ$= 1 mg/l, pH=1, T_f = 45°C, t=60 min and F=5 ml/min

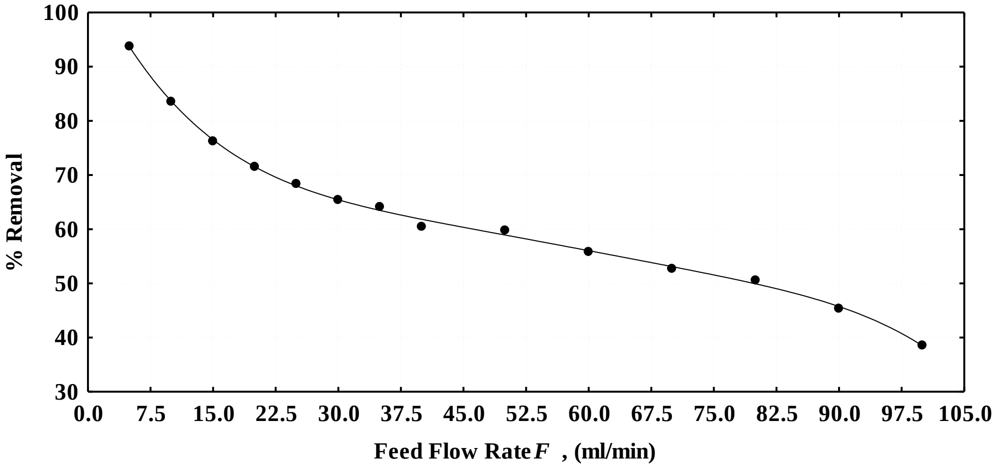

Fig- 4: Effect of aqueous solution flow rate (*F*) on the percent removal of Cr (VI)
@ $C_\circ$= 1 mg/l, pH = 1, T_f= 45°C, l = 1 m and t=60 min

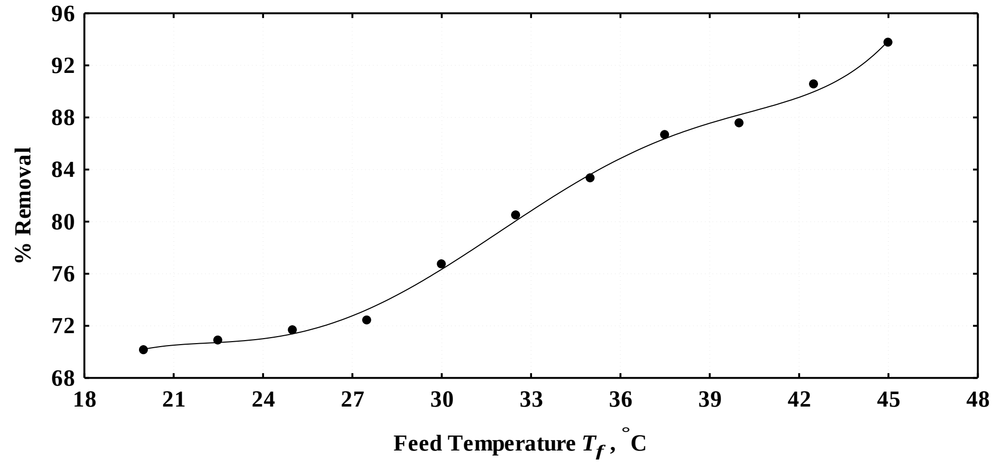

Fig-5: Effect of feed temperature (T_f) on the percent removal of Cr (VI)
@ $C_\circ$ = 1 mg/l, pH = 1, l = 1 m, t=60 min and F=5 ml/min

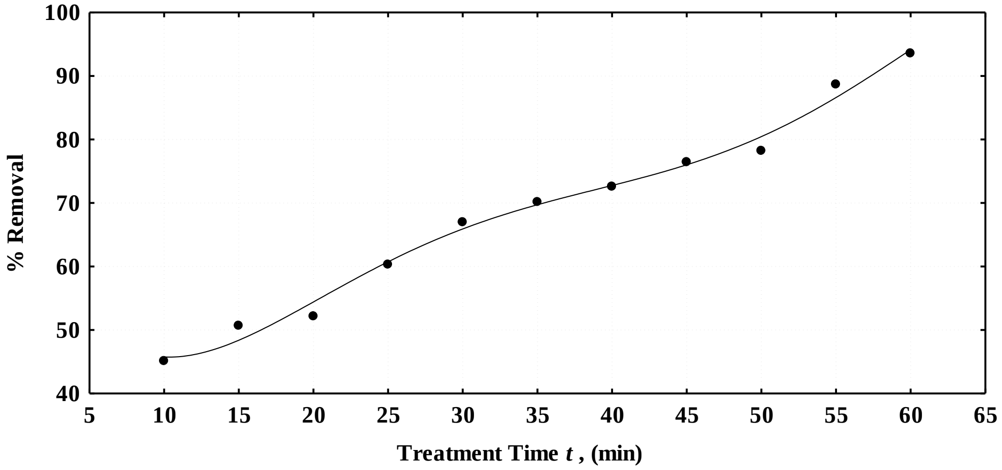

Fig-6: Effect of treatment time (t) on the percent removal of Cr (VI)
@ $C_\circ$ = 1 mg/l, T_f =45°C, pH=1, l = 1 m, and F=5 ml/min

Utilization of BP waste remaining after using in Cr (VI) adsorption

Utilization from these banana peels waste residue can be achieved by using it in synthesis of cheap type of liquid varnish and preparation of active rodenticide. Liquid varnish synthesis show a good sheen for the lather used on it because the active of banana peel waste and Cr (VI) together on the lather which have the ability to polish the surfaces which rubbed with them. On another hand the BP used as a rodenticide show good ability to kill the laboratory rat due to the toxic effect of Cr (VI) on these animals. The results were fate the rats in a different periods as shown in Table 1.

Table 1: Hours lead to kill rat when it nurtured with treated banana peel waste

Different Types of Cr (VI) to BP Waste Remaining Ratio (wt %)									
0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
107	92	80	72	50	44	36	24	18	10

STATISTICAL MODEL

A statistical model was carried out on the experimental results obtained from this study for removing Cr (VI) by BP waste remaining. Regression Analysis and π Theorem was adopted to maintain a relation between the percent removal of Cr (VI) ions and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of Cr (VI) ions, adsorbent media (BP) bed height, treatment time column diameter and other parameters. These relations are shown in equation 1 below with R^2=0.9923.

$$\%\boldsymbol{R} = \boldsymbol{9.125 \times 10^{-6}} \left(\frac{\boldsymbol{\rho_{sol}}}{\boldsymbol{C_{\circ}}}\right)^{0.1953} . \left(\frac{\boldsymbol{l}}{\boldsymbol{d}}\right)^{0.2004} . \left(\frac{\boldsymbol{T_f . C_{P_{sol}} . t}}{\boldsymbol{\vartheta}}\right)^{0.0985} . \left(\frac{\boldsymbol{K_{sol} . T_f}}{\boldsymbol{\gamma . u}}\right)^{0.1728} . \left(\frac{\boldsymbol{1}}{\boldsymbol{pH}}\right)^{0.0114} \quad \dots (\boldsymbol{1})$$

where:	$\%\boldsymbol{R}$	Percent Removal of Cr (VI)from SSAS
	$\boldsymbol{\rho_{sol}}$	Density of SSAS, $(\mathrm{kg/m^3})$
	$\boldsymbol{C_{\circ}}$	Initial Concentration of Cerium , $(\mathrm{kg/m^3})$
	$\boldsymbol{l}$	Adsorbent Material Bed Height, (m)
	$\boldsymbol{d}$	Internal Diameter of Sorption Column, (m)
	$\boldsymbol{T_f}$	Feed Temperature, (K)
	$\boldsymbol{C_{P_{sol}}}$	Heat Capacity of SSAS, (kJ/kg. K)
	$\boldsymbol{t}$	Treatment Time, (s)
	$\boldsymbol{\vartheta}$	kinematic viscosity of SSAS, $(\mathrm{m^2/s})$
	$\boldsymbol{K_{sol}}$	Thermal Conductivity of SSAS , (W/m. K)
	$\boldsymbol{\gamma}$	Surface Tension, (N/m)
	$\boldsymbol{u}$	Velocity of SSAS, (m/s)

CONCLUSIONS

The following conclusions can be drawn:

1. BP can be considered as available and valuable source for extraction of PPO enzyme which can be used in another uses.
2. BP waste remaining after extracted PPO enzyme showed a good ability to remove Cr (VI) from SSAS using fixed bed adsorption unit. So, it could be recommended for removal of Cr (VI) from wastewater instead of other material because it is valid, cheaper, economical, easy and simplicity for using, and has a high ability to adsorb Cr (VI), can be used by non-costly method and can be used finally in another benefit uses.
3. Maximum removal of Cr (VI)with BP waste remaining was 93.75% at initial concentration of 1 mg/l.
4. The percentage removal of Cr (VI) was increased with decreeing pH, flow rate of SSAS, and initial concentration of Cr (VI)while the percentage removal was increasing with increasing of treatment time and the height of adsorbent material BP waste remaining.
5. There is ability to produce benefit materials by using these BP waste remaining like liquid varnish and active rodenticide.

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