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Adsorption of Chromium Ion from Industrial Effluent Using Activated Carbon Derived from Plantain (*Musa paradisiaca*) Wastes

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Abstract Plantain (*Musa paradisiaca*) wastes are readily available in Nigeria and if not properly managed, they constitute nuisance to the environment. They could be used, however to produce resource materials, such as activated carbon that are of public health importance. Therefore, this study assessed the use of plantain wastes in the bio-sorption of chromium from battery recycling effluent. Plantain wastes were collected from a plantation, sun-dried and ground. These were then carbonized and activated using phosphoric acid at high temperature. Samples of effluent from Ogunpa River were subjected to physico-chemical (pH, conductivity, Total Dissolved Solid (TDS) and Chromium (Cr)) analyses, using standard methods. Batch experiment studies were used in determining the adsorption isotherms of the adsorbents at varied effects of pH (2 to 12) and adsorbent doses (0.1 to 2.0g) with treatments by plantain prepared activated carbons. Data was analysed using descriptive statistics, paired t-test and ANOVA at 5% level of significance. Means of pH, conductivity, TDS and Cr^{+6} of the effluent sample were: 2.0 ± 0.2, 2164.7 ± 0.6 µs/cm, 895 ± 0.00 mg/l and 13.5 ± 0.0 mg/l respectively. The highest quantities (68.02%) of Cr were removed at pH 10 while the optimum adsorbent dose (2.0g) removed 68.91% of Cr. The adsorbents showed satisfactory fits of adsorption to Langmuir and Freundlich models. Adsorbents had capacity for the uptake of chromium from effluent generated from battery recycling plant with plantain peel activated carbon having the highest adsorption capacity. Conversion and treatment of effluent with plantain wastes should be encouraged in battery recycling plant, to reduce its menace in the environment and promote effective waste management.

Keywords: *chromium removal, battery recycling effluent, Musa paradisiaca, Langmuir model, freundlich model*

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1. Introduction

Heavy metals are pollutants of very high priority concern in the scientific community because apart from being non-biodegradable, they are toxic to the entire ecosystem. They have the ability to bio-accumulate in biological species even at very low concentrations such as chromium. The presence of heavy metals and other waste pollutants can be traced majorly to urbanization and industrialization. A variety of industries are responsible for the discharge of heavy metals into the environment through their waste water [26] and through various routes [6]. These heavy metals also get into natural surface and ground waters from agricultural run-off, chemical spills, industrial effluents and municipal waste water [33]. Various methods have been applied in the removal of heavy metals from water and waste water. These methods include precipitation, coagulation and filtration, ion exchange, electrodialysis, biomineralisation and phytoremediation and adsorption on activated carbon. The choice of the method is based on the concentration of the metal ions, efficiency/cost ratio and the adsorption capacity of the adsorbent. Out of these methods, adsorption appears to be most widely used for the removal of heavy metals [10,32].

Adsorption technology is being used extensively for the removal of heavy metals from aqueous solutions because it is a cleaner, more efficient and cheap technology. Previously, various researchers have studied the possibility and efficiency of utilisation of agricultural fibres as an adsorbent for heavy metals removal in polluted water. Some of the low cost agricultural wastes that have been studied include; rice husk [30], sugar bagasse [18] and soya bean hulls [17]. These agricultural wastes which are generated in large quantities and which in some cases might become difficult to dispose, have proved very effective in the adsorption of heavy metals removal in water/polluted water. With the vast array of bio-sorbents currently available for the removal of metal ions, there is a dearth of information on the adsorptive potential of *Musa paradisiaca*. Therefore, this study assessed the potential of activated carbon derived from plantain wastes for the removal of chromium (VI) ions from battery recycling effluent, including the determination of optimum conditions (pH, contact time, adsorbent dose and initial metal ion concentration) necessary for the adsorption efficiency.

2. Materials and Methods

2.1. Collection of Effluent and Analysis

Industrial effluent from the point of discharge into Ogunpa Stream from Acid-Lead battery recycling plant, Ogunpa, Ibadan North-West Local Government, Oyo State was collected and taken to the laboratory for treatment and analysis. The effluent was characterized for pH, total dissolved solids (TDS), total suspended solids (TSS), conductivity, alkalinity, chloride, nitrate and chromium according to the standard methods (APHA, 1998). The results obtained were compared with Nigerian Environmental Standard, regulation and Enforcement Agency (NESREA). Effluent was digested using nitric-acid-hydrochloric acid digestion methods and its concentration determined by Atomic Absorption Spectrophotometer (AAS; Hanna C-100). The remaining effluent required for the adsorption studies were preserved with 5ml concentrated HNO_3 and refrigerated.

2.2. Collection of Plantain Wastes

Plantain wastes (ripe plantain, fruit stalk, bract and leaves) were collected from market within Ibadan in Oyo State, Nigeria. They were washed with distilled water, sun dried for 7 days and then oven dried at 45°C to constant weight. The samples were ground, passed through a 0.14mm mesh size and, stored in polythene container for analysis and treatment of effluents.

2.3. Carbonization and Activation of Plantain Wastes

The samples were prepared according to method by Salami and Adekola (2002) with little modification. Fifty grams of each raw ground plantain waste samples was prepared by contents into carbon at in temperature of 400°C for 1hour in a muffle furnace using a porcelain crucible and then cooled to room temperature. The charcoal was subjected to H_3PO_4 activation. The charcoal was agitated in H_3PO_4. Thereafter, the pre-carbonized charcoal slurry was left overnight at room temperature and dried at 110°C for 24 hours. The samples were activated in a closed system. Consequently, the samples were activated in a muffle furnace of 400°C for 1hour before cooling. After cooling down, the activated charcoal was washed successively several times with distilled water to remove the excess activating agent and impurities.

Raw ground plantain wastes

$$\xrightarrow[\Delta]{400^{\circ}\text{C, 60 minutes}} \text{C}(\text{s}) + \text{CO}_2\,(\text{Carbonization})$$

Carbonized – ground plantain wastes

$$\xrightarrow[\Delta]{\text{AA, }400^{\circ}\text{C, 60 minutes}} \text{AC} + \text{CO}_2\,(\text{Activation})$$

Where AA represent Activating Agent and AC represent Activated Carbon. Other reagents used were prepared as per standard methods. Four different types of plantain wastes were used as adsorbents; Peel Activated Carbon (PAC), Bract Activated Carbon (BAC), Leaf Activated Carbon (LAC) and Fruit Stalk activated carbon (SAC) were prepared. A commercial activated carbon (CAC), which served as control, was also used for this study. The prepared activated carbons were then subjected to various physical and chemical analyses.

2.4. Surface Chemistry of the Plantain Waste Activated Carbon

Surface chemistry of the activated plantain wastes was characterized by adopting Boehm titration and pH drift (or pH_{pzc} - point of zero charge). Boehm titration method is described as follows: Activated plantain waste (0.5g) was dispersed in duplicate in 50 ml each of 0.05M $NaHCO_3$, 0.025M Na_2CO_3, 0.05M NaOH and 0.05M HCl contained in 250 ml capacity glass bottles with tight glass corks. The bottles were shaken using an end-to end shaker at 180rpm for 24hours. Thereafter, the samples were filtered using Whatman No.1 filter paper and titrated with 0.05M NaOH and 0.05M HCl depending on the starting solution used. The amount of acidic groups on the surface of the plantain waste adsorbent were approximately probed as following $NaHCO_3$ (carboxylic group), Na_2CO_3 (carboxylic and lactonic groups) and NaOH (carboxylic and phenolic groups). The number of surface basic sites was calculated from the amount of HCl that reacted with the filtrate.

The method used for pH_{pzc} of activated plantain waste was a modification of Prahas *et al*, [22]. The method is described as follows: 50 ml of 0.01M KCl was prepared and added into a series of glass bottles with corks. Their pH was adjusted in range between 2 and 12 at interval of 0.5 using either 0.05M NaOH or 0.05M HCl. The pH of initial solutions was measured and noted as $pH_{initial}$. After constant value of $pH_{initial}$ had been reached. 1.0g of the activated plantain waste was added to each bottle and then corked. This set up was shaken for 48 hours. Thereafter, the second pH of the extract noted as pH_{final} was measured with a pH meter. A plot of $pH_{initial}$ on the x-axis against the difference between $pH_{initial}$ and pH_{final} on the y-axis was made. pH_{pzc} was the point where the curve cuts the x-axis implying the point when $pH_{initial} = pH_{final}$.

For the surface area using iodine test, Gimba and Musa [9] method was adopted. A stock solution was prepared containing 2.7g of iodine crystals and 4.1g of potassium iodide per litre. The prepared stock solution was standardized using a standard solution of sodium thiosulphate. Into a 100ml volumetric flask, 0.5g of the activated carbon and 10ml of 5% v/v hydrochloric acid was introduced. The flask was swirled until the carbon was wetted. Then $100cm^3$ of the stock iodine solution was added and agitated at a fast speed, using an electric shaker for a period of 60 minutes. The mixture was filtered through a sintered glass crucible. An aliquot portion (20 ml) was titrated with 0.1M sodium thiosulphate using starch as indicator. The concentration of iodine adsorbed by the activated carbon at room temperature was calculated as amount of iodine adsorbed in milligrams.

$$\frac{tmg}{g} = \frac{(B-S)}{B} \cdot \frac{VM}{W} \times 253.81$$

Where, B and S are the volumes of thiosulphate solution required for blank and sample titrations respectively. W is the mass of activated carbon sample, M is the concentration (mol) of the iodine solute, 253.81 is the atomic mass of iodine and V is 20 ml aliquot.

2.5. Adsorption Studies

A series of batch adsorption studies were carried out to determine the adsorption isotherms through the operating conditions necessary for the uptake of chromium (VI) ion. Also, the optimum operating conditions for the removal was determined.

Effect of pH

The pH values of the samples were adjusted at 2, 4, 6, 8, 10 and 12 using 1M NaOH. Effluent sample (50 ml) was collected into 250ml conical flask each and 1.0g of each prepared activated carbon was added into the flasks and agitated intermittently for the desired time periods. The mixture was shaken thoroughly at 200 rpm with rotary shaker for 90 minutes to attain equilibrium. The treated effluent was filtered through Whatman No 1 filter paper, then the chromium ions was determined by Atomic Absorption Spectroscopy (AAS). The study was performed at ambient temperature (28±2°C) to be representative of environmentally relevant condition. To avoid the fluctuation of pH due to the exchange of gases during the experiment, the flasks were covered with lids.

Effect of Contact time

One gram of each activated carbon was added into 250ml conical flask each containing 50ml of effluent. The pH used was obtained from the best value received from previous experiment. The mixture was agitated thoroughly at 200 rpm with rotary shaker for 30, 60, 90, 120 and 150 minutes. The treated effluent was filtered through Whatman No 1 filter paper, then the chromium ions was determined by Atomic Absorption Spectroscopy (AAS). The study was performed at ambient temperature (28±2°C) to be representative of environmentally relevant condition.

Effect of adsorbent doses

50ml of sample was taken into 250ml conical flask and known amount of each activated carbon 0.1g, 0.5g, 1.0g, 1.5g and 2.0g was added into each flask and agitated thoroughly at 200 rpm with rotary shaker. The pH and contact time used were obtained from the best value received from previous experiments. It was assumed that the applied shaking speed allows all the surface area to come in contact with heavy metals ions. The treated effluent was filtered through Whatman No 1 filter paper, then the chromium ions was determined by Atomic Absorption Spectroscopy (AAS). The study was performed at ambient temperature (28±2°C) to be representative of environmentally relevant condition.

Effect of initial metal ion concentration

The stock solution of 1000 mg/1 of the standardized Cr^{6+} was prepared using effluent sample. The solution was adjusted to pH 6.0 ± 0.2 with 1M HCl. Volume of effluent (50ml) was measured into each 250ml conical flask, dose of the adsorbent was added and the mixture was agitated at 200 rpm with rotary shaker. The pH, contact time and adsorbent dose used were obtained from the best value received from previous experiments. The treated effluent was filtered through Whatman No 1 filter paper, then the chromium ions was determined by Atomic Absorption Spectroscopy (AAS). The study was performed at ambient temperature (28±2°C) to be representative of environmentally relevant condition.

2.6. Adsorption Isotherms

The amount of metal ion adsorbed (Q_e) during the series of batch investigations was determined using a mass balance equation:

$$Q_e = \frac{(C_v - C_f) \times V}{M}$$

The definition of removal efficiency is as follows:

$$\text{Removal efficiency } (\%) = \frac{(C_v - C_f)}{C_v} \times 100 \text{ [14]}$$

Where Q_e is the metal uptake (mg/g); C_V and C_f are the initial and final metal equilibrium concentration in the effluent sample (mg/l) respectively, M is the mass of the adsorbent (g) and V is the volume of the effluent sample [1]. The result of batch equilibrium obtained from initial metal ion concentration was used to obtain metal adsorption isotherms. The adsorption isotherm was used to characterise the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate.

2.7. Adsorption Models

In this study, the experimental isotherm data set obtained was fitted using adsorption models including the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibria [19,23].

2.7.1. Langmuir Principle and Equations

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place.

The linearized equation is described by:

$$\text{Qe} = \frac{1}{\text{Qe}} = \frac{1}{Q^o b C_e} + \frac{1}{Q^o} \text{ [24]}$$

The Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants. Where Q*e* is the amount of metal ion adsorbed per unit mass of adsorbent; C*e* is the equilibrium concentration of adsorbate (mg/l); Q^o and **b** are the Langmuir constants and are the significance of adsorption capacity (mg/g) and energy of adsorption (l/mg) respectively. Also, constant **b** could be used to compare the removal efficiency of each adsorbent. Q^o and b are obtained from the intercept and slope of the plot $1/Qe$ and $1/Ce$.

2.7.2. Characteristics of Langmuir Isotherm

The characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L, which describes the type of isotherm and is defined by:

$$R_L = \frac{1}{1+KLC_o}$$

Where R_L is a dimensionless separation factor, C_o is initial Cr^{6+} in mg/l and K_L is a Langmuir constant (Lmg^{-1}). The parameter R_L indicates the shape of the isotherm accordingly:

Values of R_L	**Type of isotherm**
$R_L > 1$	Unfavourable
$R_{L = 1}$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

2.7.3. Freundlich Principle and Equations

The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface.

A linear form of this expression is given as

$$\text{Log } Q_e = \log k + \frac{1}{n}\log C_e$$ [24]

k and n are the Freundlich constants and represent the significance of adsorption capacity and intensity of adsorption respectively. Also **k** could be used to compare the removal efficiency of each adsorbent and n is qualitatively related to the distribution of site bonding energies. Values of k and n were calculated from the intercept and slope of the plot log Q_e and log C_e

A comparison of isotherm parameters for all adsorbents was done to determine the effectiveness of the adsorbents. The coefficients of correlation (r^2) and the isotherm constants were obtained. The high values of r^2 (>95%) show that the adsorption of Cr^{6+} could be well described by the Langmuir and Freundlich isotherms.

2.8. Statistical Analysis

A summary index was used to determine the mean values of results obtained from various parameters. One-way ANOVA was used to test for significant differences in characteristics of the prepared plantain wastes. The results were investigated by using the least significant difference at a 95% confidence level using SPSS 16.

3. Results and Discussion

3.1. Physico-chemical Characteristic of the Effluent

The physico-chemical characteristics of the effluent were presented in Table 1. The pH of the effluent was strongly acidic than the limits recommended by NESREA.

Table 1. Physico-chemical Characteristic of the Effluent

Parameters	Mean Value	NESREA Standards
pH	2.0 ±0.15	6-9
Temperature (°C)	30.0 ± 1.5	<40
TSS (mg/l)	2001.7±25.2	28
TDS (mg/l)	895.0± 0.0	2000
Conductivity (µScm-3)	2164.7 ± 0.6	1000
Chemical Oxygen Demand (mg/l)	1125.0±35.2	1000
Chloride (mg/l)	18.5±0.5	600
Nitrate (mg/l)	2.5±0.4	20
Chromium (Cr^{+6}) (mg/L)	13.1 ± 0.0	<1

All data were mean ± standard deviation of triplicate determinations.

The recreational uses of water and aquatic life in the receiving stream are adversely affected at low pH. Decreased in pH also decreased the solubility of certain essential elements such as selenium, while at the same time low pH increases the solubility of many other element such as Copper, Cadmium and iron [7]. pH being a function of hydrogen ion concentration, the high acidity was probably due to the high concentration of hydrogen ion [H^+] in the effluent, attribute to sulphuric acid, which one of the major raw materials in lead acid battery.

The averaged total suspended solids (TSS) value of the effluent is very high. Literature classified TSS of effluent as follows: TSS less than 100mg/l as weak, TSS greater than 100mg/l but less than 220mg/l as medium and TSS greater than 220mg/l as strong wastewater. The mean temperature value of the effluent is within the range of NESREA limit of 30°C. The mean COD value of the effluent is very high. It is above the NESREA limit of 1000mg/l for the discharge of wastewater into stream. High COD concentration observed in the wastewater might be due to the use of chemicals, which are organic that are oxygen demand in nature. The mean concentration of nitrate in the effluent is lower than the standards. The levels of nitrate may give rise to methemoglobinemia infants (Blue eye syndromes) and pregnant women [25] and when combined with phosphate can cause eutrophication. This would pose great problems for the users of the stream.

The level of chromium ions in the sample was low but exceeded the NESREA standards. Ingestion of chromium in low value is carcinogenic. When inhaled, hexavalent chromium can damage the lining of the nose and throat, and irritate the lungs as well as the gastrointestinal tract. Nasal irritation has been observed following acute exposure at levels less than 0.01mg/m^3. When swallowed, it can upset the stomach and damage the liver and kidneys.

Some people have an allergic skin reaction after touching material containing chromium. The direct use of water from this receiving river (Ogunpa) for domestic purposes without treatment could be detrimental to the users in the vicinity of the catchment.

3.2. Physical and Surface Chemistry of the Adsorbents

The result of the study showed a neutral pH which was found to be acceptable since that for most applications, carbon pH 6-8 is acceptable also for pH_{pzc} (pH at point of zero charge) [3,21]. The bulk density is important because activated carbon with high bulk density has ability to filter more liquor volume before available cake space is filled [8]. The prepared adsorbents have a low amount of ash content reduced the overall activity of activated carbon and the efficiency of reactivation (Table 2). The lower the ash value therefore the better the activated carbon. The values of porosity of the prepared adsorbents are almost the same when compared to commercial activated carbon. Porosity describes the number of pores present in a sample, hence, enhances adsorption capacity of the adsorbent.

Table 2. Characteristics of the prepared activated carbons

Parameters	BAC	LAC	PAC	SAC	CAC
Ph	6.5 ± 0.10^{a}	6.8 ± 0.10^{b}	7.0 ± 0.10^{c}	7.0 ± 0.10^{b}	6.8 ± 0.20^{c}
pH_{pzc}	6.6 ± 0.10^{a}	6.8 ± 0.20^{b}	7.0 ± 0.01^{c}	6.5 ± 0.11^{a}	7.1 ± 0.10^{c}
Ash (%)	$5.0\pm0.01^{b*}$	$5.0\pm0.01^{a*}$	$5.2\pm0.01^{c*}$	$6.2\pm0.01^{e*}$	5.4 ± 0.01^{d}
Bulk density (kg/m^3)	$0.8\pm0.00^{c*}$	0.7 ± 0.001^{a}	$0.8\pm0.01^{d*}$	$0.8\pm0.01^{b*}$	0.6 ± 0.01^{a}
Porosity (kg/m^3)	$0.7\pm0.01^{c*}$	$0.6\pm0.01^{a*}$	$0.6\pm0.01^{a*}$	$0.7\pm0.01^{b*}$	0.8 ± 0.01^{d}
Surface Area (m^2/g)	$486.1\pm0.01^{b*}$	$524.7\pm0.01^{c*}$	$625.6\pm0.01^{e*}$	$530.7\pm0.01^{d*}$	200.4 ± 0.01^{a}
Carboxylic	$0.1\pm0.01^{a*}$	0.1 ± 0.01^{b}	$0.1\pm0.01^{a*}$	0.1 ± 0.01^{b}	0.1 ± 0.01^{b}
Phenolic	$0.2\pm0.01^{b*}$	0.3 ± 0.01^{c}	$0.1\pm0.0^{a*}$	0.3 ± 0.01^{c}	0.3 ± 0.01^{c}
Lactones	0.6 ± 0.01^{c}	$0.5\pm0.01^{a*}$	0.6 ± 0.01^{b}	$0.6\pm0.01^{d*}$	0.6 ± 0.01^{b}
Acidic	$0.9\pm0.01^{b*}$	0.9 ± 0.01^{b}	$0.8\pm0.01^{a*}$	10.0 ± 0.01^{c}	10.0 ± 0.01^{c}
Basic	$0.5\pm0.01^{a*}$	$0.6\pm0.01^{c*}$	$0.6\pm0.01^{d*}$	$0.6\pm0.01^{c*}$	0.5 ± 0.01^{b}

All data were mean ± standard deviation of triplicate determinations

^{a,b,c,d,e} are means from least to the highest. Means of the same row with the same alphabet(s) are not significantly different.

Means within the same row with the different alphabet(s) are significantly different at $P<0.05$

* = The mean difference is significant at the 0.05level.

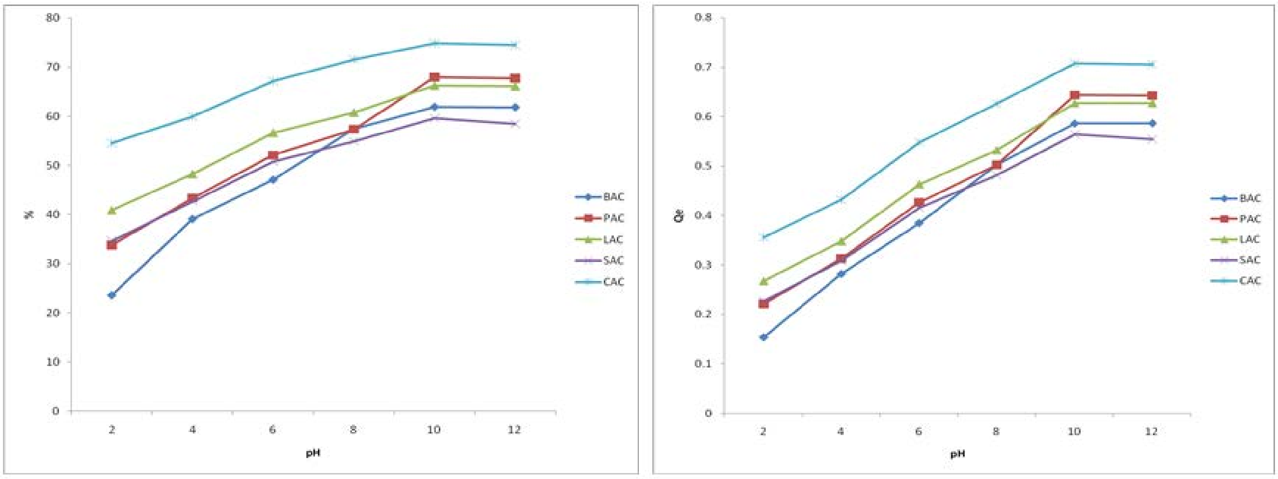
Iodine number is a measure of the micropores content of the activated carbon and is obtained by the adsorption of iodine from solution by the activated carbon sample. The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micropores that adsorption largely takes place. The surface chemistry of carbon materials is basically determined by the acidity and basicity of their surface. The type and concentration of surface functional groups of activated carbons was determined by the Boehm titration technique. Table 2 highlights the quantitative surface chemistry analyses of plantain wastes adsorbents consisting of the amount of acidic and basic functional groups. The pH at which the H^+ and OH^- were equal, known as the pH of zero charge (pH_{pzc}), was also determined. The acidic pH_{pzc} shown by the plantain wastes adsorbents is consistent with the Boehm titration result that presented dominance of this acidic group of the surface of the plantain. This is in accordance with Unuabonah *et al.*, [29] and Mahir *et al.*, [16] who observed the same trend on activated carbon from defatted *Carica papaya* seeds and fibre samples respectively. The surface titration method stipulates that only strongly acidic carboxylic groups are neutralized by sodium bicarbonates (Na_2HCO_3), whereas those neutralized by sodium carbonate (Na_2CO_3) are thought to be lactonic and carboxylic group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide (NaOH). Neutralization with hydrochloric acid (HCl) characterizes the amount of surface basic group (pyrones and chromenes) that are present in the activated carbon [12,27].

The carbon matrix does not consist of carbon atoms alone but is also formed by other heteroatom like hydrogen, oxygen, nitrogen, halogen, sulphur, phosphorus, etc. These heteroatoms bonded to the edges of the carbon layers, which govern the surface chemistry of activated carbon. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, etc., has been postulated as constituting the source of surface acidity. Whereas the basic properties of activated carbon is associated with two types of structures: (i) the presence of oxygen containing groups, i.e. pyrone, chromene and carbonyl structures, at the edge of carbon crystallite; and (ii) oxygen free Lewis basic site on the graphene layers.

3.3. Optimum Conditions Necessary for the Removal of Chromium (VI) ion by the Adsorbents

Effect of pH

pH, being an important controlling parameter in the adsorption process and thus the role of H^+ concentration was examined from samples at different pH covering a range of 2-12. The result showed that the percentage removal and adsorption capacity (Q_e) of Cr^{6+} increased at a steady rate as pH increased up to 10, attaining a maximum value of 68.02% and 0.64 respectively (Figure 1a & b). This may be as a result of increased overall negative charge on the surface of activated plantain wastes between pH 2 and 10. In addition, increasing pH decreases the concentration of H^+ therefore reducing the competition between metal ions and protons for adsorption sites on the particle surface. Another factor that could contribute to enhancing metal ion adsorption is the increasing pH which encourages metal ion precipitation from the solution in the form of hydroxides. The formation of soluble hydroxyl complexes causes the decrease in the adsorption which was observed after pH 10. At low pH, the surface of the adsorbent would be closely associated with hydroxonium ions (H_3O^-) by repulsive forces, to the surface functional groups, thereby lowering the percentage removal of metal [15]. It is possible that the lone pair of electrons (Lewis base) on some of the functional groups in defatted plantain waste adsorbents may have played a major role in the removal of the metal ions by (Lewis acid) defatted plantain waste adsorbents. It should be noted that the removal of Cr^{6+} from effluent by adsorbents involves a complex mechanism that is partly controlled by adsorption and partly chemical precipitation at the solid-effluent interface and the mechanism of its pore filling.



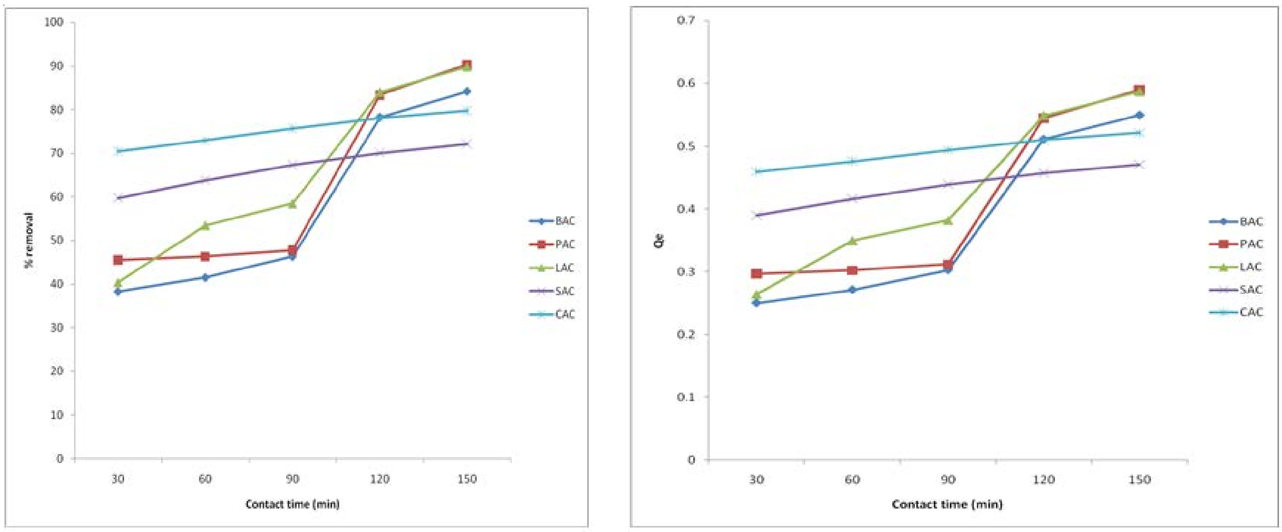
a b

Figure 1. Effect of pH on the percentage removal and adsorption capacity

It is possible that the lone pair of electrons (Lewis base) on some of the functional groups in defatted plantain waste adsorbents may have played a major role in the removal of the metal ions by (Lewis acid) defatted plantain waste adsorbents. It is therefore thought that there could have been the formation of inner sphere complexes between plantain waste adsorbent and metal ion. The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups. This replacement occurs after the removal of the outer hydration sphere of metal cations. In addition, the results obtained agreed with the findings of some researchers showing that the dependence of metal ion adsorption on wider range of pH [1,13].

Effect of contact time

Increasing the contact time correspondingly increase the percentage removal and adsorption capacity of activated plantain wastes. The percentage removal and adsorption capacity (q_e) of Cr^{6+} increased at a steady rate as contact time increased up to 150minutes, attaining a maximum value of 90.35% and 0.60 respectively (Figure 2a & b). The higher initial sorption rate may be due to an increased numbers of vacant adsorption sites available at initial stage of the adsorption process which result in an increased concentration gradient between the solute in solution and the solute on the adsorbent surface [28]. This increased concentration gradient tends to increase the rate at which Cr^{6+} is adsorbed at the initial stage of adsorption, since the adsorption kinetics depends on the surface area of the adsorbents. Similar observations were reported by Wang and Xing, [31] and Okareh and Adeolu, [20].

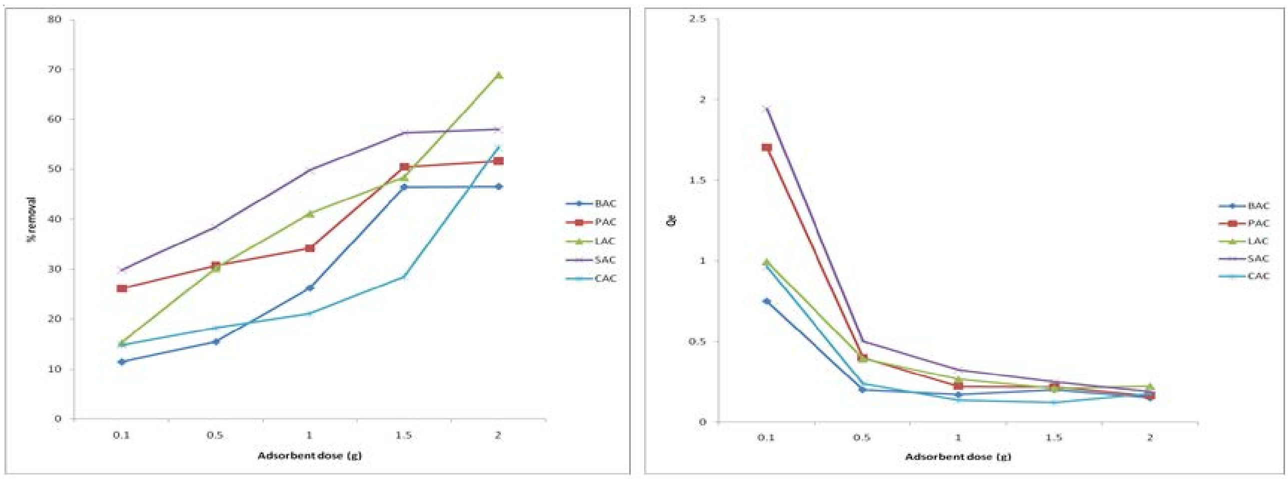


a b

Figure 2. Effect of contact time on the percentage removal and adsorption capacity

Effect of adsorbent dose

Increasing bio-sorbent dosage decreased the amount of chromium ions absorbed. However, the percentage of metal ion adsorbed was observed to follow the reverse trend. The percentage removal of Cr^{6+} increased at a steady rate as adsorbent dose increased up to about 2.0g for Cr^{6+}, attaining a maximum value of 68.91% while the adsorption capacity (q_e) decreased at corresponding increase in adsorbent dose, attaining a minimum value of 0.25 (Figure 3a & b). Similar trend has been observed by Ho *et al*, [11], Adebowale *et al*., [2], Okareh and Adeolu, [20]. It should be noted that after a certain dose of adsorbent, the maximum adsorption set in and hence the amount of ions bounds to the adsorbent and the amount of free ions remain constant (equilibrium) even with further addition of the dose of adsorbent except LAC and CAC. The increased percentage adsorption by adsorbent was as a result of increased surface area and increased adsorption site occasioned by increased adsorbent dose. However, the observed decrease in adsorption capacity may be due to decrease in liquid–solid ratio which directly resulted in this trend since amount adsorbed, qe, has an inversely proportional to the weight of biosorbent, but directly proportional to the percentage adsorbed [29]. This could also due to increase in surface negative charge, as well as a decrease in the electrostatic potential near the solid surface.



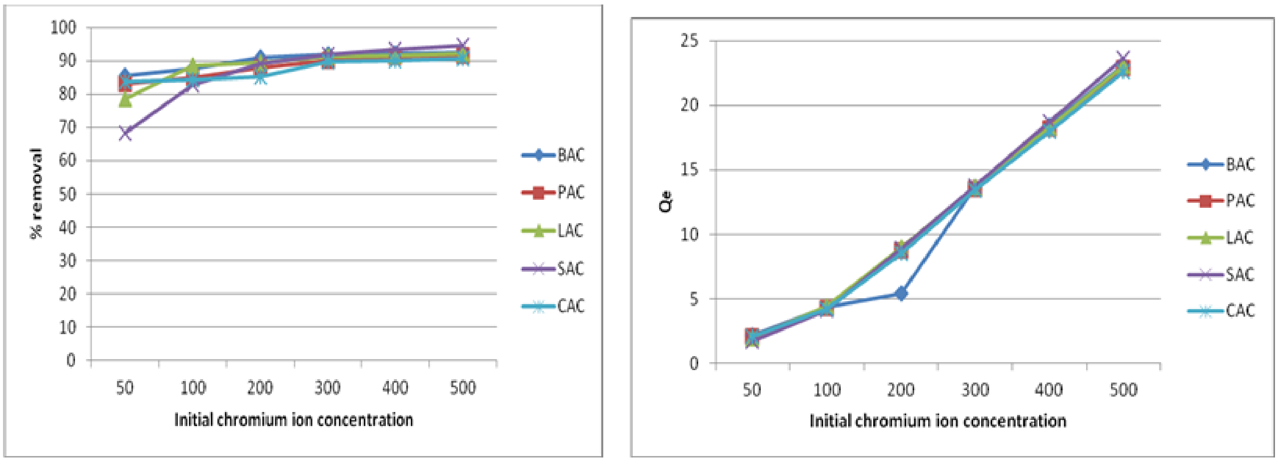
a

b

Figure 3. Effect of adsorbent dose on the percentage removal and adsorption capacity

Effect of initial metal ion concentration

The percentage removal and adsorption capacity (q_e) of Cr^{6+} increased at a steady rate as initial concentration increased up to 500mg/L, attaining a maximum value of 94.49% and 23.62 respectively as shown in Figure 4a and 4b. With increasing metal ion concentration, there is increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on the defatted plantain waste adsorbents [2].



a

b

Figure 4. Effect of initial chromium ion concentration on the percentage removal and adsorption capacity

Adsorption isotherms

All the adsorbents showed satisfactory fits to both models except LAC and SAC which showed poor fit to Langmuir isotherm (Table 3). From the correlation coefficient (r^2), there is strong indication that the adsorption data obtained fits both the Freundlich and Langmuir models. PAC has potential for removing the chromium from effluent generated from battery recycling plant with highest adsorption capacity.

Table 3. Adsorption isotherm constants and coefficient of determination (r^2) of adsorbent

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants		
	Q^o (mgg^{-1})	b (Lg^{-1})	r^2	k (Lg^{-1})	1/n	r^2
BAC	16.1031	0.0163	0.9879^*	9,8673	0.6710	0.9719^*
PAC	12.8866	0.0165	0.9992^*	13.9766	0.6506	0.9920^*
LAC	8.4317	0.0220	0.8024	18.5225	0.6012	0.9400
SAC	1.5903	0.0366	0.82.15	51416.20	0.2367	0.9604^*
CAC	18.9036	0.0122	0.9917^*	9.2939	0.7280	0.9713^*

*= Fit at r^2 (>95%).

The value of R_L for each adsorbent obtained were found to be less than 1 and decreased with increasing initial concentration of Cr^{6+} (Figure 5). This confirmed that the adsorption of Cr^{6+} into plantain waste adsorbents is favourable for higher initial ion concentrations with respect to lower ones. The values of 1/n were also found to be less than 1; again that the adsorption is favourable.

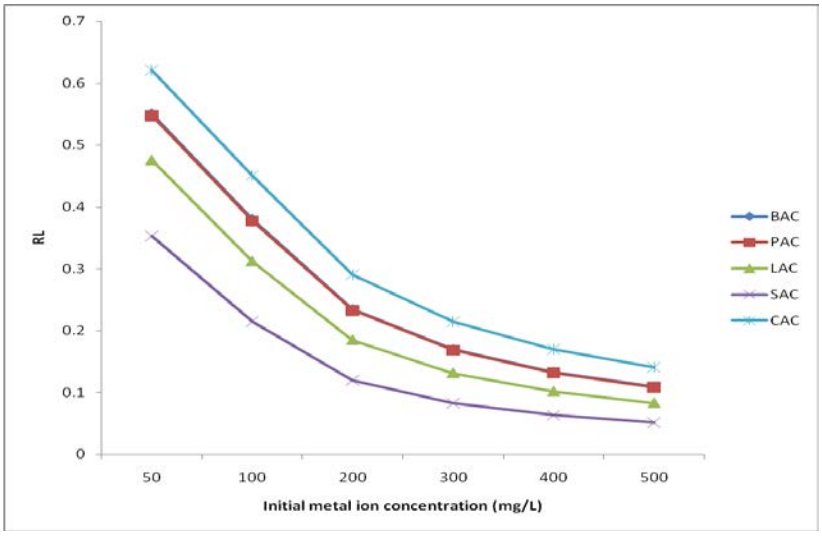


Figure 5. Separation factor ($R_{L)}$ of initial chromium ion concentration for plantain waste adsorbent

4. Conclusion

Plantain wastes have been successfully used to produce high quality activated carbon because of its inherent high densities and carbon content. From the analysis of the result, it is evident that the plantain wastes, processed into activated carbon have great potential for the uptake of chromium (VI) ions from the industrial effluent which depends on the operating conditions such as pH, initial metal ion concentration, adsorbent dose and contact time. Modeling data obtained from isotherms indicated that very good fits were produced with the Langmuir and Freundlich at high chromium ion concentration. This implies that the sites on plantain wastes adsorbents available for the adsorption of high concentrations of Cr^{6+} may be either homogenous or heterogeneous in nature. Therefore, the plantain wastes adsorbents have the potential of adsorbing heavy metal ions from industrial effluent and it offers an application in the treatment of heavy metals in situ.

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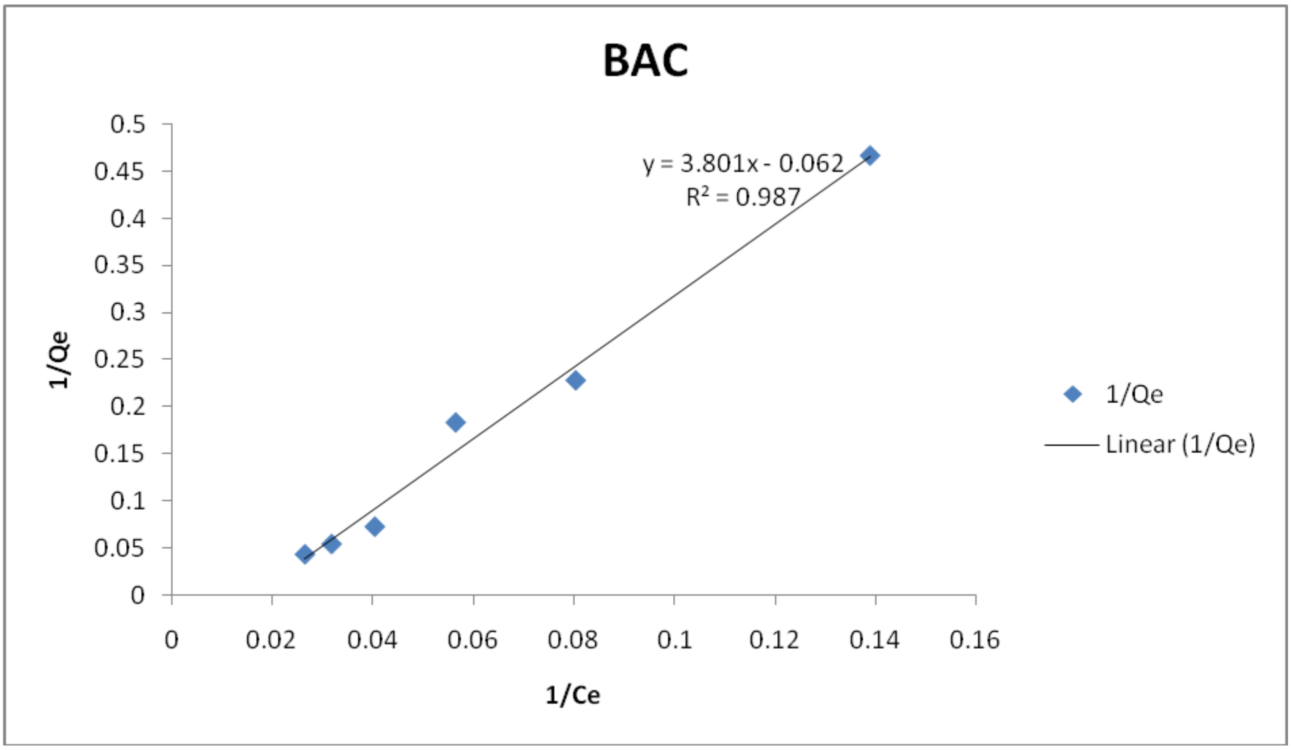
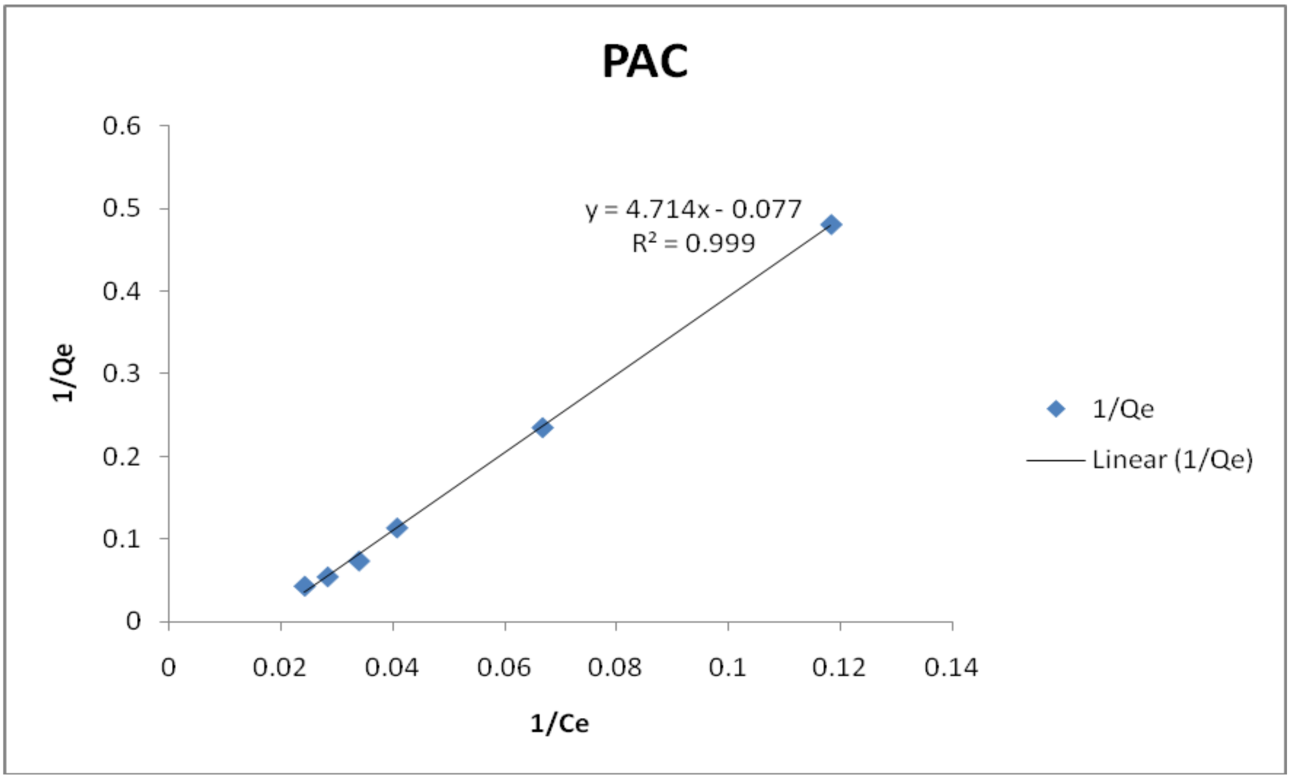
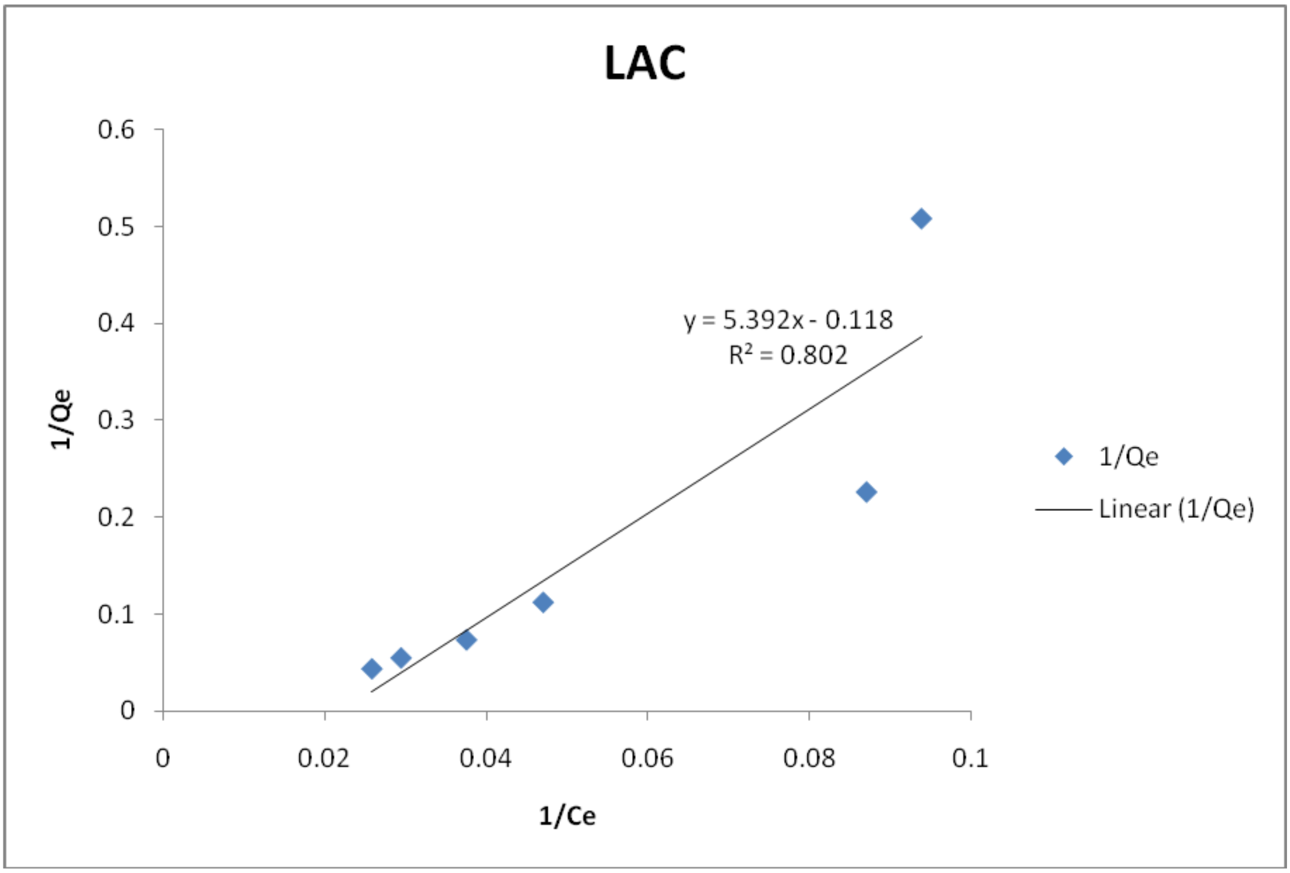
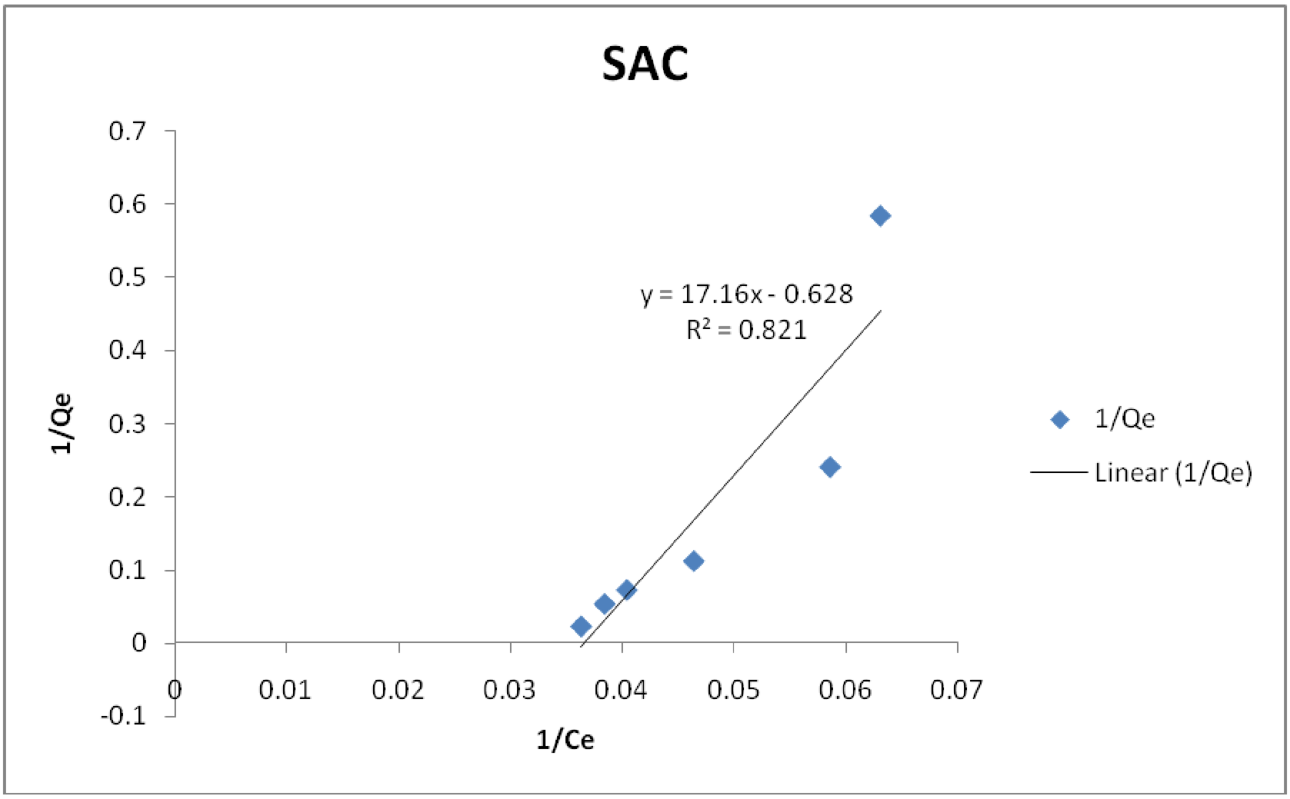
Appendixes

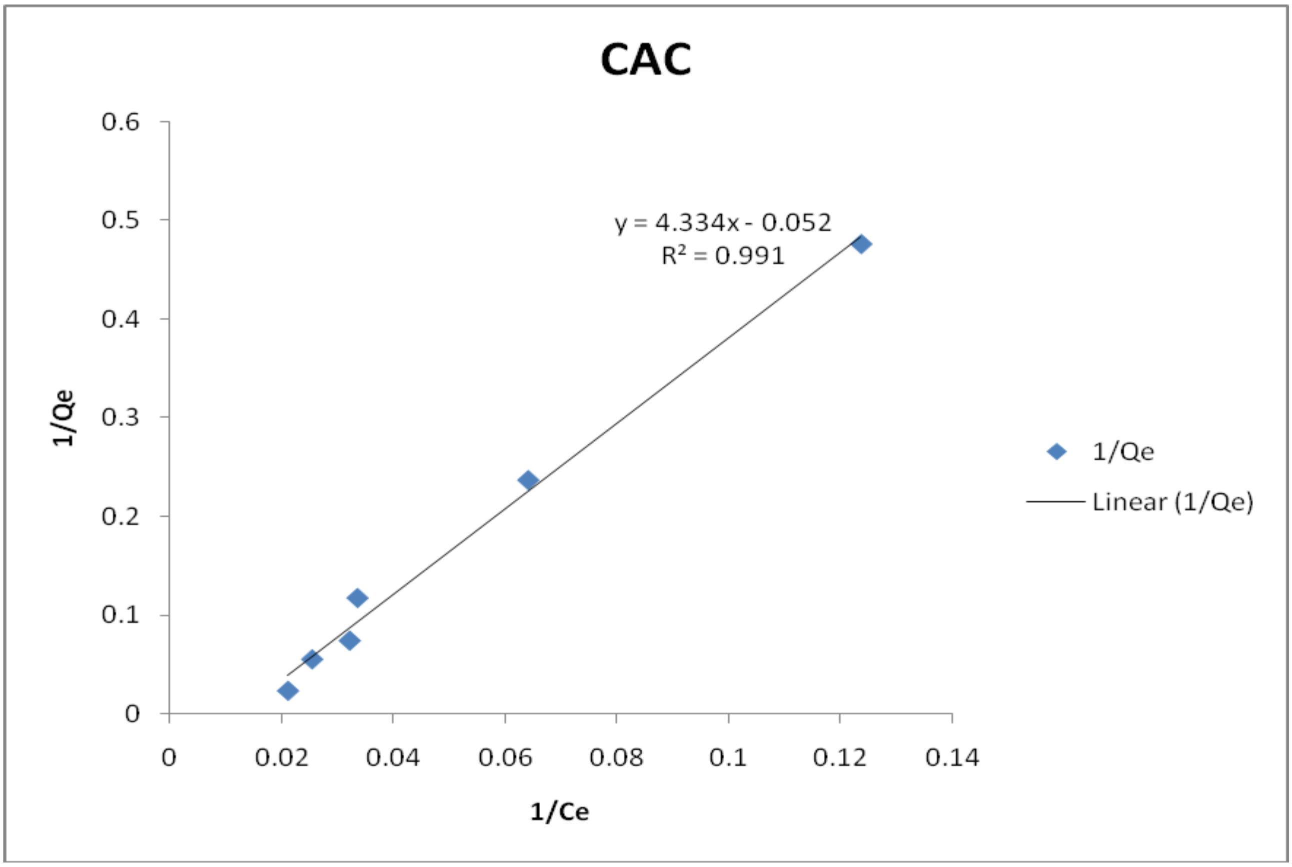
Plot of Langmuir model for adsorbents for chromium



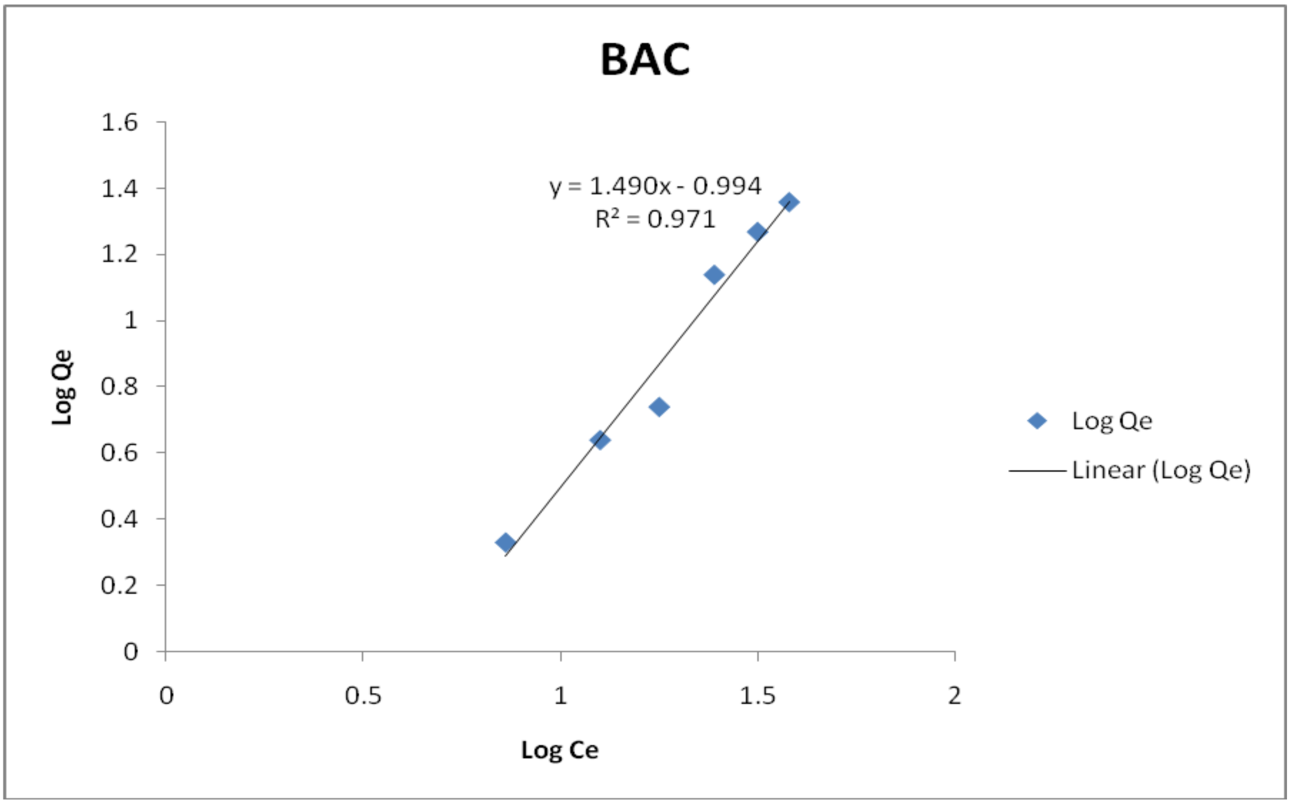

PAC
y = 4.714x - 0.077
R² = 0.999
1/Qe
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
1/Ce
1/Qe
Linear (1/Qe)

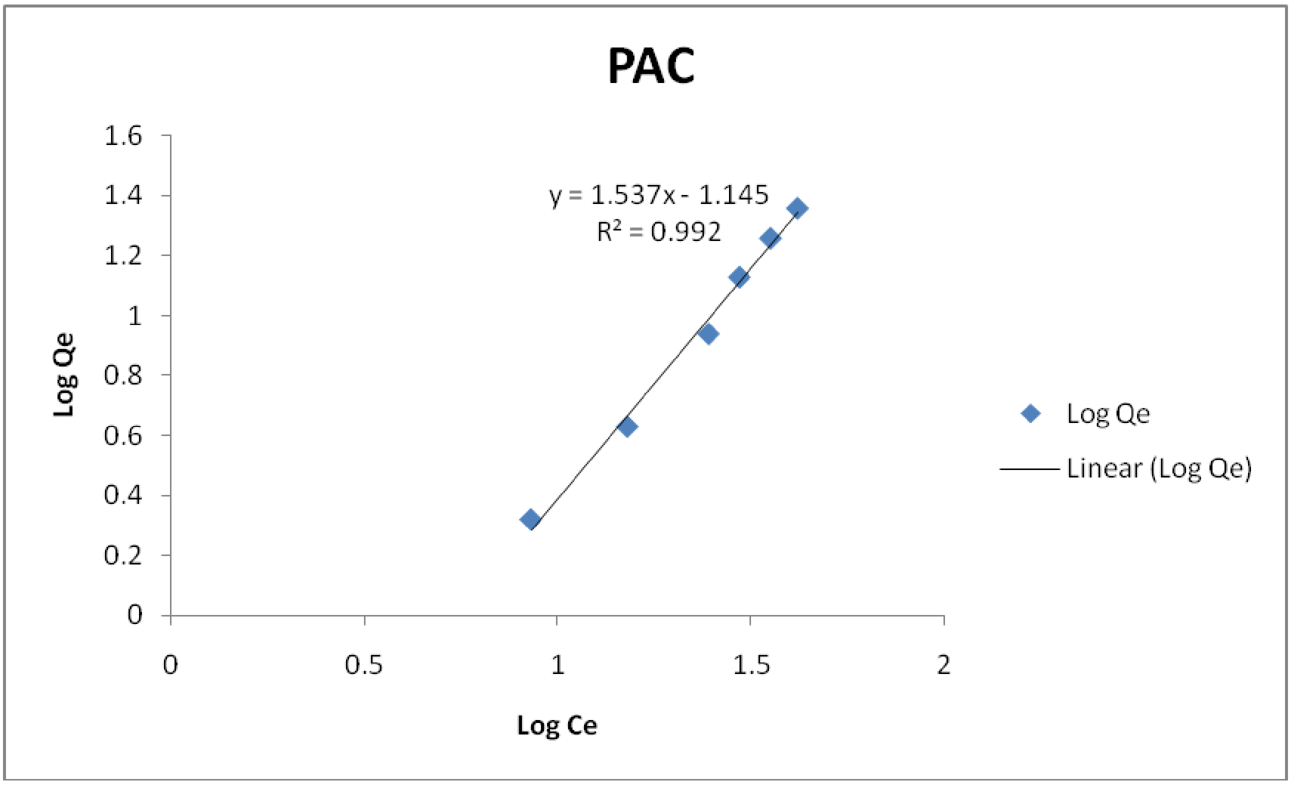

LAC
y = 5.392x - 0.118
R² = 0.802
1/Qe
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.02
0.04
0.06
0.08
0.1
1/Ce
1/Qe
Linear (1/Qe)

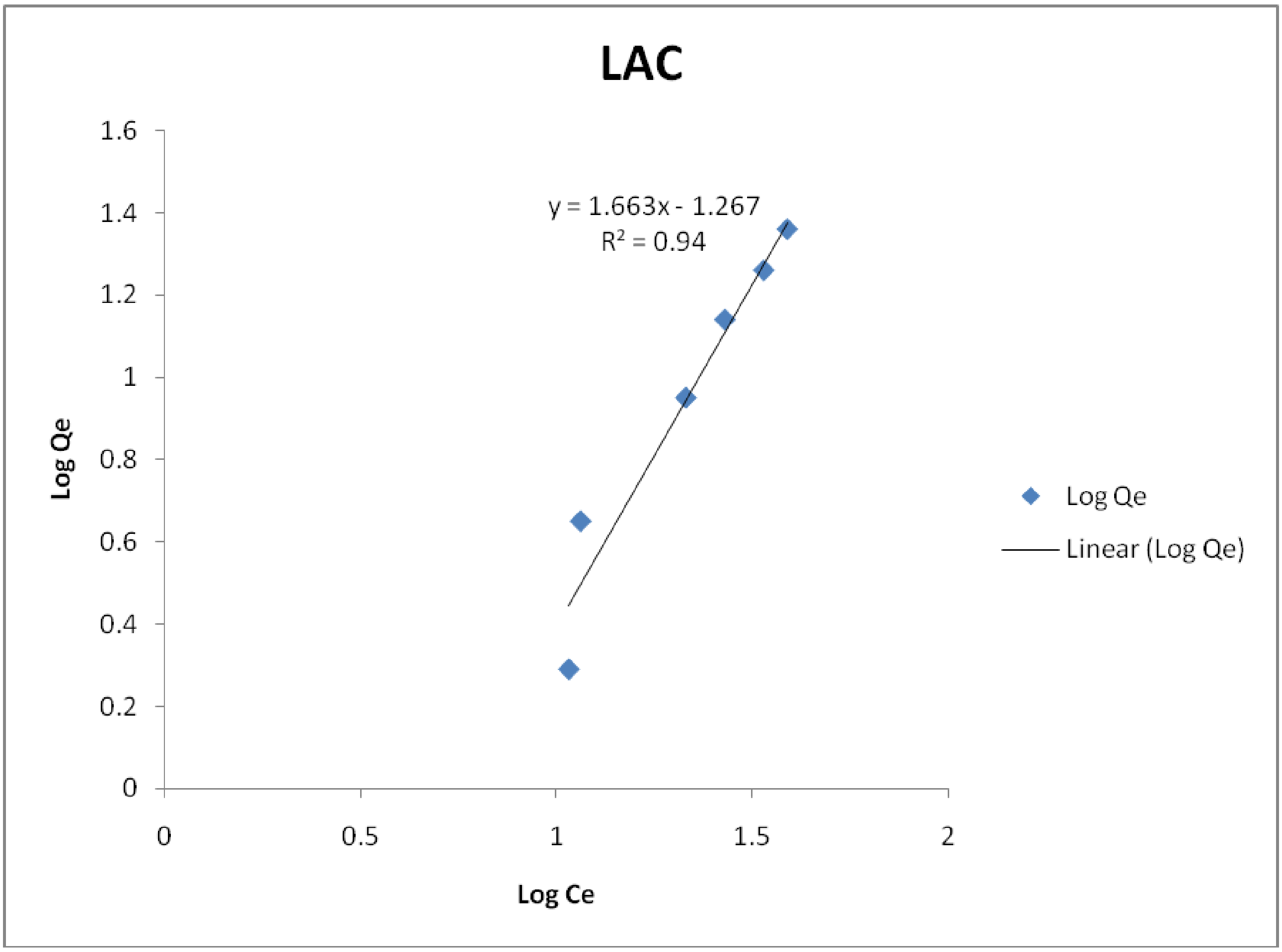

SAC
y = 17.16x - 0.628
R² = 0.821
1/Qe
1/Ce
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
◆ 1/Qe
Linear (1/Qe)

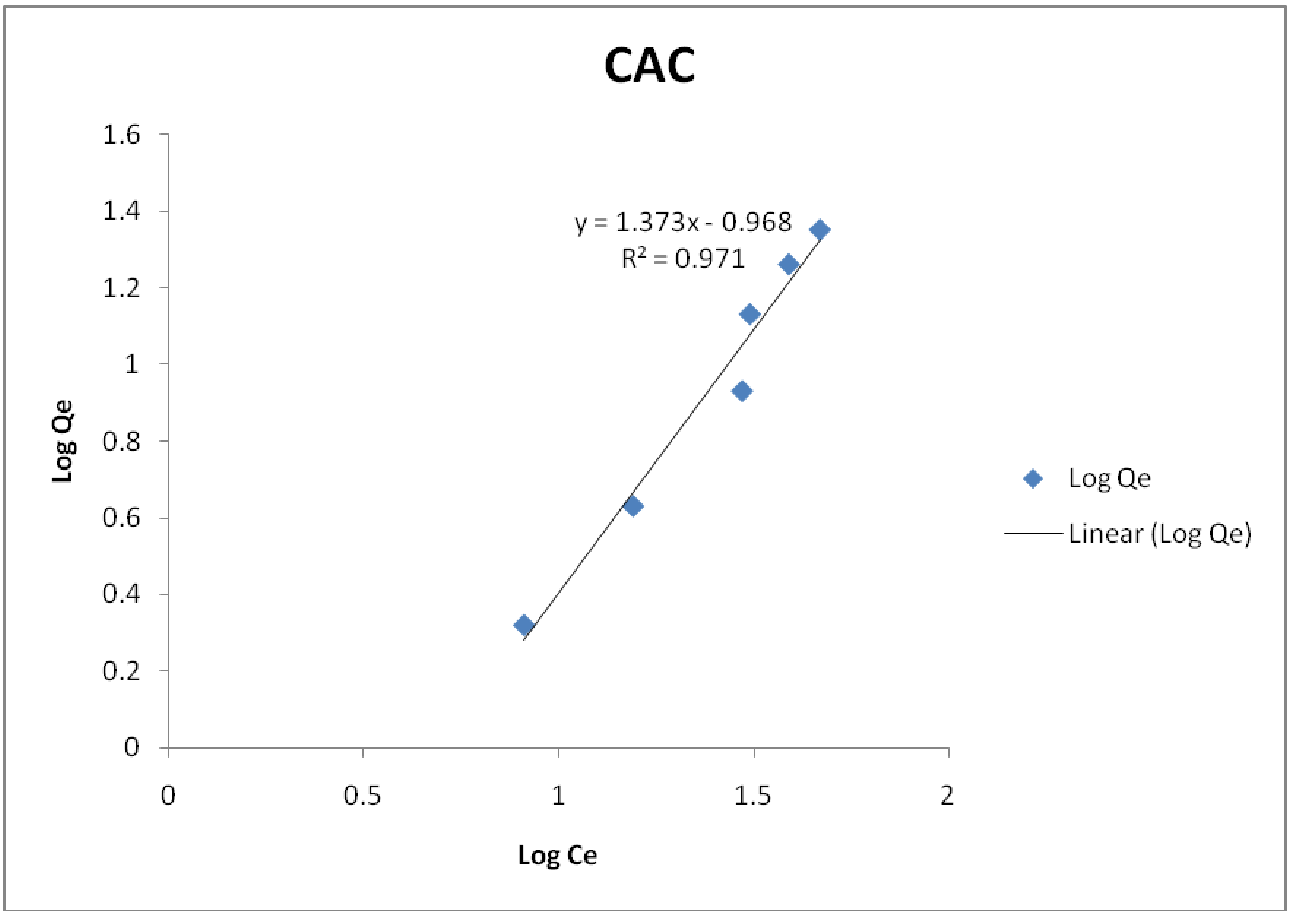

CAC
y = 4.334x - 0.052
R² = 0.991
1/Qe
1/Ce
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
◆ 1/Qe
Linear (1/Qe)

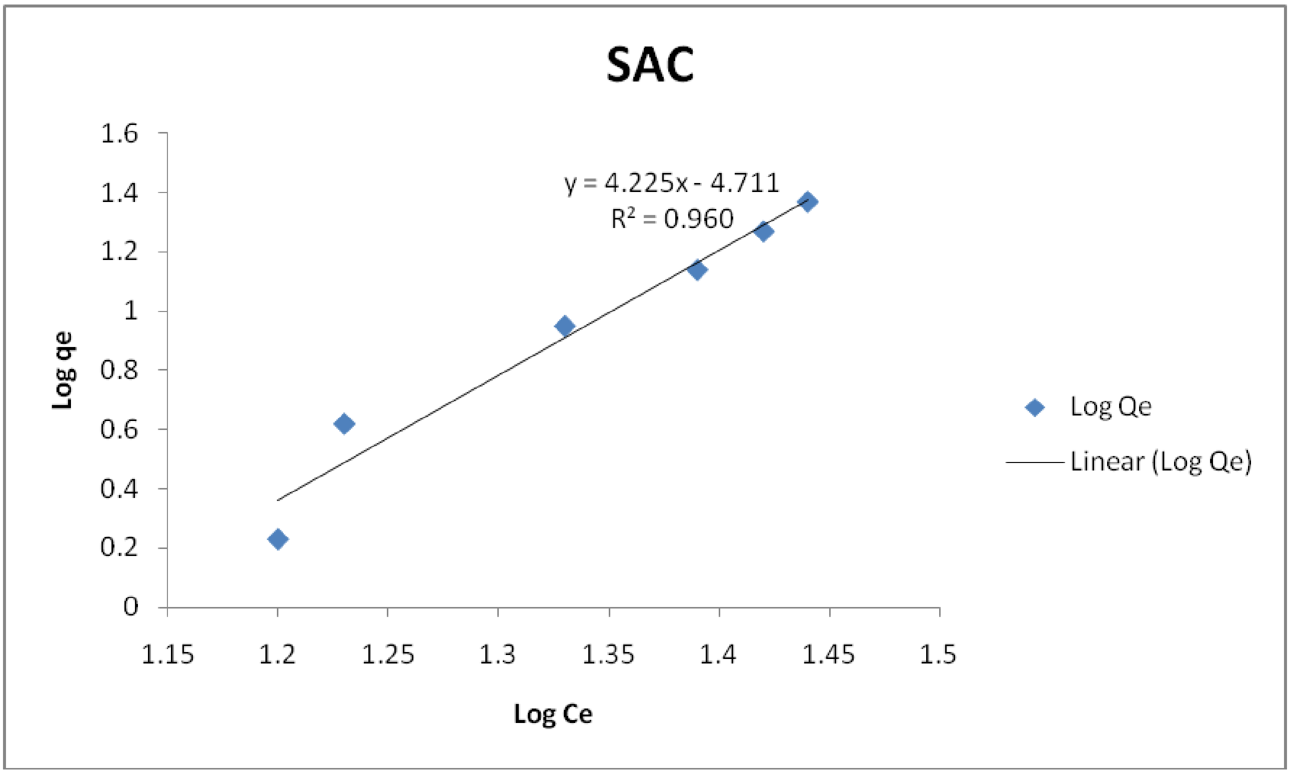
Plot of Freundlich model for chromium






LAC
y = 1.663x - 1.267
R² = 0.94
Log Qe
Log Ce
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
◆ Log Qe
Linear (Log Qe)


CAC
y = 1.373x - 0.968
R² = 0.971
Log Qe
Log Ce
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
◆ Log Qe
Linear (Log Qe)


SAC
y = 4.225x - 4.711
R² = 0.960
Log qe
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1.15
1.2
1.25
1.3
1.35
1.4
1.45
1.5
Log Ce
Log Qe
Linear (Log Qe)