SYNTHESES AND USING OF ACTIVATED CARBON FROM RICE HUSK AND PURE SILICA FOR POLLUTION REMOVAL PROCESS

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Abstract

Activated carbon Rice Husk ACRH and Silica powder of Rice Husk SRH has been successfully synthesized from Iraqi Rice Husk RH through physical and chemical activation processes using potassium chloride KCl and N2 gas as activating agents, and carbonized for production of activated carbon at 500C0 for 2hrs. The production of activated carbon (AC) appeared to be one of the most important phases of this study. SRH was carried out by treatment with acidic and basic solution and pyrolysis at 500 Co for 2hrs. Three kinds of adsorption materials was studyed with the removal of polluted water (RH , ACRH and SRH) . FT-IR, UV-Visible Spectra were performed for characterized and studying adsorption, which calculated with using an Langmuir and Freundlich Equations. Frandash equation isotherms was largely applied or fitted on the behavior of adsorption processes.

تحضير واستخدام الكاربون الفعال من قشور الرز والسليكا النقية في عمليات إزالة التلوث

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كلمات مفتاحية : كاربون فعال ، سلكا ، قشور الرز ، امتزاز الفينول

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المستخلص:

تم في هذا البحث تحضير الكاربون الفعال والسليكا النقية من قشور الرز العراقي . وأجريت له عمليات التنشيط الكيميائي والفيزيائي باستخدام كلوريد البوتاسيوم KCl وغاز النيتروجينN_2 كعوامل للتنشيط في درجة حرارة 500م ولمدة ساعتين. كما تم استخلاص السليكا على شكل بلورات نقية بالمعالجة الحامضية والقاعدية ثم التحلل الحراري بدرجة حرارة 600م ولمدة ساعتين . استخدمت المواد المازة الثلاثة لأزاله الملوثات مثل الفينول من الماء و تم الاستعانة بمطيافية U.V , FT-IR لتشخيص ودراسة خواص الكاربون المحضر ، وجرى حساب عمليات الامتزاز باستخدام معادلة لانكميروفرندش . وأظهرت هذه الدراسة أن السليكا هي الأفضل في عمليات الامتزاز . وأن آيزوثيرمات معادلة فرندش تنطبق بشكل كبير على سلوك عمليات الامتزاز .

INTRODUCTION

Activated Carbon(AC)has a very large surfacearea and various surface functional groups. It has been widely used as the adsorbent withwide range ofapplications adsorption method may be one of the ecofriendly economic and efficient techniques with considerable potential for the removal of organic pollutants from contaminated water. (Iang etal, 2009), (Zong etal, 2011), (Chiang Maie,2008), commercially activated carbon is produced frombituminous or lignite coal. Thelong-term availability of coalenvironmental impacts and potentially increasing costhasencouraged researchers to find other alternatives, which maybe cast effective and equally potential. Activated carbon canbe manufactured from any material that has reasonableelemental carbon content. Any lingo cellulosic material can beconverted to an activated carbon,The literature mentions many precursors for activatedcarbon such as (Gergov.1994), Grag etal, 2007), Thuadaig and Chiang Maie.2008), (Tsaietal, 2001), (Gergova etal, 1994). It is used for purification (decolorization) and removal of the toxic organics and heavy metal ionsrecently.

Activatedcarbon is widely used as adsorbent in gas and liquid phaseseparation.(Qureshia etal ,2008).

AC obtained from pyrolysis is considerably improved by activation treatment. There are two distinct ways of activation, termed as physical and chemical activation in physical activation. The activating agents in the physical way are oxidizing gases: CO_2 or H_2O, and are mainly inorganic compounds, and for the chemical was can use (KOH, H_3PO_4, $ZnCl_2$). ([Khezami etal, 2009). Phenols are a class of organicscompounds common herbicides and insecticides and resistant to biodegradation.Phenol is very solublein water, also considered as prioritypollutants since they are harmful to organisms at lowconcentrations. The presence of chlorine indrinking water, phenols form chlorophenol, which form akind of medicinal taste, (Wu etal, 2005).

RH are an agricultural waste product produced by milling industry be to more than thousandtones in Iraq. The main components of ricehusk are carbon and silica (15-22%) SiO_2 in hydratedamorphous form like silica gel, it has the potential tobe used as an adsorbent, When rice husk isburnt, about 20 wt% of the husk remains as ash. Therice husk ash has more than 95 wt.% of silica with highporosity and large surface area, (Saritayadav and Ttagy, 2011).

The overall purpose of this study is the developmentof value-added, industrially useful products from low- value agricultural residues. This investigated the useof activated carbon produced fromrice husk for the possible removal of dissolved organic compounds from aqueoussolution.

EXPERIMENTALMaterials and Methodology

Chemicals:

phenol , KCl from Fluka company, ethylene glycol and mono ethyl ether from Sigma –Aldrich . All chemicales used as received without are purification.

Equipment's:FTIR-8400spectrophotometer (Shimadza) was used for RH, ACRH, XRD for SRH analysis , UV-VIS. spectroscopic of a Perkin Elmer Lamba. rotary incubator shaker 2model wmx8 manufactured by xteelment industries 38, laboratory vacuum line provide with desiccator, were used for surface area measurement and muffle Furnas (Carbolate - England).

Raw materials (RH):

Activated carbon was prepared from Iraqi Rice Husk (RH) obtained from the local rice processing mill in NasiriyaGovernoratearea. Shown Table ,(Garag,U..2007) the RH was washed with tape water in order to release dust, and then washed twice with distiled waterand subsequently dried at 90 C^0 for 24 h to remove moisture content. The dried RH was ground and sieved to a particle size of 106µm, and then stored in desiccator (Glass Dryer) until used in adsorbed.

Synthesis of the Activated Carbon Rice Husk (ACRH):

The washed and dried rice husk was grounded and sieved through106µm and was burned in electrical oven with multi temperatures at 200 C^0 for 1 hour, 300 for 1 hour and 500 C^0 for 2 hours.The rice husk ash was stored in a desiccator until use. Table. 2. showingchemical composition of the mineral ash.

Extraction of Pure Silica from Rice Husk (SRH) :

Rice husk silica was extracted by using 15g of RH stirred in 200 ml of distilled water for 1hr then filtrated, Pretreatment of the husk in an aqueous solution with 5.0 wt% of sulfuric acid at 200°C for10hrs was boiled in a covered 250 ml Erlenmeyer flask. The solution was filtered and the residue was washed with 150 ml boiling waterfor several times, The filtrate was allowed to cool down until the last rinse to aH =6 –7 .The solid Grains RH treatment with 5N Sodium Hydroxide andwas boiled in a convert 250 ml Erlenmeyer flask for 10hrs , filtrated the solution and thenwashed the solid Grains with distilled water until the last rinse to PH = 7. Filtrate was then dried at 120C^{o}with oven for 6hrs,The treated husk was burned at 500°C for 3hrs the resulting white powder was dried ball milled with zirconia balls in plastic bottles, The resulting silica powders was characterized by FT-IR and XRD.

Determinationof Surface area:

Specific surface area was measured using ethylene glycol and monoethyl ether method(EGME). (Qing etal, 2007).

Measurements of PH :

PH was determined by mixing 1gm of sample with 10 ml distilled water ,then measured by PH meter.

Adsorption Studies:

0.5gm of active carbonwas placed in 250 mlconical flask containing phenol solution (15 mg phenol were prepared by serial dilution of stock solution) in different concentration (40, 80, 120, 160, 200) ppm were carried out by shaking and were placed on rotary shaking machine using for 10hrs80 rpm at room temperature. The progress ofadsorption during the experiment was determined by removing the flask, and the amount of removed phenol achieved at varying dosages of carbon,.This gave an indication of the active carbon usage rate required to treat a phenol pollution to a specified effluent quality. As well as the type of solid – fluid phase equilibrium that exists for the particular case under consideration.

Data Analysis:

A spectrophotometer UV-VIS. was used todetermine,the absorbance of different phenol concentrations.A calibration curve of phenol concentrations versus absorbance was constructed,this run was thought to be useful in testing the ability of the producedactivated carbonto remove phenol, The Langmuir and Freundlich equations was used to determine the models of adsorption isotherm.

RESULTS AND DISCUSSION

Three kinds of adsorption materials were produced from RH, Firstly simple granularly RH was heated under atmospheric oxygen at 100 C^{o}without pyrolysis, Secondly ACRH was heating under nitrogen at 500 C^o, and thirdly pure silica SRH , was extracted from Rice Husk and Characterizated by XRD in state Enterprise for phosphate Factory in al – Quaim. Chemical properties of RH, ACRH and SRH are indicated in tables (1,2,3).

Table. 1. Chemical Oxide % for RH , ACRH and SRH .

Componets	RH %	ACRH %	SRH
SiO_2	71.82	93.21	98.22
MgO	1.6	0.93	0.03
CaO	1.84	0. 73	0.08
K_2O	1.81	0.10	0.05
Fe_2O_3	0.63	0.09	0.042
Al_2o_3	2.89	0.76	0.15

Table. 2 . Properties of the ACRH

Ash Content Wt%	20 .24
Density Kg / L	0.48
PH	6.2
Moister Wt %	9.7
Iodine Number	645

Table. 3 . Chemical Properties of the RH .

Ash	23.8
Carbon	35.9
Oxygen	41.07
Hydrogen	5.11
Nitrogen	0.28
Moister	9.32

Rice Husk pyrolysis:

Three types of activated carbons (RH, ACRH,SRH) were prepared under different conditions.Rice husk was washed with distilled water and dried at 90 C^0 for 24 hrs, the dried material were divided into three portions rate, The first portion was RH without pyrolysis was gave the lowest value in the adsorption because it had the lowest surface area, second portion was carbonize in $500C^0$for 2hrs , This showed some increase in adsorption rate and surface area. The third was carbonized in 950 C^0 for 2hrs. This appear to produce purecrystals SRH. This seems to have a high rate of adsorption and largest in surface area.

Adsorption Kinetics:

The suggested mechanism for the adsorbign of phenol is That atmospheric oxygen and phenol are adsorbed on the surface of ACRH.Each molecules of oxygen adsorbed may have resulted in the conversion of two molecules of phenol. into two molecule of phenoxide. It had been know on thatthe negative charge of the oxygen atom bound to the silicon atom on the surface of active carbon and subtract the proton from the solution .

Chemical and Physical Activation:

Chemical activation of ACRH was carried out by impregnatedwith KCl in different concentration(5 , 15 , 25) % for 24hrs. This broughtabout a large decrease in the ash content and an increase in the carbon content, with high surface area.and hot deionized water sequentially toremove the residualKCl. Finally theACRHactivated carbons were dried in$90C^0$ .and also physical activation was carried out under atmospheric nitrogen for 2hrsat high temperature to gave more increasing in surface area .The effects ofnitrogengas on carbonization active carbon at $500C^0$, which aregaveing an improving in adsorption Susceptibility.

Surface area.

Thiswas carried out by determining the specific surface area using(EGME) method,which seem to be proportional with the increased concentration of KCl as a chemical activation reagent

Table .4 . Surface area of active carbon

NO	KCl. Conc. %	RH	ACRH	SRH
1	5	265.4	335.25	370.4
2	15	278.5	350.33	328.3
3	25	293.2	365.5	396.7

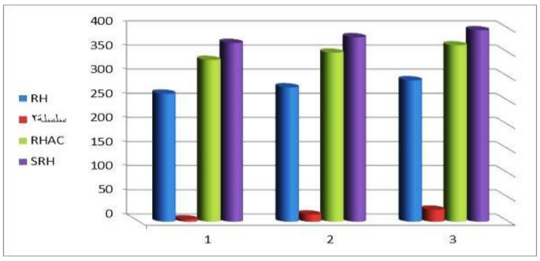

Fig. 1. Relationship between KCl % via Surface area

Adsorption Isotherms:

The mathematical interpretation of the adsorption isotherms was studied using Langmuir and FreundlichEquations The mathematical expression for the Langmuir equation[9] :

$$q_e = \frac{QbC_e}{1 + bC_e}$$

Ce(mg/L) is in equilibrium with that on solid , where Q(mg/g)is the maximum amount of adsorbed , whichFreundlich equation [9]:

$$q_e = K_F C_e^{\beta}$$

where KF and β are constant. There are a few models to describe the experimental data during adsorption isotherms in the literature. The adsorbed molecules distributed between the liquid phase and the solid phase can be described by adsorption isotherms when the adsorption process reaches at equilibrium state .The adsorption capacity in this study was investigated with theFreundlich and Langmuir adsorption isotherms .

Freundlich equation is shown by the Log Q_e = log K_f + 1/Log c_e,where the intercept Log k_f is a measureof adsorbent capacity and the slope 1/n is the sorption intensity . Fig (3 – 7). (Boonpoke, et al..2011)

The Langmuir equation relates the solid phase adsorbate concentration (Q_e) or uptake to the equilibrium liquid concentration (c_e) as follows

$$\frac{1}{Qe} = \frac{1}{a} + \frac{1}{ab} \times \frac{1}{ce}$$

Where a and b are the Langmuir constants representing the maximum adsorption capacity for the solid phase loading. (Fig. 8 – Fig .12)

Table. 5 .The Langmuir and Freundlich constant.

Materials	Freund lich constant			Langmuir constant	
	K_f	1/n	R*2	Q_o	A
RH	8.63	0.052	0.81	0.012	0.128
ACRH	8.66	0.03	0.9	0.011	0.133
SRH	7.6	0.09	0.81	0.029	0.144

The results in Table .5. show that the rate of adsorption of phenol in rice husk ,rice husk ash and its pure silica obeys The Freundlich adsorption isotherm. The isotherm data fit well with the Freudlich models R*2=0.95 for rice husk ash. The constants $K_f$and 1/n were calculated to be 0.866 and 0.03 respectively for rice husk ash . The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that amount of adsorbate. Adsorbed increase in infinity with an increase in concentration .

In the previous application of the equation, shapes shown of the Freundlichmore than equivalent to the Langmuir. This was expected for The adsorption o organic materials on solid surfaces,The adsorption Isotherm for Langmuir shows that adsorption was increased with concentration, at higher concentrations of the adsorbent substance. The rate of adsorption was up to a specific value and then the solid material was covered with a single layer of adsorbent materials .This means that a saturation of the surface was reacted for the adsorbent,so that the adsorbent may be needed for to other time in order to install other layer from The adsorbent materials. In general the adsorption process from aqueous solutions is essentially

the link process adsorbent for surfactant molecules .and activated carbon with salts chlorides leads to the formation of a variety of functional groups on the surface of coal .which including groups such as oxygen , polycarboxylic ,lactones , and carbonate, These groups are multiple patterns of alternating influence absorbed / adsorbent . Three mechanisms imposed for the adsorption of organic compounds on active carbon surface , a mechanism constitute: hydrogen bonding linking , complexes donor – accepter electron and polarized effected π – π* (Amy etal, 2002), (Nasehir etal, 2011).

The effect of initial phenol concentration in the range of (40, 80, 120, 160, 200) mg/l on adsorption is shown in fig(7) .The evidence that the percentage phenol removal decreased with the increase in initial concentration of phenol .The initial phenol concentration provides the necessary driven force to overcome the resistance to the mass transfer of phenol between the aqueous phase and the solid phase.

Spectral Study:

The FT-IR spectrum of RH , ACRH and SRH have similarity in the absorbed peak but they are differ in the intensity of the peaks(.Fig .2)for SRH peak at 3471 CM^{-1} are due to the OH –Vibration of the silica as well as the adsorption of H_2O on the surface. In 1647 CM^{-1} for bending of the H_2O, peak at 1066 CM^{-1} to the bond of Si - O - Si , 968 CM^{-1} is the bending vibration of Si - O – Si and 601 stretching vibration of Si - O – Si . (Giraldo and Moreno Pirajane. 2011).

CONCLUSIONS:

In this study, the ability of RH, ACRH and pure SRH to adsorbe of the polluted water. The Physical and chemical adsorption data were correlated with the Freundlich and Langmuir type isotherm equationat 24°C. The adsorption capacityto bind phenol was investigated as a function of PH.RHAC carbon and pure SRH had ahigher adsorption capacity for phenol. The experimental results indicate that rice Husk was ability toadsorb phenol and, consequently, it's possible utilizationin the treatment of phenol-contaminated solution. The experimentaldata showed that the Freundlich equation bestrepresented phenol adsorption data and the adsorption ofphenol onto both the sorbents follows first-order kinetics. Therefore, rice husk (RH , ACRH . SRH) could be used aslow-cost and natural product .

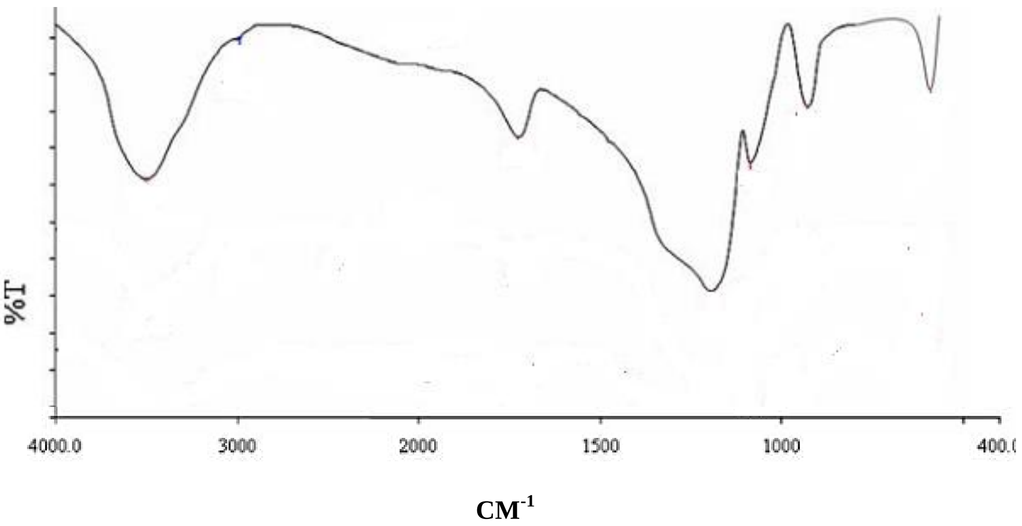

Fig . 2. FT-IR Spectrum of pure silica SRH

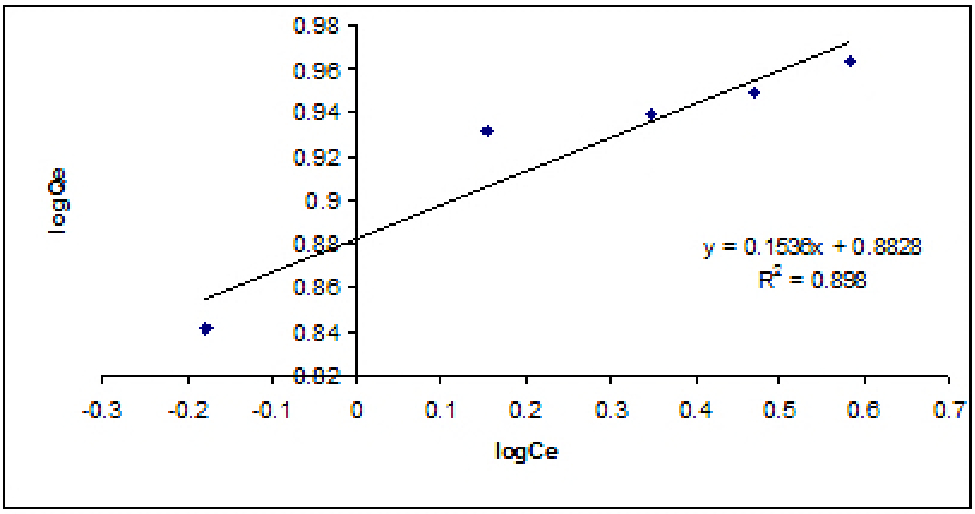

Fig.3. ACRH 25% KClFrandlish equation at 25 C^0

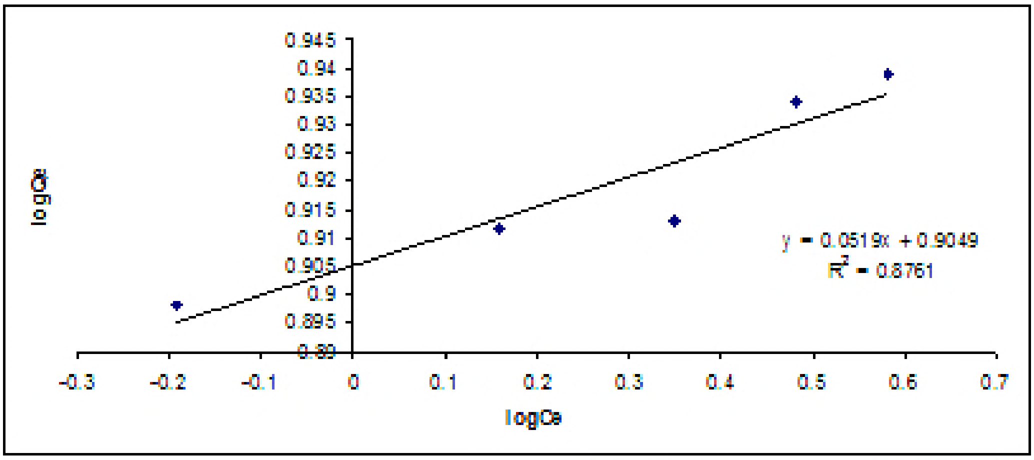

Fig. 4. RH Granular with 25% KClFrandlish equation at 25C^0

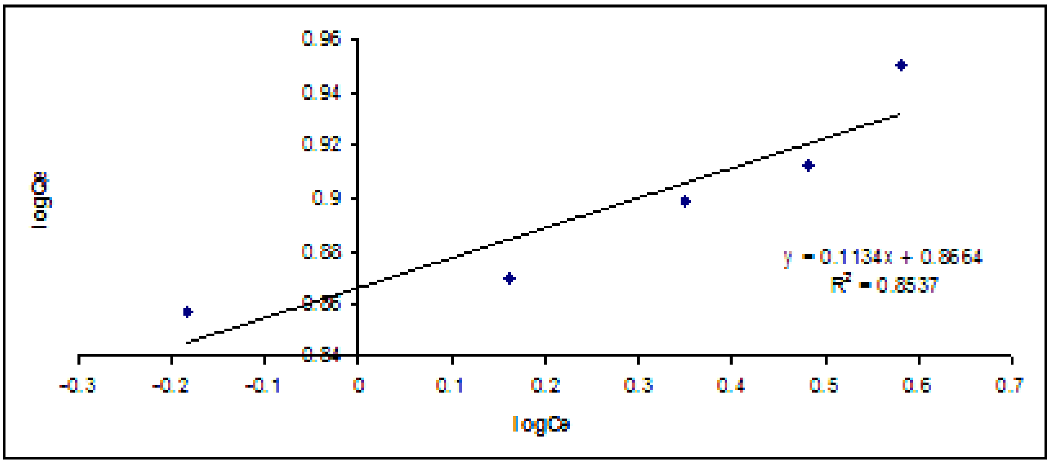

Fig. 5. SRH with 25% KClFrandlish equation at 25C^0

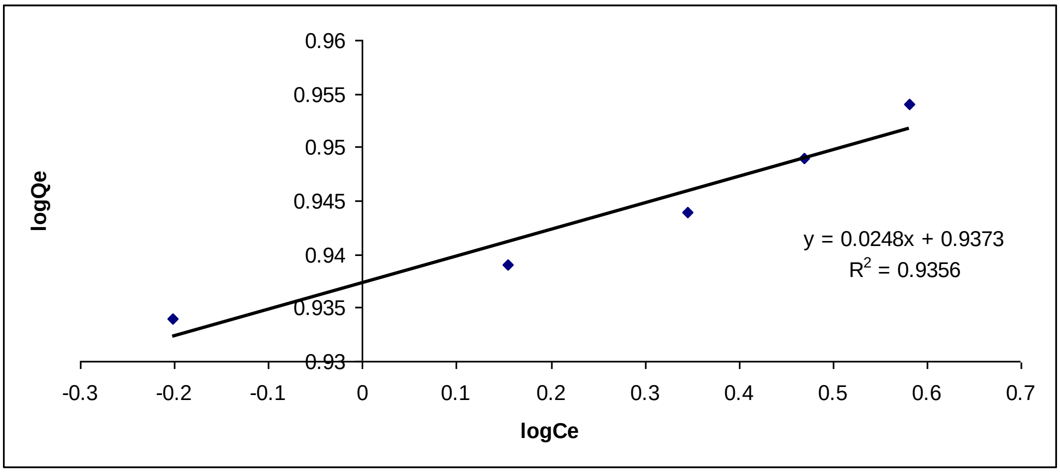

Fig.6. ACRH with 5% KClFrandlish equation at 25C^0

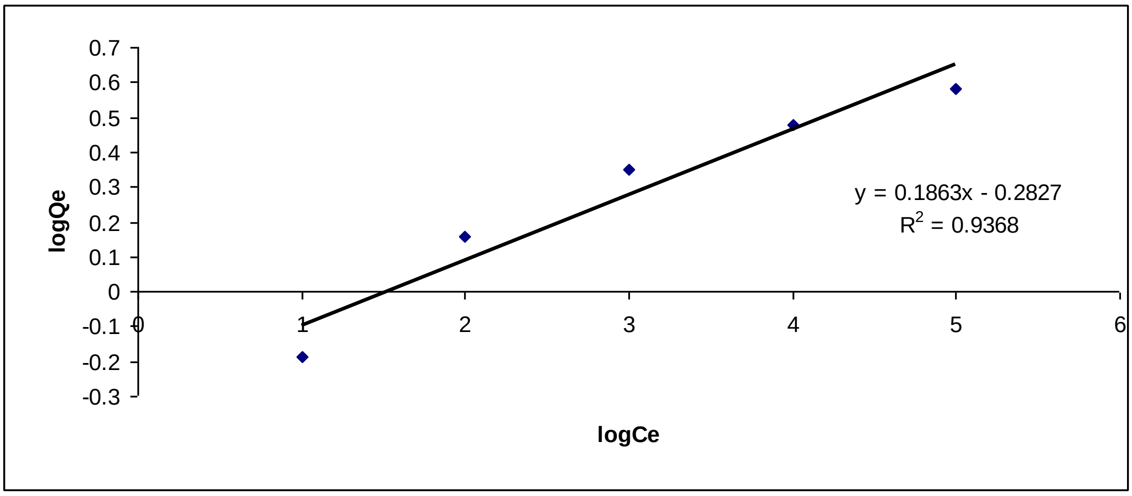

Fig. 7. ACRH with 15% KClFrandlish equation at 25C^0

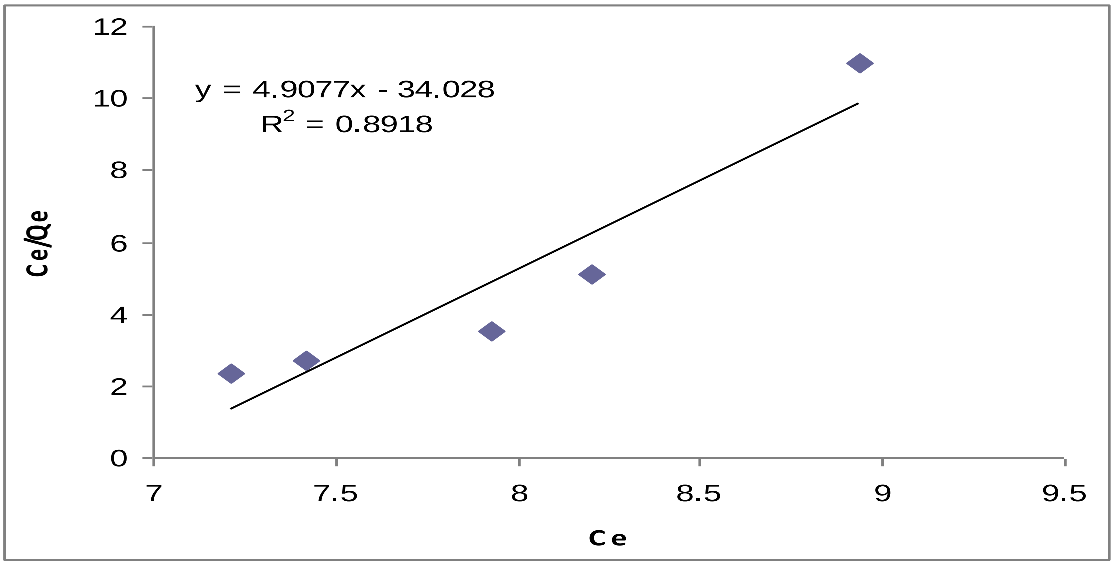

Fig.8. SRH with 15% KCl Langmuir equation at 25C^0

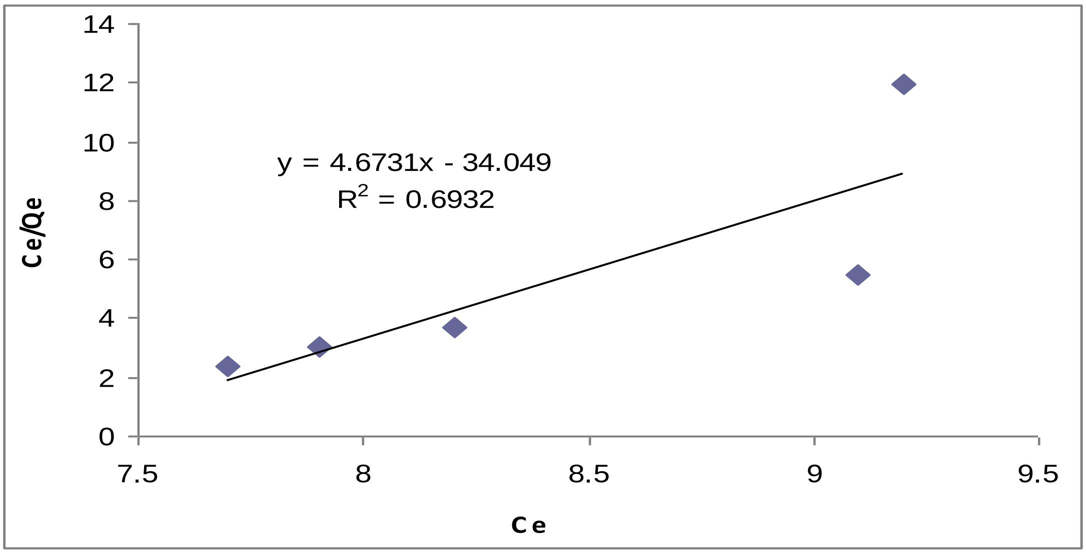

Fig.9. ACRH with 15% KCl Langmuir equation at 25C^0

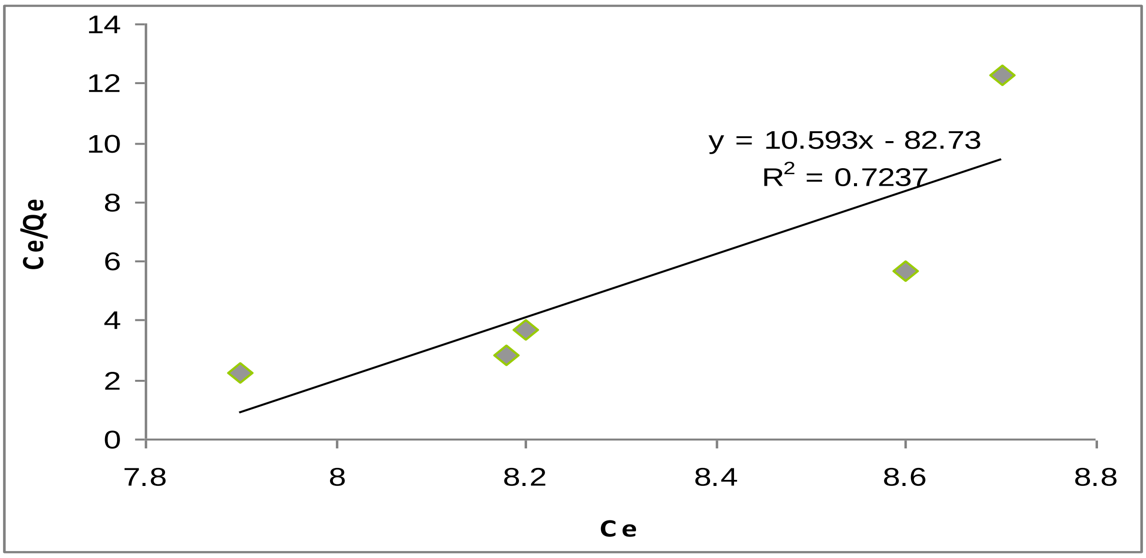

Fig . 10 . RH Granular with 5% KCl Langmuir equation at 25C^0

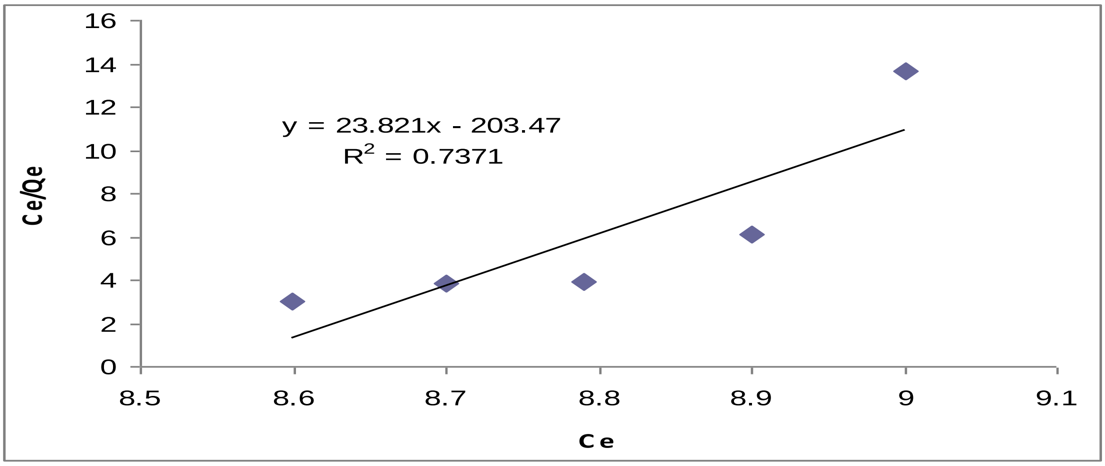

Fig . 11 . RH Granular with 15% KCl Langmuir equation at 25C^0

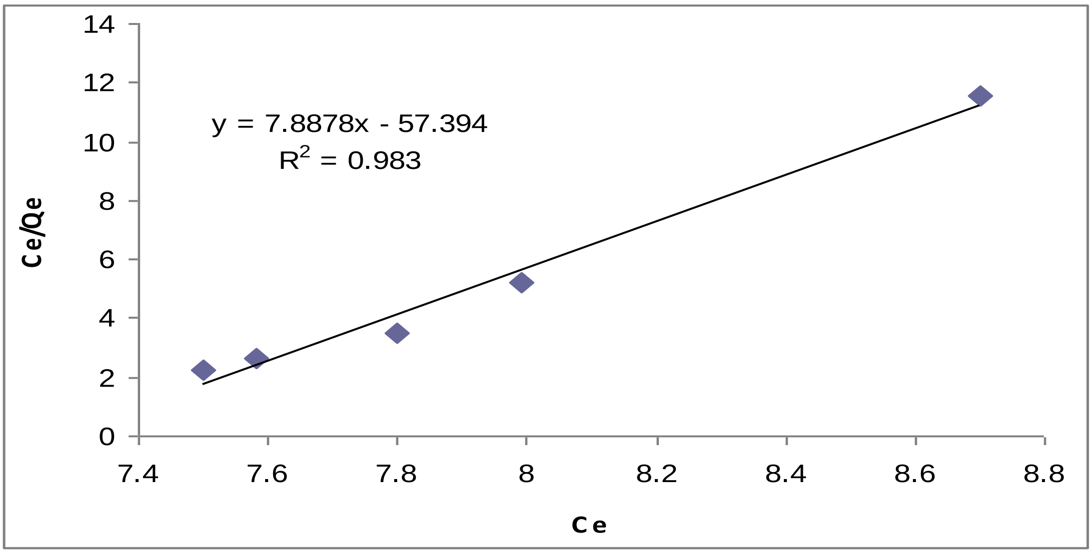

Fig . 12 . RH Granular with 25% KCl Langmuir equation at 25C^0

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