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Evaluation of parameters affecting the rice husks performance on cyanide ion removal from wastewater

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Abstract This research is designed to investigate the Rice husk (RH) adsorption capability on cyanide ion (CN -) removal from wastewater. Several operating parameters were investigated in order to obtain the optimal removal efficiency using such agricultural by product media. The operation parameters were pH, initial concentration of the cyanide ion (Ci), adsorbent media height (Hm), Process time (tp), and Temperature (T) of the wastewater. The results showed that the removal efficiency could reach 97 % at the optimum operating conditons. Removal efficiency increased with increasing of adsorbent media height, increasing of pH also shows increasing in removal efficiency till pH 7 and then decreased slowly. Increasing temperature has a good effect on enhancing removal efficiency but such effect weakens when temperature exceeds 40oC. For process time the removal efficiency shows steep increasing rate till 40 min and then the rate slowed down. Removal efficiency decreased rapidly with increasing of initial concentration ($Ci \leq 20$ mg/l), then it shows slower decreasing rate.

Key Words: *rice husk, rice hulls, cyanide ion, adsorption, wastewater treatment and pollution control.*

تقييم العوامل المؤثرة على أداء قشور الأرز في إزالة أيون السيانيد من مياه الصرف الصحي

محمد ابراهيم بشير

الخلاصة: تم تصميم هذا البحث لتقييم قدرة الامتزاز لقشور الأرز (RH) على إزالة أيون السيانيد (- CN) من مياه الصرف الصحي. تم التحقق من عدة معلمات تشغيلية من أجل الحصول على أفضل كفاءة إزالة باستخدام هذه المخلفات الزراعية، و شملت المعلمات التشغيلية التي تم التحقيق منها درجة الحموضة، والتركيز الأولي لأيون السيانيد (Ci)، ارتفاع المادة الممتزة (Hm)، زمن التشغيل (tp)، و درجة الحرارة (T) لمياه الصرف الصحي. أظهرت النتائج أن كفاءة الإزالة يمكن أن تصل إلى ٩٧٪. لوحظ زيادة كفاءة الإزالة مع زيادة ارتفاع المادة الممتزة ، وزيادة الرقم الهيدروجيني حتى الرقم الهيدروجيني ٧ ثم تنخفض بعدها كفاءة الازالة . زيادة درجة الحرارة له تأثير جيد على تعزيز كفاءة الإزالة ولكن هذا التأثير يضعف عندما تتجاوز درجة الحرارة اربعون درجة مئوية وهذا صحيح أيضا لزمن التشغيل حيث ان كفاءة الإزالة تظهر ارتفاع حاد حتى ٤٠ دقيقة ثم تظهر زيادة طفيفة بعد ذلك. كفاءة الإزالة كانت تنخفض بسرعة مع زيادة التركيز الأولي ($Ci \leq 20$ mg/l) ثم تظهر تباطؤ في معدل الانخفاض.

I. INTRODUCTION.

Cyanide ion (CN^-) is an extremely toxic ion that ties with the catalyst cytochrome C oxidase. This compound hinders cell breath and vitality generation, leading to cytotoxic hypoxia influencing the nervous system (CNS) and heart [1] Cyanide compounds are used in many industrial sectors. Hydrogen cyanide is used in the production of plastics. Potassium or sodium cyanide is used in mining processes, cyanide salts are used in metal plating. Many other industrial processes such as: petroleum refining, steel production, and pharmaceutical production also uses cyanide.

There are several methods that are proven to be effective in cyanide ion removal from polluted water such as: sulfur dioxide and air process, hydrogen peroxide process, peroxymonosulfuric acid (H_2SO_5) process, Alkaline chlorination, and last but not least adsorption using activated carbon [2]. Adopting a specific removal process usually depends on cost, technical availability, and cyanide ion concentration.

adsorption method has many advantages over previous mentioned methods for removing contaminants from polluted water and wastewater. Activated carbon is a very popular adsorbent and has been mostly used in cyanide removal process. However, this adsorbent as many researchers mentioned that it has a low capacity for cyanide removal, costly and loses more than 10% of its mass during the regeneration process, and this is what make it unsuitable in a large scale usage [3,4].

Rice husk has been successfully used by many researchers as an adsorbent matter for phenol removal [5], copper removal [6], arsenic removal [7], lead, zinc, and nickel removal [8]. The purpose of this study is to investigate the rice husk capability in cyanide ion removal from polluted wastewater, and the effect of some important operation parameters such as initial pH of the wastewater, initial cyanide ion concentration (C_i), adsorbent media height (H_m), process time (t_p), and temperature (T), on the removal efficiency, in order to obtain the optimal operating conditions. A Polymath 6.1 computational system was then used in order to simulate the effect of the previous mentioned operation parameters on the cyanide ion removal and hence obtain a reliable mathematical model that would help in predicting the expected removal efficiency under specific operating conditions.

II. MATERIAL AND METHODS.

A. Materials

- *Rice husk (RH).*

Rice husks were collected from the local market, which is dealing with domestic rice in Al distilled water [9] and dried by spreading it on an open area exposed to the sun for 48 -Qadisiyah province. The rice husk was subjected to impurities removal, washed with tap water followed by hours, Figure 1. shows part of rice husks stacks throughout the preparation process.

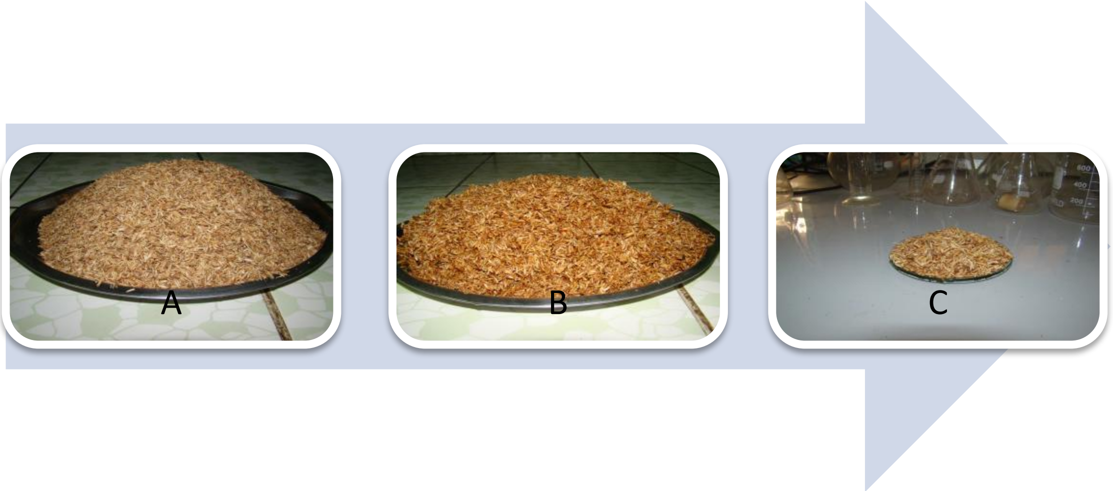

Fig.1: Rice husks stacks: (A) Raw rice husks stack; (B) Washed rice husks stack ; (C) Dried and ready to use rice husks stack.

Table 1. shows the physical properties and chemical compositions of the used rice husks, while Table 2. shows the sieve analysis of the raw rice husks which is ready to be used in the experiments.

TABLE1: PHYSICAL PROPERTIES AND CHEMICAL COMPOSITIONS OF EXPERIMENTAL RICE HUSK

Physical properties		**Chemical compositions**	
Surface area (BET)	542.02 m^2/g	Compound	Composition wt %
Bulk density	0.1405 g/cm^3	SiO_2	15.46
Moisture content	6.455%	Al_2O_3	0.65
Carbon	35.2 %	Fe_2O_3	0.03
Ash	20.5 %	CaO	0.93
Volatile matter	37.85 %	MgO	0.52
		Na_2O	0.1
		K_2O	1.33
		LOI	80.98

TABLE 2: SIEVE ANALYSIS OF THE RICE HUSK.

Sieve Size (mm)	1	2	4	8
Passing %	0	40	60	100

- *Preparation of cyanide ion solutions*

A stock solution cyanide ion of 1000 mg/ l cyanide ion concentration was prepared by dissolving 1.8846 grams of reagent grade NaCN crystals in 4 ml Ionic Strength Adjuster (10 M NaOH) finally adjust the volume of the solution to one liter using distilled water. This stock solution is used to prepare the cyanide standard solutions needed , the solutions are stored in a well-sealed flask in a dark cabinet [10].The cyanide ion concentrations were measured using spectrophotometer thermo – genesys 10 UV [11] .

B.Methods.

Adsorption experiments were carried out using 1 inch (2.54 cm) diameter PVC chemical resistance pipe with 100 cm height (Fig 2).

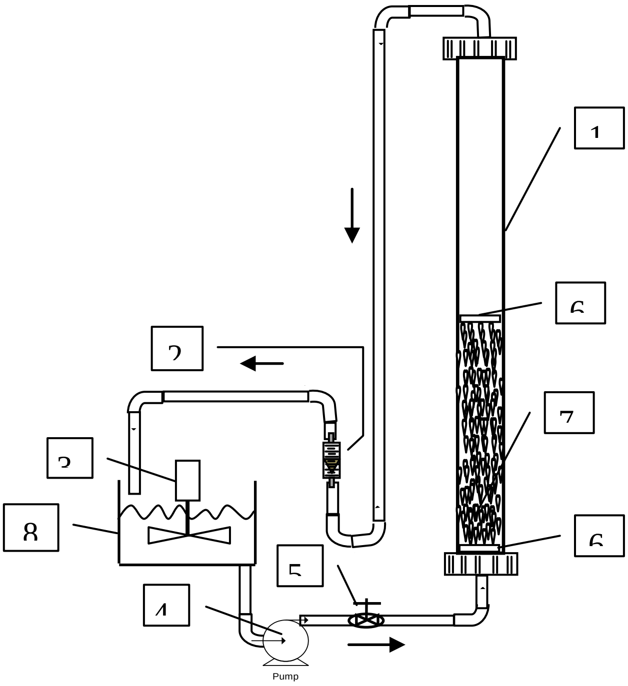

Fig.2: Fixed bed adsorption column unit: (1) Chemical resistance PVC pipe; (2) Flow meter; (3) Motor with paddle mixer; (4) Peristaltic pump; (5) Gate valve;m (6) Perforated steel plate; (7) Rice Husk media; (8) Tank filled with experimental solution

The pipe is packed with desirable adsorbent media height (H_m) (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm), shaken gently to insure the final settlement of the media to the desired height. Perforated steel plates were placed above and below the media to prevent flotation. The experiments were done by pumping the cyanide ion solution upward using peristaltic pump, control and measuring flow using gate valve and flow meter.

Fixing the flow rate at 55 ml/min requires 9.2 min for the solution to travel through the experimental column, then using a syringe to collect the samples after (10, 20, 30, 40, 50, 60 min) from the fully mixed solution tank. The removal efficiency (R_e) is calculated using the following equation:

$$\boldsymbol{R_e}\% = \frac{C_i - C_e}{C_i} * 100 \qquad (1)$$

Where C_e represents the concentration of the cyanide ion in the collected samples under specific operating conditions. C_i initial cyanide ion concentration.

III. EXPERIMENTAL RESULTS AND DISCUSSION.

A.Effect of pH value.

Experiments were conducted at various initial pH values (1, 2, 3, 4, 5, 6, 7, 8, 9, 10) for cyanide ion solution while other parameters are maintained fixed (C_i =1mg/l, process time (t_p) = 60min, H_m = 1m, T = 40 ^oC), the previously mentioned pH values are obtained by adjusting the prepared solutions using 0.1 N NaOH and 0.1 N HCl solutions, and the pH values were traced using portable pH Tester (Hanna instruments , HI 98108).

Figure 3. shows that the removal efficiency clearly increased with pH increase and the max removal efficiency of about 90% was achieved at pH = 7, and that is because decreasing of pH will make the surface charge of the particles more positive and due to the composition of hydrogen ions for the binding sites [12]. After that, the removal efficiency tends to slow down, such behavior may refer to the formation of soluble cyanide complexes, which remain in solution as dissolved matter [12].

B. Effect of Temperature.

Increasing temperature of the feed solution clearly tends to increase the removal efficiency of the cyanide ions (Figure .4), the experiments set was conducted for various temperatures (20, 25, 30, 35, 40, 45, 50, 55 ^oC) while other parameters kept fixed (C_i =1mg/l, t_p = 60min, H_m = 1m, pH =7). The increase in removal efficiency due to temperature increase may refer to two major phenomena. First is that increasing solution temperature will increase the ions mobility [13], second is that increasing solution temperature would lead to tear the rice husks leaf leading to increases its absorption susceptibility due to the increasing of the leaf surface area, however after temperature 40^oC the removal efficiency shows a slow increase rate.

C. Effect of Initial Concentration.

A set of experiments were conducted for different initial concentration of cyanide ions (1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/l) other parameters kept fixed (pH =7, t_p= 60 min, H_m = 1m, T = 40 ^oC). The results show (Figure .5) that maximum removal was 92 % at C_i = 1mg/l. From this figure the removal efficiency decreases rapidly with increasing of initial concentration till C_i = 10 mg/l, then the reduction rate tends to be slower. Noticing that the results are about the removal percent not the total removal amount.

The decrease of cyanide ion removal efficiency with increase of initial concentration refers to the limitation of available active free sites of adsorbent media where the cyanide ion molecules to compete for a fixed mass of adsorbent, in addition to the increase in intra-particle diffusion [14]**.**

D. Effect of Adsorbent Media Height.

A set of experiments were designed to investigate the effect of adsorbent dose on the removal efficiency, to do so the adsorbent media height (H_m) has been changed for every run (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 cm) while other parameters were kept fixed during these set of experiments (C_i =1mg/l, t_p = 60min, T = 40 ^oC, pH =7).

The results shown in Figure .6 indicate that increasing the adsorbent height lead to increase the cyanide ion removal efficiency and this is due to the increment of available surface area (active sites) for adsorption by increasing the adsorbent dose [15]. Maximum removal was 97% which was conjugated with 1m height of adsorbent media.

E. Effect of Process Time.

As it was mentioned before; fixing the flow rate at 55 ml/min will require 9.2 min for the solution to travel through the experimental column, so collecting the samples should be after 9.2 min to insure the complete circulation. A syringe was used to collect the samples after (10, 20, 30, 40, 50, 60 min) from the fully mixed solution tank.

Figure .7 shows the effect of process time (t_p) on removal efficiency of cyanide ion. The results show that increasing process time enhance the adsorption process and so increasing the removal efficiency. However the removal rate shows negligible increment after 40 min which is called equilibrium time where the interactions between the solution and adsorbent media reaches to an equilibrium phase [15]. The removal efficiency increased from 92 to 95 % within 20 min as it increased from 50 to 92 within 30 min.

IV. MATHEMATICAL MODEL.

Mathematical modelling can help in reducing the needs for field or laboratory experiments to investigate a specific scientific problem under specific conditions, and so reducing time and cost. However, such modelling processes need sufficient experimental data for model input information. A Polymath 6.1 computational system software (Fig .8) was used to apply a regression analysis on the experimental data that were obtained from the experiments.

A non linear approach was chosen to model the relationship between three independent variables (C_i, t_p, H_m) and one dependent variable which is the removal efficiency (R_e). Other independent variables such as pH and T were kept constant at their values which achieved the optimal removal efficiency from the lab experiments (i.e. , pH = 7. T =40 ^oC).

The model output gave the following equation which represents the relationship between cyanide ion removal efficiency (R_e) with the independent variables.

$$R_e = A*C_i^B + C* H_m^D + E* t_p^F \qquad (2)$$

Table 3 shows the values of the constants (A, B, C, D, E, F):

TABLE 3: VALUES OF THE CONSTANTS WHICH APPEARS IN EQUATION (2).

Constant	A	B	C	D	E	F
Value	-82.65785	0.0654519	-0.0002821	3.336158	110.4785	0.1193157

The model required 64 iterations to produce an equation (2), Figure .9 shows the relation between R_e calculated from the model and experimental R_e . The results of the statistical analysis for this model shown in Table 4.

TABLE 4: STATISTICAL ANALYSIS FOR CALCULATED AND EXPERIMENTAL REMOVAL EFFICIENCY.

Parameter	Determination coefficient(R^2)	Root mean square deviation (Rmsd)	Variance (σ^2)
Value	0.9959142	0.2250015	1.446448

The statistical analysis shows that the determination coefficient (R^2) was very close to 1, R^2 is a measure used in statistical analysis that defines how well a model explains and predicts experimental data, its value ranges from zero to one, noting that the closer the determination coefficient value is of one the best the fit was indicated. Root mean square deviation (Rmsd) closer to zero, noting that Rmsd which measures the average error and typically vary from zero to infinity with a value closer to zero indicates a better fit. Variance (σ^2) equal to 1.446448 which indicates that the variability of the data from the mean value is relatively small.

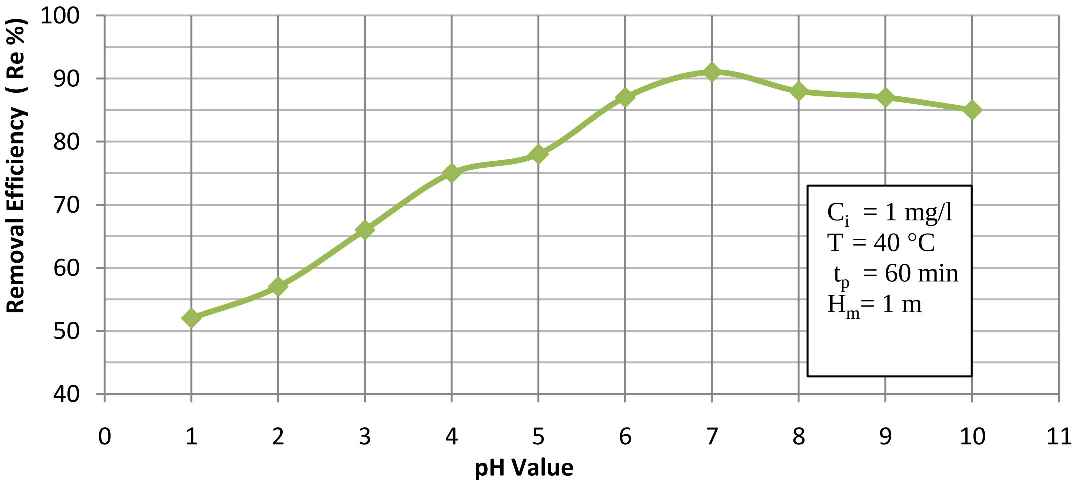

Fig .3: Effect of initial pH value for cyanide ion solution on removal efficiency

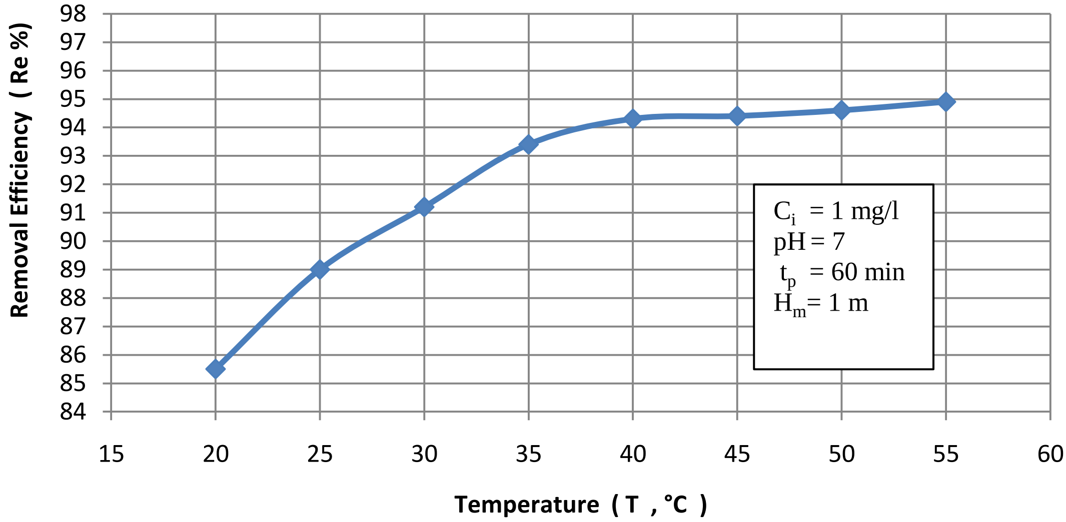

Fig .4: Effect of cyanide ion solution temperature on removal efficiency

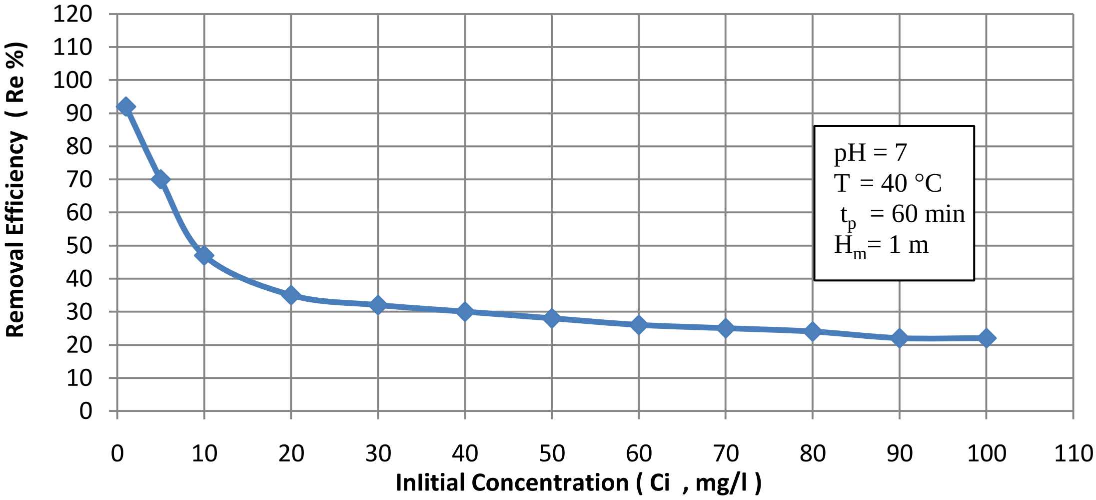

Fig..5: Effect of initial concentration of cyanide ions on removal efficiency

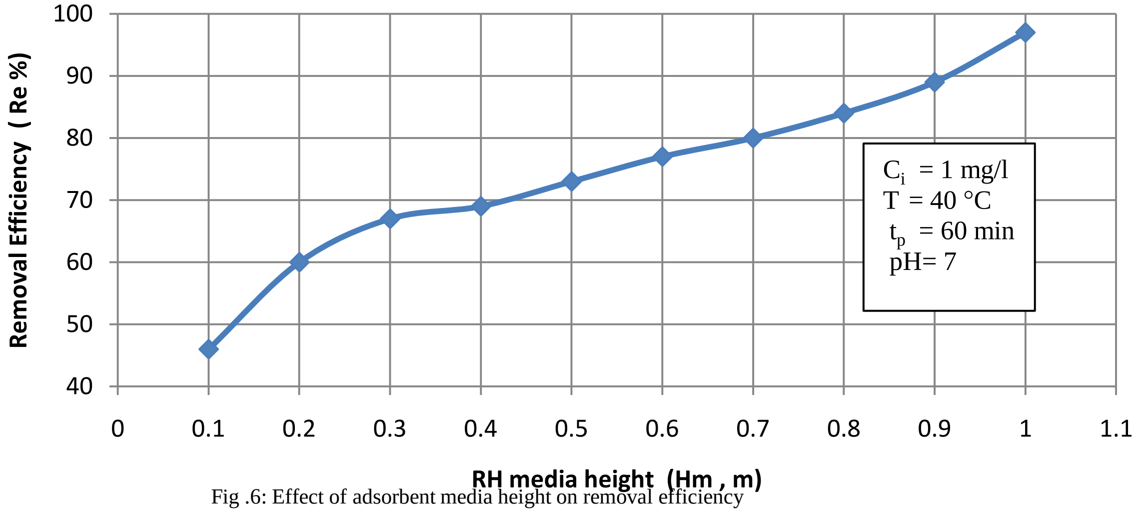

Fig .6: Effect of adsorbent media height on removal efficiency

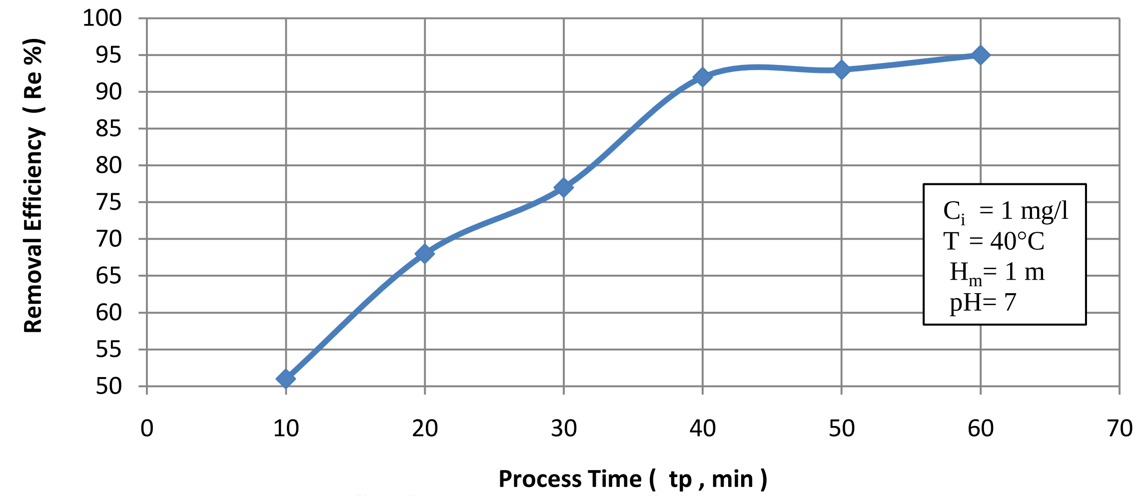

Fig .7: Effect of process time on removal efficiency

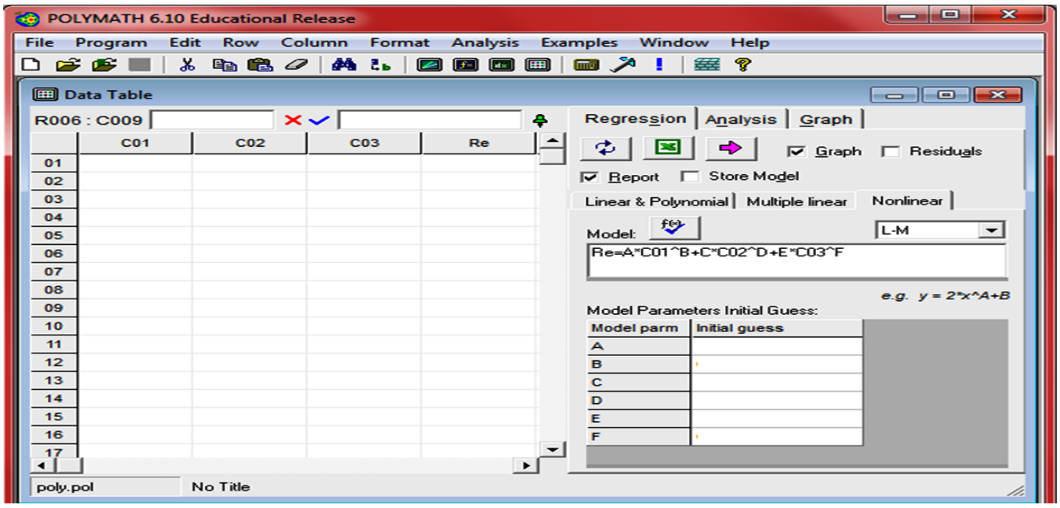

Fig.8: Polymath 6.1 computational system software interface

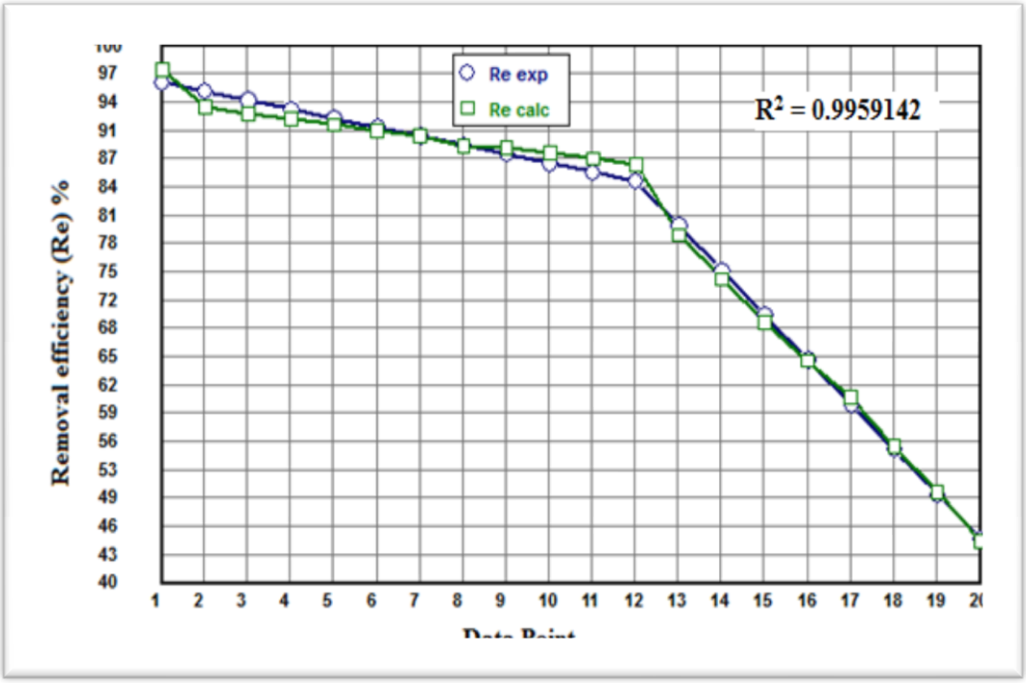

Fig .9: Relation between experimental and calculated Re as it was produced by polymath program.

V. CONCLUSIONS.

From this study, rice husks show effective capability in removing the cyanide ion from wastewater, according to the results obtained the following conclusions can be deduced:

1- The removal efficiency would reach as high as 97 % under specific conditions (C_i = 1 mg/l, T = 40°C, t_p = 60 min, pH= 7, H_m = 1m).
2- Optimum pH for removal efficiency was 7, RH shows dramatically high removal capability under acidic environment, and mild removal under alkaline environment.
3- High cyanide ion concentration requires a high RH dose in order to maintain effective removal efficiency.

4- Increasing cyanide ion solution temperature would show high removal efficiency, but after T = 40 ^{o}C the removal rate does not justify the additional cost that requires to improve the removal efficiency.
5- The developed model introduced from the application of polymath software shows an excellent correlation between the experimental parameters. This model would help to predict the required operation conditions in order to obtain best removal.

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