Research Article

The Adsorption Kinetics and Thermodynamics Study of some Metal Ions (Cr^{+6}, Pb^{+2}, and Co^{+2}) on to Activated Carbon derived from Lemon Peel (*Citrus limonum*)

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Abstract The adsorption, kinetics, and thermodynamics of some metal ions (Cr^{+6}, Pb^{+2}, and Co^{+2}) on to activated carbon derived from lemon peel (*Citrus limonum*) was studied. Energy dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition of the adsorbents while Scanning Electron Microscope (SEM) was used for surface texture and morphological characteristics of the lemon peel. The optimal parameters such as initial concentration, agitation time and adsorbent particle size was studied by using Atomic Absorption Spectroscopy (ASS). And removal efficiencies were calculated. Freundlinch and Langmuir adsorption models were employed to study adsorption pattern. The equilibrium data results of metal ions were fitted well to Freundlinch and Langmuir adsorption models. Coefficient of correlation (R^2) for Freundlinch and Langmuir adsorption models was fallen within $0<R^2<1$. The values of Gibbs were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The positive values of Enthalpy, indicating the endothermic nature of the biosorption Cr^{+6}, Pb^{+2}, and Co^{+2} onto Lemon peel. The positive values of entropy, shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process. The study was concluded that activated carbon derived from lemon peel, have potential as an adsorbent to remove toxic heavy metals like, (Cr^{+6}, Pb^{+2}, and Co^{+2}) from waste water.

Keywords *Citrus limonum,* Cromium, Lead, Cobalt, Adsorption Kinetics, Thermodynamics

Introduction

Environmental pollution by heavy metals due to industrial activities tends to persist indefinitely circulating and eventually accumulating through the food chain which results in serious ecological and health hazard [1]. Heavy metals are not hazardous at lower concentration however, at higher concentration they can bio-accumulate and enter into human being through the food chain and can cause several health problems. Depending on the nature and quantity of the metal ingested, heavy metals toxicity is related to the formation of complexes with proteins, in which carboxylic acid (COOH), amine ($-NH_2$), and thiol ($-SH$) group are involved. When metal binds to these complexes, important enzymes and protein structures are affected [2]. Among these heavy metals Cr^{+6}, Pb^{+2}, and Co^{+2} was found to be most toxic in the environment. It has been reported that hexavalent chromium is most toxic than trivalent

chromium and widely recognized as carcinogen. Lead can cause anemia and brain disorder and finally lead to death of human being. Cobalt is toxic to the heart muscle. It can cause heart muscle disease (toxic cardiomyopathy) after too much exposure. Lead is present at about 20ppm in the earth's crust and the medium of its transport in the air are fine particulates (4um diameter). Chromium occurs in nature mostly as chrome iron ore. Its concentration in the earth's crust is about 60ppb. Cobalt is found in the Earth's crust only in chemically combined form, save for small deposits found in alloys of natural meteoric iron. The free element, produced by reductive smelting, is hard, lustrous, silver-gray metal. The permissible limits of Cr^{+6}, Pb^{+2}, and Co^{+2} have been recommended in drinking water is 0.005 mg/l [3].

Therefore, researchers have developed various methods such as chemical precipitation, coagulation, adsorption, ion exchange and membrane filtration for removal of heavy metals from waste water [4]. The limitations associated with these methods are high operational cost, sludge production and they differ in their effectiveness, especially when metals are present in solution at very low concentrations of all treatment methods mentioned above, adsorption had been reported as an efficient method for the removal of heavy metals from aqueous solution because of their effectiveness even at low concentration [5].

The origin of the lemon is unknown, though lemons are thought to have first grown in Assam (a region in northeast India), northern Burma or China. A genomic study of the lemon indicated it was a hybrid between bitter orange (sour orange) and citron. Lemon entered Europe near southern Italy no letter than the second century AD, during the time of ancient Rome. However, they were not widely cultivated. They were later introduced to Persia and then to Iraq and Egypt around 700AD. Lemons are rich source of vitamin C, providing 64% of the daily value in a 100g serving. Other essential nutrient, however, have insignificant content. Lemons contain numerous phytochemicals, including polyphenols, terpenes, and tannins. Lemon juice contain slightly more citric acid than lime juice (about 47g/l), nearly twice the citric acid of grapefruit juice, and about five times the amount of citric acid found in orange juice. Lemon juice, ring, and peel are used in a wide variety of foods and drinks. The whole lemon is used to make marmalade, lemon curd and lemon liqueur. Lemon slices and lemon ring are used as a garnish for food and drinks [6].

Adsorption is the adhesion of atoms, ions, or molecules from a gas liquid, or dissolved solid to a surface. Adsorption is one of the physicochemical treatment processes found to be effecting in removal of heavy metals from aqueous solutions. The emerging process of bio-sorption uses nonviable or viable biological materials to bind contaminants via physicochemical mechanisms, whereby factors like pH, size of bio-sorbent, ionic strength and temperature influence metal bio-sorbent, plant wastes are inexpensive as they have no or very low economic value and most of the adsorption studies have been focused on untreated plan wastes [7].

In this research, the adsorption kinetics and thermodynamics of some metal ions (Cr^{+6}, Pb^{+2}, and Co^{+2}) on to activated carbon derived from lemon peel (*citrus limonum*) was studied.

2. Materials and Methods

2.1 Sample collection

Lemon peel was collected from a lemon tree in G.R.A Gashua, Yobe state Nigeria. The lemon peel was removed from the collected lemon, and then was sun dried, cut, ground and sieved to three particle sizes of 150, 212 and 300 μm. Commercial activated carbon (GAC F-300) produced by Boncaki Nigeria Limited was purchased. Synthetic wastewater was employed for the adsorption studies. 500 mg/L each of stock solution of analytical grade, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $Co(Cl_2)$ was prepared by dissolving exact quantity of the salts in deionize solution.

2.2 Preparation of lemon peel char

The char of the lemon peel was prepared using the modified methods of Amuda and Edewor [8]. About 15g of lemon peel powder was placed in a crucible, and put into a furnace. The furnace temperature was increased at a rate of 10°C/min from room temperature to 500°C in a nitrogen environment to ensure nitrogen free environment and the temperature was held at this temperature for 2h, after, then was washed with distilled water to remove any leachable impurities due to free acid and adherent powder.

2.3 Adsorbent characterization

The elemental composition of the prepared lemon peel was determined using Energy Dispersive X-ray Micro Analysis (EDX) while Scanning Electron Microscope (SEM) (High resolution SEM EVO MA 10 carlZeiss) was used to study the surface morphological characteristics.

2.4 Activation of lemon peel char

The char samples was treated with 2% H_2SO_4 in an incubator for 24h at a temperature of 110°C. The treated char sample was first soaked in deionized water until the pH was stabilized and thereafter soaked in 2% $NaHCO_3$to remove the residual acid. This acid treated lemon peel carbon was dried overnight in an oven at 110°C, and was stored in desiccators for further use [9].

2.5 Adsorption studies

The method used is as described by Ameh and Odoh [10]. Experiments was conducted in 5 different 250 ml Conical flasks containing 100 ml varied concentration (5, 10, 15, 20 and 25 mg/L) of Cr^{+6} solutions and then, used150 μm lemon peel with dosage of 1.5 g was added to the different flasks. Flask was agitated on a shaker at 400 osc/m constant shaking. The mixture was filtered using Whatman no.1 filter paper, after 30 min, and the filterate was analysed using Atomic Absorption Spectroscopy (AAS). The adsorption procedure was repeated using different adsorbents (150, 212 and 300 μm) sizes of unmodified lemon peel, modified lemon peel and activated carbon), dosages (0.5, 1.0, 1.5, 2.0 and 2.5 g) and different adsorbent, contact period (30, 60, 90, 120 and 150 min) in turns. Triplicate analyses was carried out for each adsorption. Batch adsorption studies for varied concentration of Pb^{2+} and Co^{2+} was also carried out. Adsorbent on Cr^{+6}, Pb^{+2}, and Co^{+2} was calculated as follows:

$$A(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

(2.1)

Where C_o and $C_f$are the initial and final concentrations of Cr^{+6} and Pb^{+2} (mg/L), respectively.

2.6 Data Evaluation

The amount of metal bound by the adsorbent was calculated as follows:

$$Q_e = V\frac{C_0 - C_e}{m}$$

(2.2)

Where Q_e is the metal uptake (mg metal per g adsorbent), v is the volume of solution containing the metal (ml), C_o is the initial concentration of the metal in the solution (mg/L), C_f is the final (equilibrium) concentration of the metal in the filtrate (mg/L) and m is the amount of the added adsorbent on the dry basis (g) [9].

3. Result and Discussion

3.1 Sample characterization

The result obtained from the EDX study is as presented in Figure 1 and Table 1. The results revealed the presence of C, K, Ca, Mg, Al, Si, O, P and Cl in the adsorbent. The presence of the element mentioned above had been reported to enhance adsorption of metals through ions exchange, chelation coordination, and complexation reactions [1, 11]. Elements such as Al, K, Ca and Mg could exchange for the heavy metals while element like P, O, Si could prompt chalation, coordination and complexation [1]. The Scanning electron micrograph study revealed that the surface texture and morphological characteristic of the adsorbent (Lemon Peel char). The SEM image obtained for the adsorbent and presented in figure 2 reveals the porous structure of the lemon peel char. The porosity and agglomeration of lemon peel char particles enhanced metal uptake and encourage mass transportation of heavy metals through the inside of the sorbent [2].
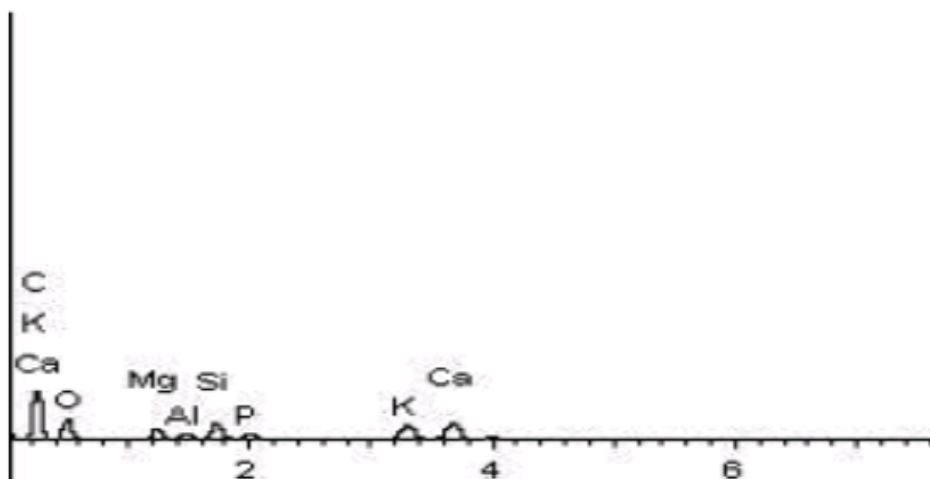
Figure 1: The Energy Dispersive X-ray spectroscopy EDX Lemon Peel Char

Table 1: The Energy Dispersive X-ray spectroscopy (EDX)

Element	Lemon Peel	
	Weight %	**Atomic %**
C	42.04	54.13
O	37.95	36.69
Mg	2.47	1.57
AI	1.07	0.61
Si	3.36	1.85
P	1.25	0.62
K	4.71	1.86
Ca	6.32	2.44
Fe	0.82	0.23
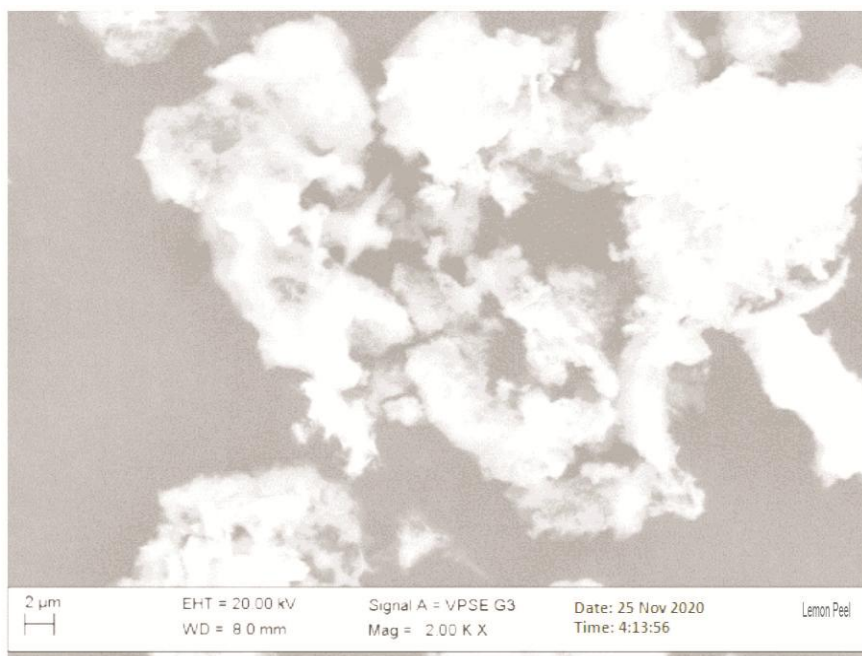
Figure 2: SEM Image of Lemon Peel Char

3.2 Effect of initial concentration

Figures 3(a), 3(b) and 3(c) show the effect of Initial metal ion concentration on the removal efficiency exhibited by the adsorbents with increase in metal ion concentration. From these Figures, commercial activated carbon show an outstanding removal efficiency over modified and unmodified lemon peel char. In Figure 3(a), 3(b) and 3(c) the removal efficiency of unmodified lemon peel char increased as the metal ion concentration increases while the removal efficiency of the modified and commercial adsorbent initially increased as metal ion concentration increased from 5 to 25 mg/L and later increased as metal ion concentration increased. The removal efficiency of both modified unmodified and commercial adsorbent increase as initial metal ion concentration increases. The increase in removal efficiency as metal ion concentration increases may be as a result of competition for the available binding site on the adsorbent by the metal ion as the concentration increases. Also, the initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase [1]. The results show that feasibility and efficiency of adsorption process depends not only on the properties of the adsorbents, but also on the concentration of the metal ion solution. It was observed that the removal efficiency of the modified lemon peel char was higher compared to the unmodified adsorbents (Figures 3(a), 3(b) and 3(c)). This may be due to the fact that modification increases the available active binding sites for metals thereby enhancing the performance of the adsorbent [8, 12]. Development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. Among these low cost adsorbents, Lemon has the high sorption capacity for several metal ions [8]. In addition, removal efficiency of Cr^{+6} Pb^{+2} Co^{+2} with the modified lemon peel char is relatively close to that of activated carbon (Figure 3(a), 3(b) and 3(c)).
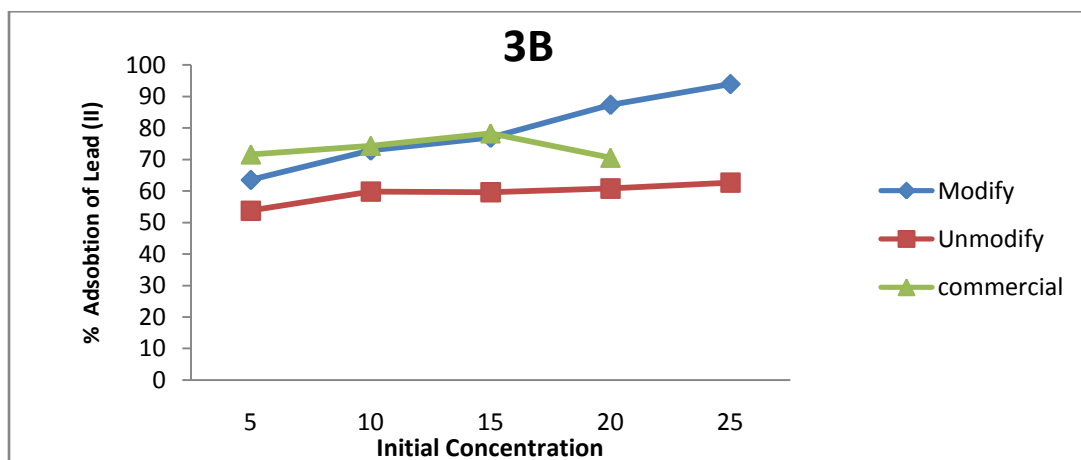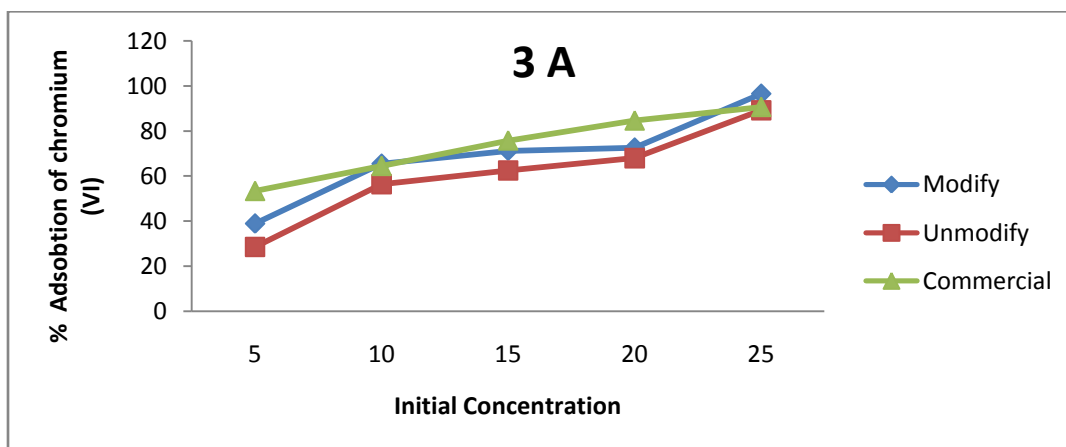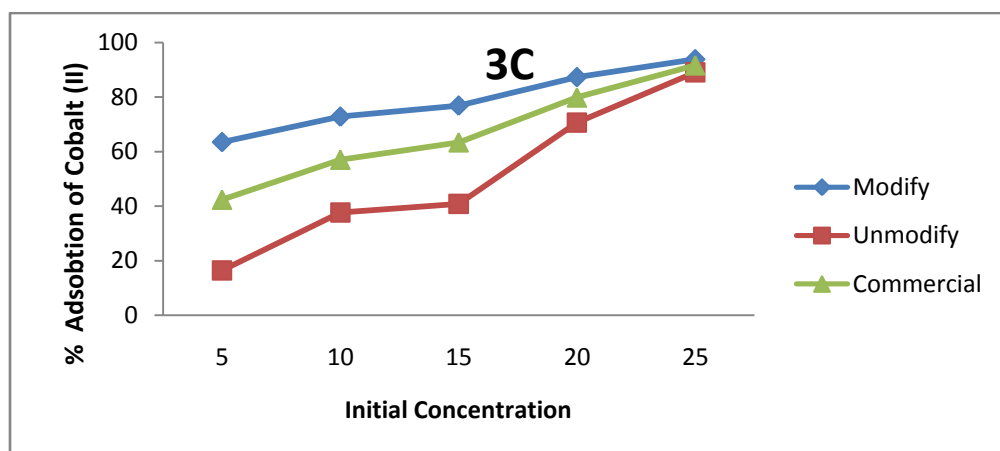
Figure 3a, 3b, 3c: Effect of Initial Concentration on Cr, Pb, Co ions biosorption respectively by activated carbon, derived from lemon peel, biosorbent dosage 5g, Particle size 150mm, agitation type 30mins, Temperature 300⁰C.

3.3 Effect of particle size

The results of the effects of particle size on the removal efficiencies of Cr^{6+}, Pb^{2+} and Co^{2+} is presented in Figure 4(a), 4(b) and (c). The particle sizes used were 150, 212 and 300 μm, respectively. Other parameters such as adsorbent dose, initial ion concentration and agitation time were kept constant; temperature and agitation speed were kept at 25°C and 400 osc/min, respectively. The removal efficiency of Cr^{6+}, Pb^{2+} and Co^{2+} by modified, unmodify decreased as particle size increased while for the unmodified lemon peel char, 300 μm particle size show higher efficiency than 212 μm. This increased efficiency as particle size decreased may be due to the fact that smaller particles give large surface areas. Sometimes, larger particle size can show higher removal efficiency over smaller particle if the particles are spherical in shape. Larger particles with spherical shape, in general, present higher external mass transfer than small particle size which therefore responsible for the higher removal efficiency [3, 13].
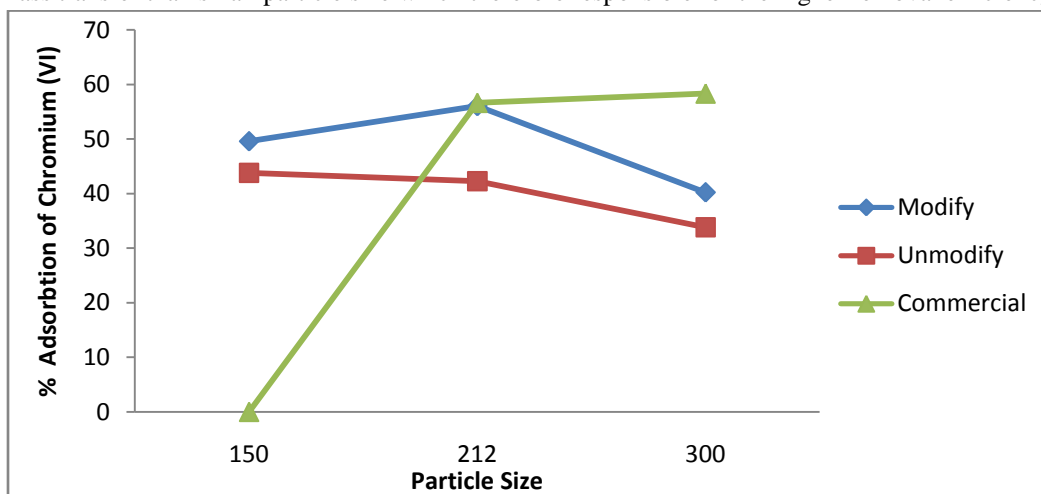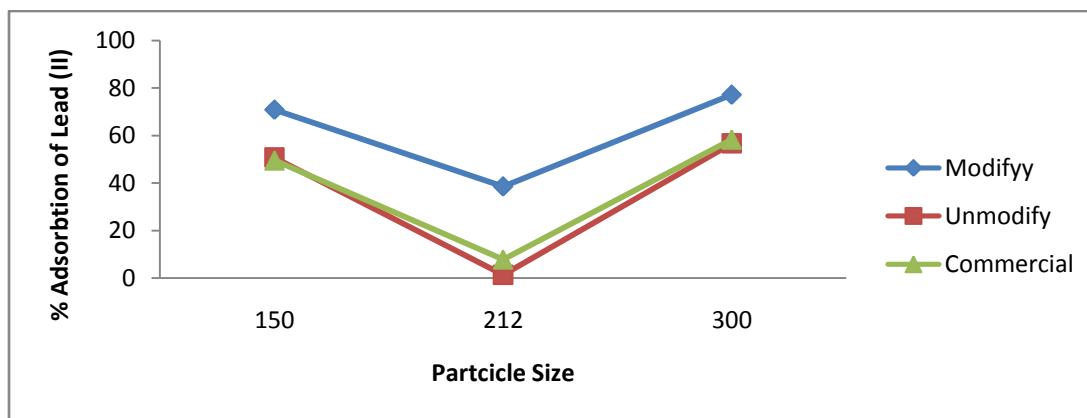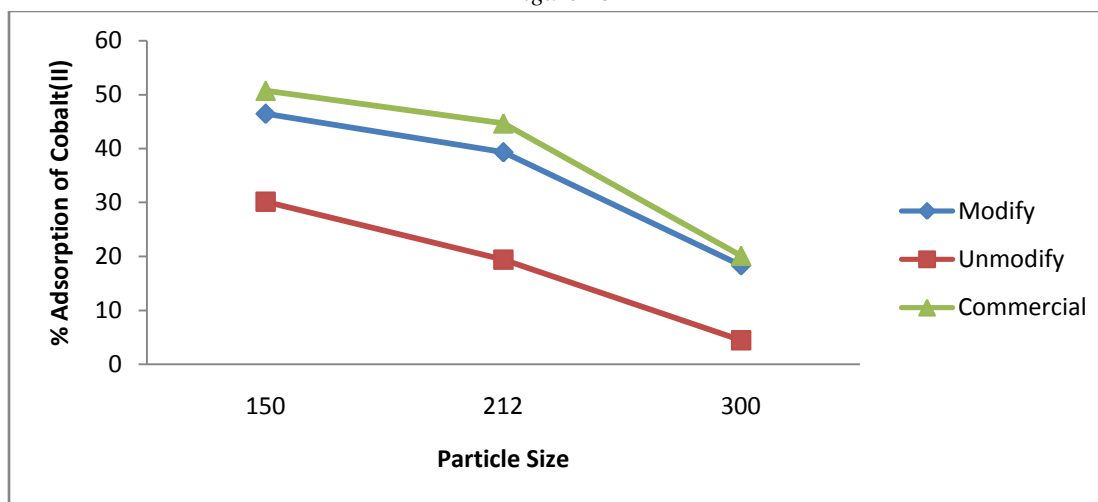

Figure 4a.

Figure 4b

Figure 4c

Figure 4a, 4b, 4c: Effect of Initial Particle size on Cr, Pb, Co ions biosorption by activated carbon, derived from lemon peel, biosorbent dosage 1.5g, Initial concentration 20mg/L, agitation type 30mins, Temperature 300^0C.

3.4 Effect of agitation time

As shown in Figure 5(a), 5(b) and 5(c), the removal efficiency of Cr^{6+}, Pb^{2+} and Co^{2+} by unmodified lemon peel char increases with adsorbent contact time from 30 to 90 min. However, it decrease within the adsorbent contact time of 120 and later increase within the adsorbent contact time of 150 min, these results showed that initially the number of vacant sites was large which later reduced as the vacant active site is been saturated [14]. Also, the fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of available binding sites on the adsorbent surface at the beginning while the decrease in efficiency may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbents [15-16].
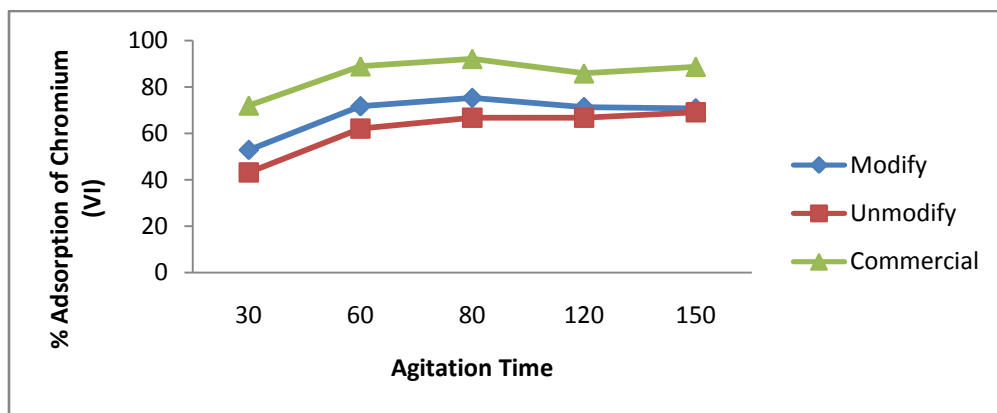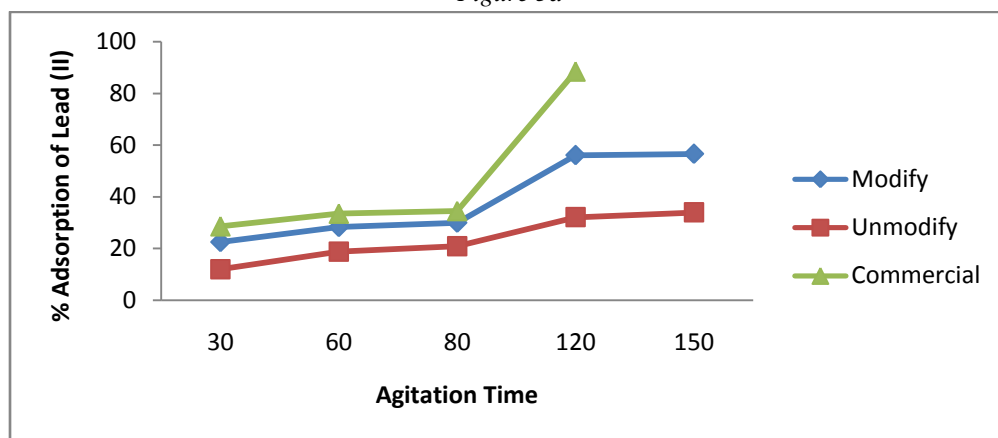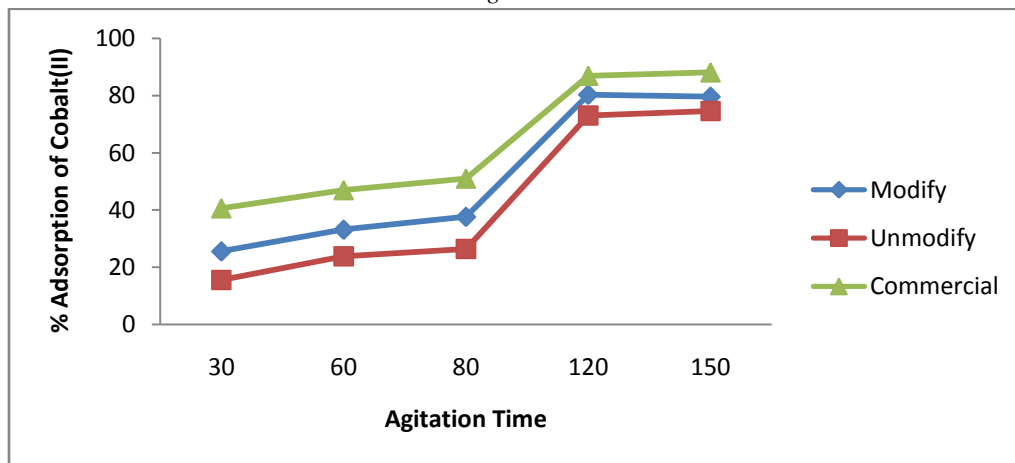
Figure 5a

Figure 5b

Figure 5c

Figure 5a, 5b, 5c: Effect of Agitation Time on Cr, Pb, Co biosorption by activated carbon, derived from lemon peel, biosorbent dosage 5g, Particle size 1.5mm, Initial Concentration 20mg/L, Temperature 300^0C

3.5. Adsorption isotherm
3.5.1 Langmuir adsorption isotherm (Langmuir 1918)
The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by;

$$q_e = \frac{q_m\, b\, C_e}{1 + b\, C_e}$$

(3.1)

Where q_m is the maximum biosorption capacity of biosorbent (mg g-1). b is the Langmuir biosorption constant (L mg-1) related to the affinity between the biosorbent and sorbate.

Linearized Langmuir isotherm allows the calculation of biosorprtion capacities and Langmuir constants and is represented as;

$$\frac{1}{q_e} = \frac{1}{q_m\, b\, C_e} + \frac{1}{q_m}$$

(3.2)

The linear plots of 1/qevs 1/ce is shown in Fig. 7 (a), 7(b), and (c). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m, b and regression coefficient (R^2) are listed in Table 2.

Maximum biosorption capacity of adsorbent (qm) is found to be 0.6745 mg per g of biosorbent which is higher than the other biosorbents used by many authors.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation;

$$R_L = \frac{1}{1 + b C_i}$$

(3.3)

Where b is the Langmuir constant and Ci is the maximum initial concentration of Cr^{+6}, Pb^{+2}, and Co^{+2}. The value of separation parameters R_L provides important information about the nature of biosorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.1503-0.8984 for concentration of 5 mg/L -250 mg/L of Cr^{+6}, Pb^{+2}, and Co^{+2}. They are in the range of 0-1 which indicates favorable biosorption [4].

3.5.2 Freundlich adsorption isotherm (Freundlich 1906)

Freundlich equation is represented by;

$$q = K C_e^{1/n}$$

(3.4)

Where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.

Linearized Freundlich adsorption isotherm was used to evaluate the biosorption data and is represented as,

$$\log q_e - \log K + \frac{1}{n} \log C_e$$

(3.5)

Equilibrium data for the biosorption is plotted as log qevs log Ce, as shown in Fig. 8(a), 8(b), and 8(c). The two constants n and K are calculated from the slope (1/n) and intercept (log K) of the line, respectively. The values of K, 1/n and regression coefficient (R_2) are listed in Table 2.

The n value indicates the degree of non- linearity between solution concentration and biosorption as followes: if n = 1, then biosorption is linear; if n < 1, then biosorption is chemical process; if n > 1, then biosorption is a physical process. A relatively slight slope and a small value of 1/ n indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 0.001-3.788. Some n > 1, and others n<1 these indicates the physical biosorptionand chemical process of Cr^{+6}, Pb^{+2}, and Co^{+2} onto lemon peel, The higher value of K (3.2006) indicates the higher biosorption capacity of the biosorbent.

Chromiun (VI) Ion
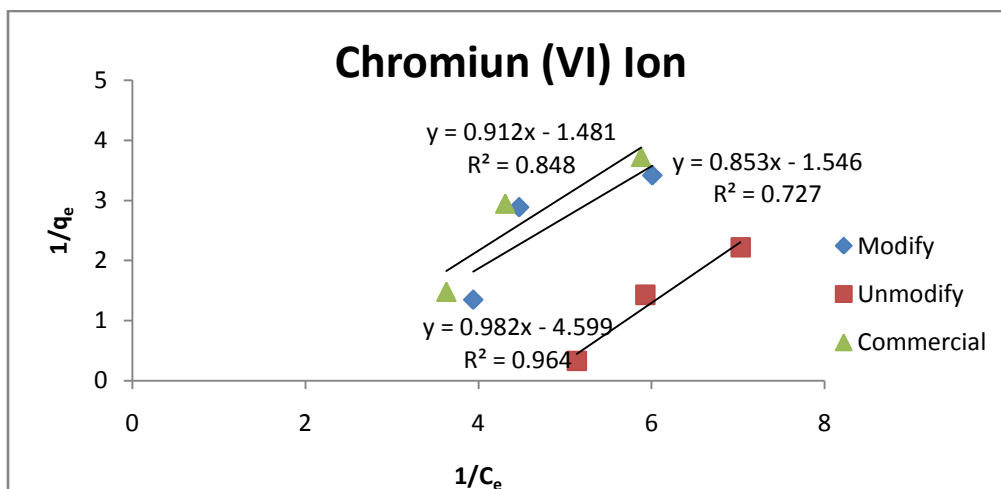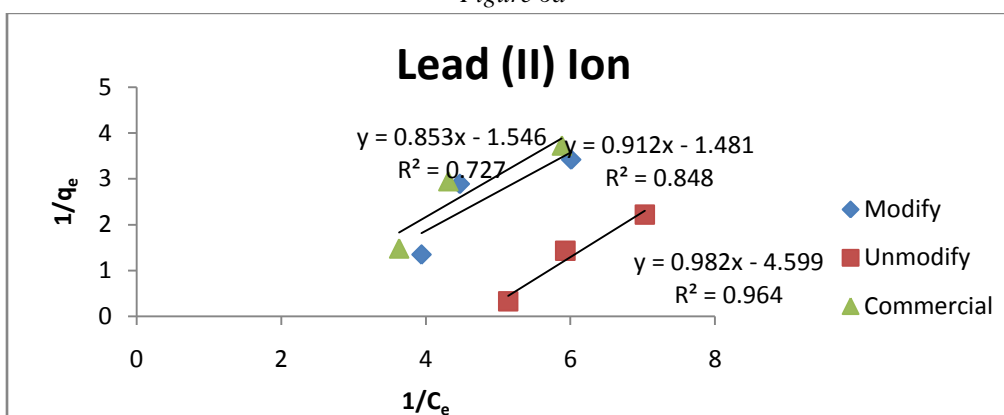
$y = 0.912x - 1.481$
$R^2 = 0.848$

$y = 0.853x - 1.546$
$R^2 = 0.727$

$y = 0.982x - 4.599$
$R^2 = 0.964$

- Modify
- Unmodify
- Commercial

Figure 6a

Lead (II) Ion

$y = 0.853x - 1.546$
$R^2 = 0.727$

$y = 0.912x - 1.481$
$R^2 = 0.848$

$y = 0.982x - 4.599$
$R^2 = 0.964$

- Modify
- Unmodify
- Commercial

Figure 6b

Cobalt (II) Ion

$y = 0.604x + 3.073$
$R^2 = 0.405$

$y = 0.668x + 2.170$
$R^2 = 0.331$

$y = 0.628x - 2.913$
$R^2 = 0.624$
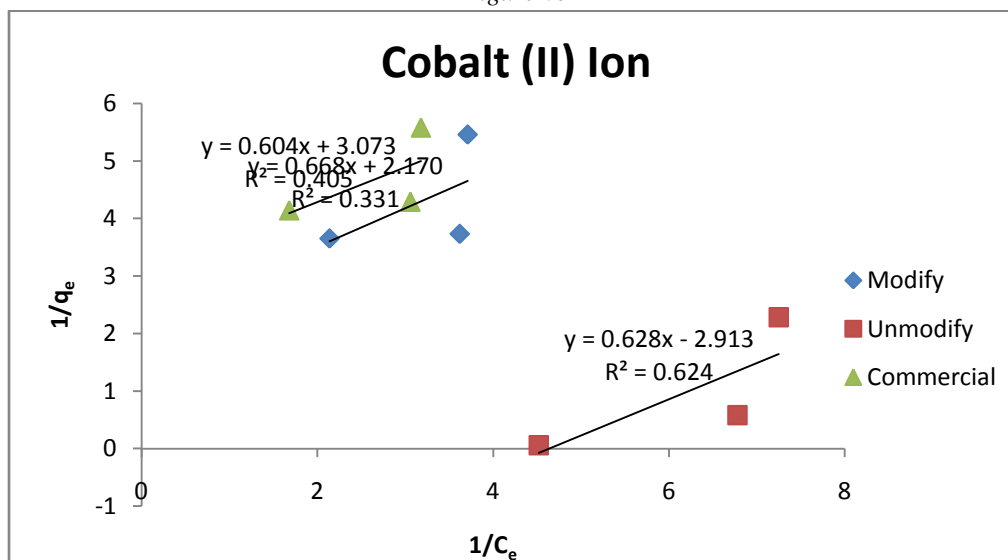
- Modify
- Unmodify
- Commercial

Figure 6c

Figure 6a, 6b, 6c: Plot of $1/q_e$ against $1/C_e$ for Langmuir adsorption isotherm of biosorption of Cr, Pb, Co, by activated carbon derived from lemon peel.
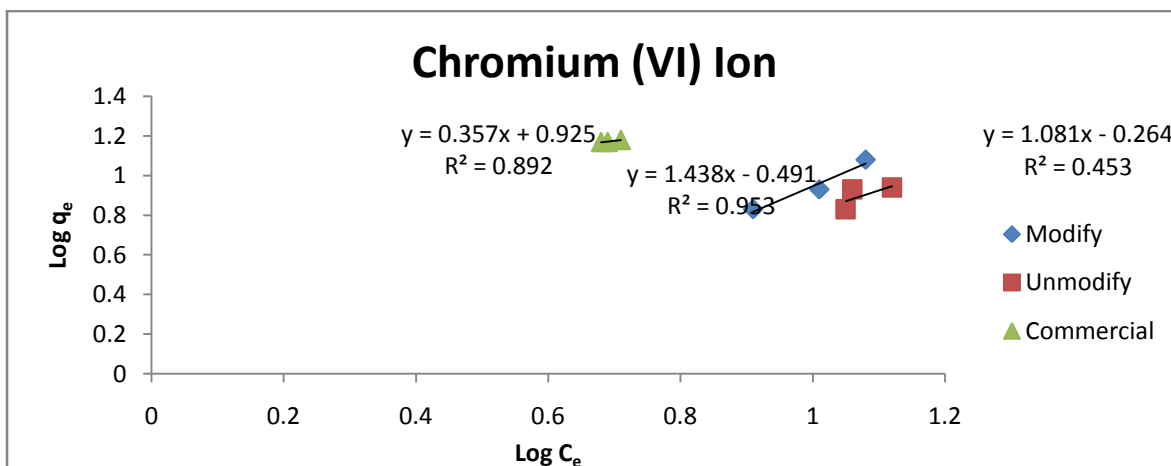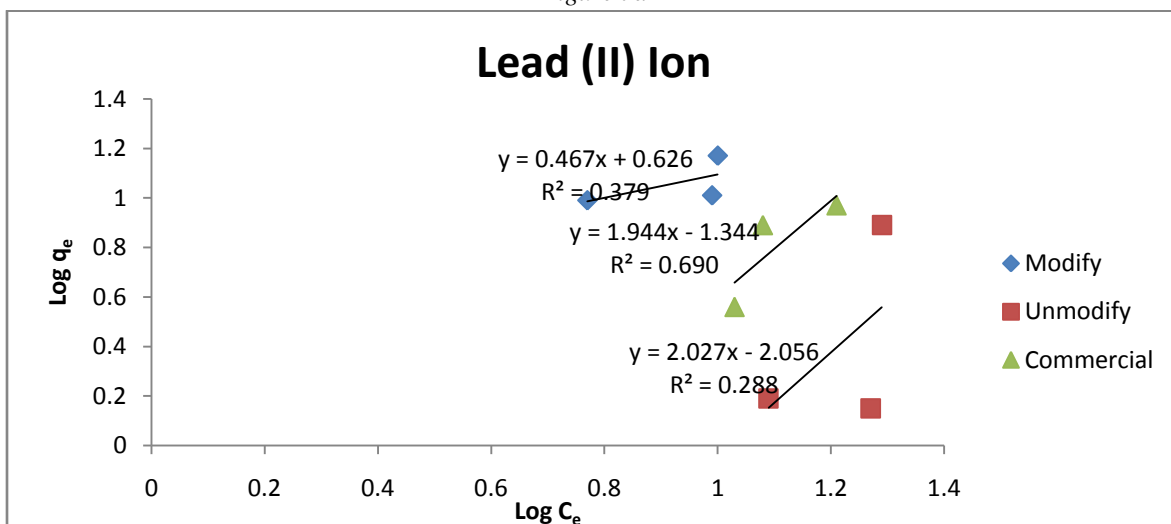
Chromium (VI) Ion
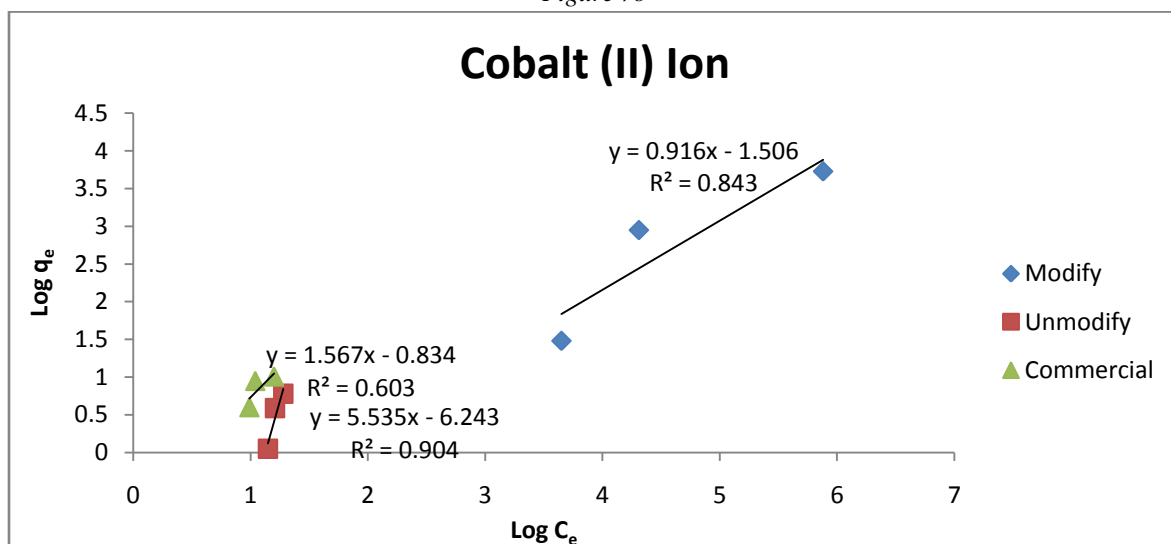

Figure 7a

Lead (II) Ion

Figure 7b

Cobalt (II) Ion

Figure 7c

Figure 7a, 7b, 7c: Plot of Log q_e against Log C_e for Freundlich adsorption isotherms for biosorption of Cr, Pb and Co by activated carbon derived from lemon peel.

Table 2: Langmuir and Freundlish Constants

Sample	Langmuir Constants				Freundlish Constants		
	Q_m	B	R^2	R_L	K	1/n	R^2
Chromium(VI)							
Modify	0.647	0.758	0.727	0.062	2.482	0.4917	0.954
Unmodify	0.217	0.229	0.964	0.185	4.558	0.264	0.453
Commercial	0.675	0.740	0.848	0.051	1.522	0.926	0.893
Lead(II)							
Modify	0.461	0.690	0.331	0.068	1.612	0.627	0.379
Unmodify	0.343	0.546	0.624	0.084	3.201	2.057	0.288
Commercial	0.345	0.571	0.405	0.081	0.831	1.345	0.379
Cobalt (II)							
Modify	0.747	1.758	1.727	0.162	2.638	1.506	0.844
Unmodify	0.317	0.329	0.974	0.285	0.346	6.243	0.904
Commercial	0.775	0.840	0.948	0.156	2.396	0.835	0.603

3.6 Adsorption kinetics

As aforementioned, a lumped analysis of biosorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first- order equation [17]. (b) the pseudo-second-order equation [4]. (c) Elovich equation [18] (d) Weber and Morris intraparticle diffusion rate equation [19]. are presented below.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3.6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3.7}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{3.8}$$

$$q_t = k_i t^{0.5} + c \tag{3.9}$$

Where q_e (mg g-1) is the solid phase concentration at equilibrium, q_t (mg g-1) is the average solid phase concentration at time t (min), K_1 (min-1) and K_2 (g mg-1 min-1) are the pseudo-first-order and pseudo-second- order rate constants, respectively. The symbols of (mg g-1 min-1) and (g mg-1) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. K_i (mg g-1 min-1/2) is the intra particle diffusion rate constant, c is intercept.

If the adsorption follows the pseudo-first- order rate equation, a plot of ln (q_e-q_t) against time t should be a straight line. Similarly, t/q_t should change lineally with time t if the biosorption process obeys the pseudo-second order rate equation. If the adsorption process obeys Elovich rate equation, a plot of q_t against ln t should be a straight line. Also a plot of q_t against t0.5 changes lineally the biosorption process obeys the Weber and Morris intraparticle diffusion rate equation.

Biosorption of Cr^{+6}, Pb^{+2}, and Co^{+2} onto biosorbent was monitored at different specific time interval. The Cr^{+6}, Pb^{+2}, and Co^{+2}uptake was calculated from the data obtained. From the Cr^{+6}, Pb^{+2}, and Co^{+2} uptake was plotted against time to determine a suitable kinetic model, the biosorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich equation and the Weber & Morris intraparticle diffusion rate equation. The pseudo-first-order equation was plotted for ln (q_e-q_t) against t (Fig. 9(a), 9(b), and 9(c)). The values of q_e and K_1 values were calculated from the slope (K_1) and intercept (lnq_e) of the plot and shown in Table 3. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the adsorbent and the ions adsorbed onto it [20]. The pseudo- second-order equation was plotted for t/q_t against t (Fig. 10(a), 10(b), and 10(c)). The values of qe and K_2 are calculated from the slope (1/qe) and

intercept ($1/K_2 q_e^2$) of the plot and values are shown in Table 3. The pseudo-second-order equation showed a strongest correlation value ($R^2 = 0.987$) being higher than the correlation coefficient for the Elovich equation, pseudo-first-order and Weber and Morris intraparticle diffusion rate equation. The Elovich equation was plotted for q_t against ln t (Fig. 11(a), 11(b), and 11(c)). The values of q_e and k_1 are calculated from the slope (k_1) and the intercept ($\ln q_e$) of the plot and values are shown in Table 3. The Elovich equation has been used with the assumption that the actual biosorption surface is energetically heterogeneous [21]. The Weber & Morris intraparticle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Fig. 12(a), 12(b), and 12(c)). The value of k_i and c are calculated from the slope (K_i) and intercept of the plot and values are shown in Table 3. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle pore diffusion is not only rate-limiting step [19]. The plot of intraparticle diffusion rate equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of biosorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption [4].
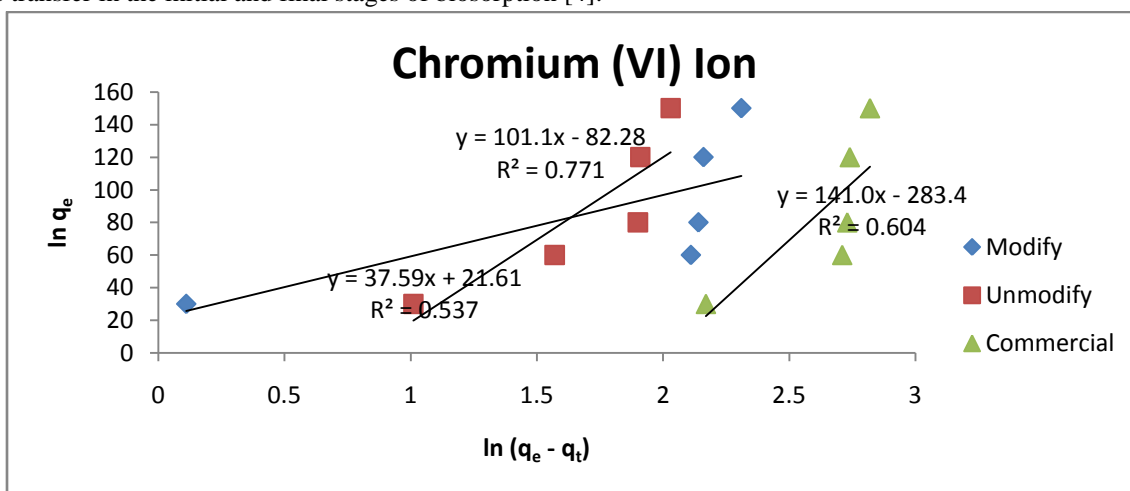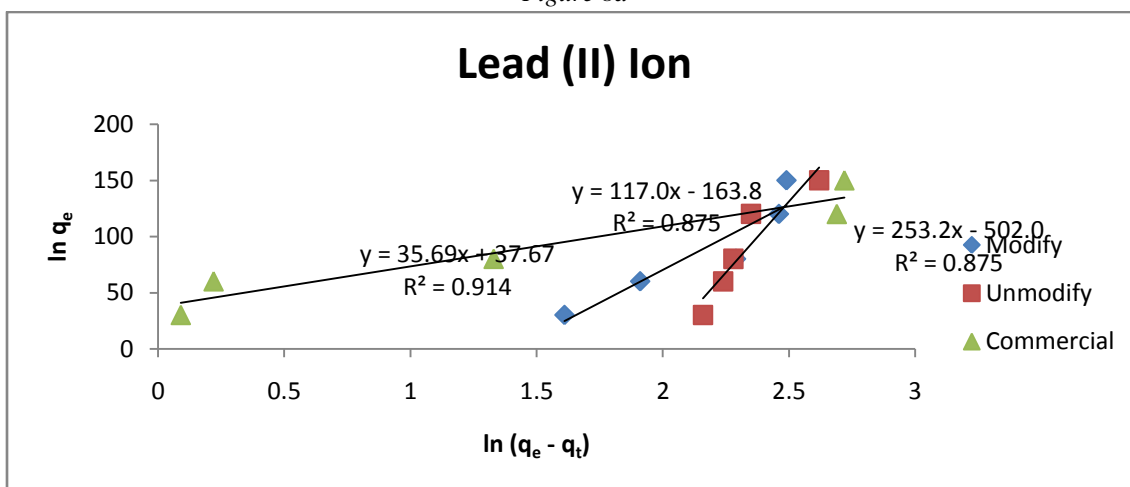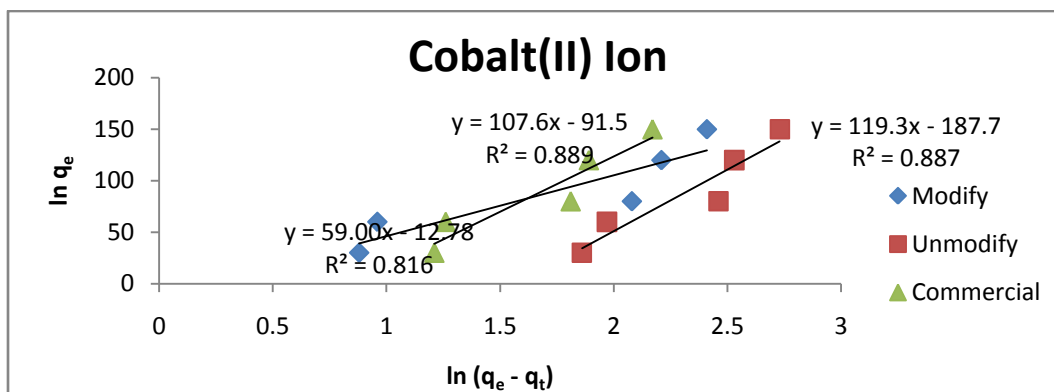

Figure 8a

Figure 8b

Cobalt(II) Ion

Figure 8c

Figure 8a, 8b, 8c: Plot of ln q_e against ln (q_e - q_t) for pseudo first order kinetic model for biosorption of Cr, Pb and Co by activated carbons derived from lemon peel
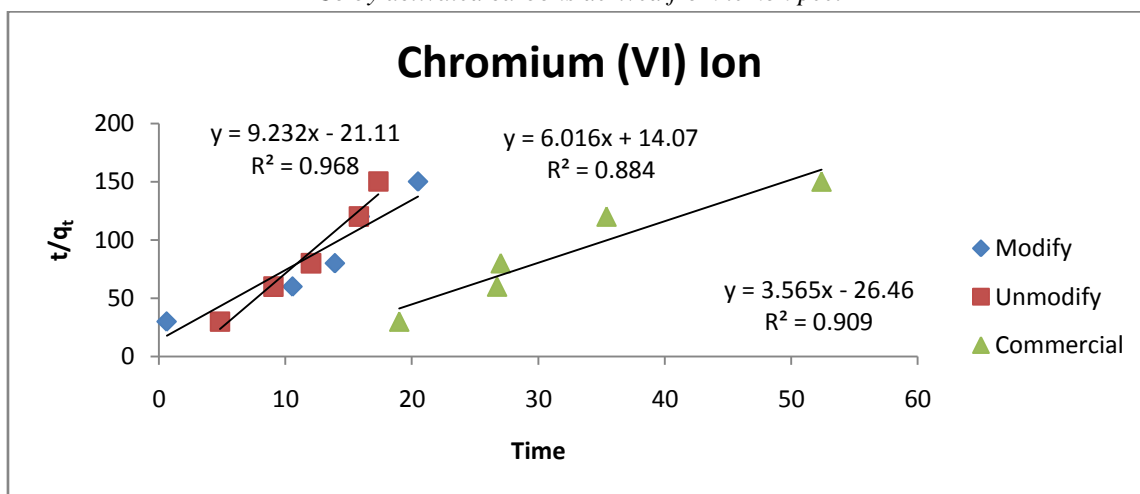
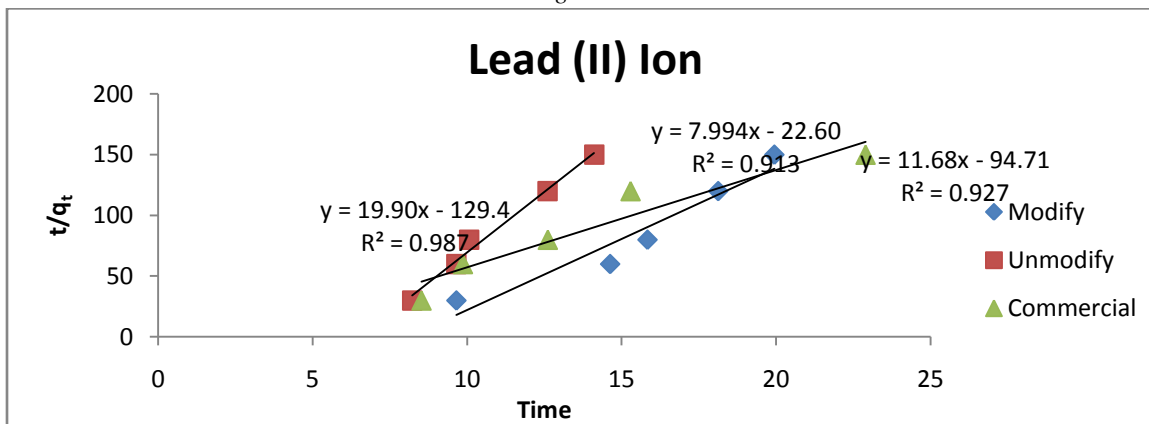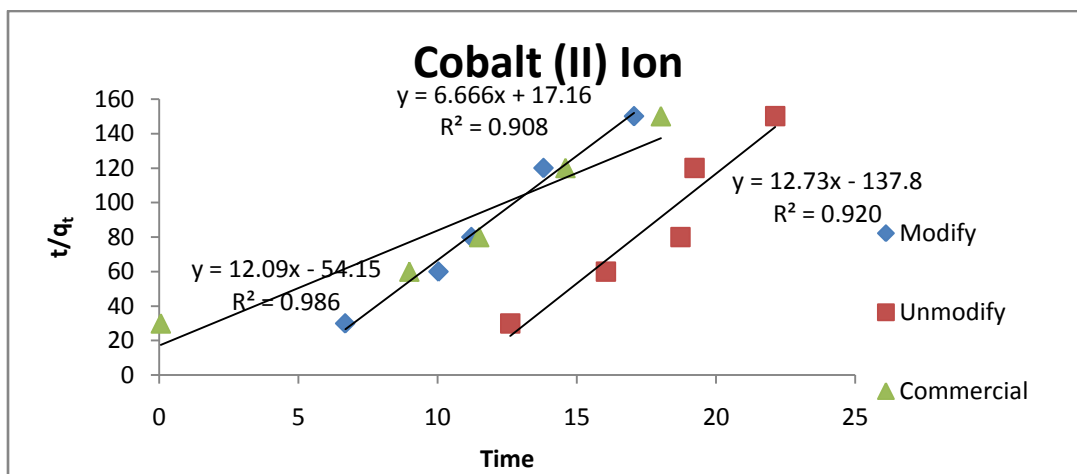## Chromium (VI) Ion

Figure 9a

Lead (II) Ion

Figure 9b

Figure 9c

Figure 9a, 9b, 9c: Plot of t/q against time for pseudo second order kinetic model for biosorption of Cr, Pb and Co by activated carbons derived from lemon peel

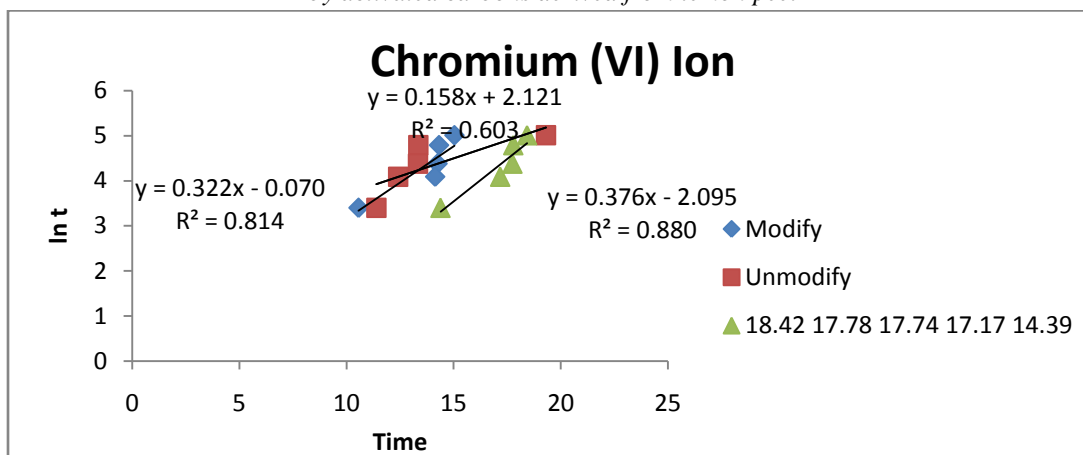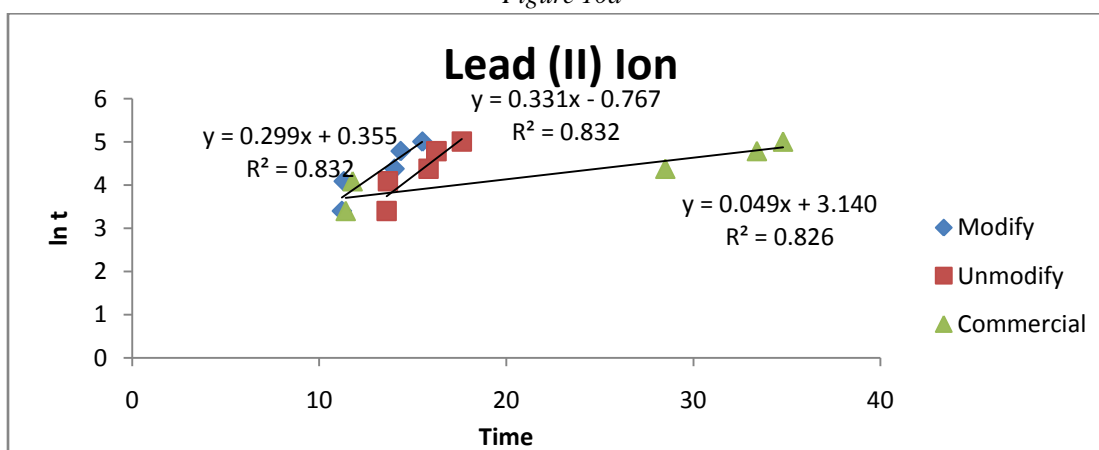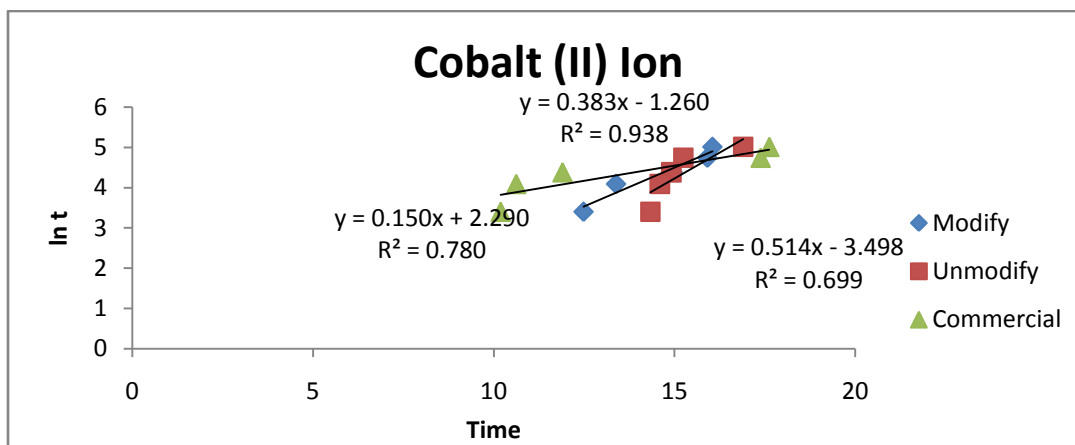*Figure 10a*

Figure 10b

Figure 10c

Figure 10a, 10b, 10c: Plot of ln t against Time for elovinch equation for biosorption of Cr, Pb and Co by activated carbons derived from lemon peel
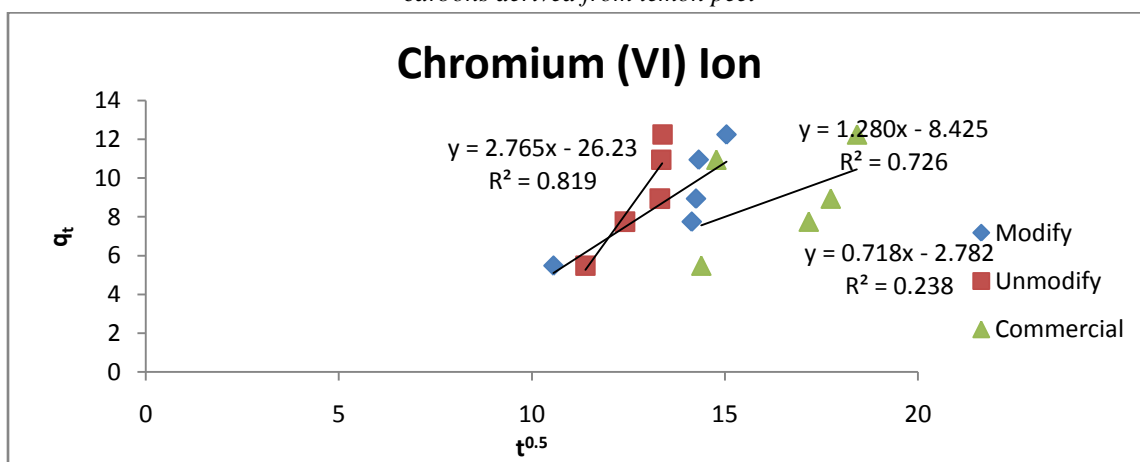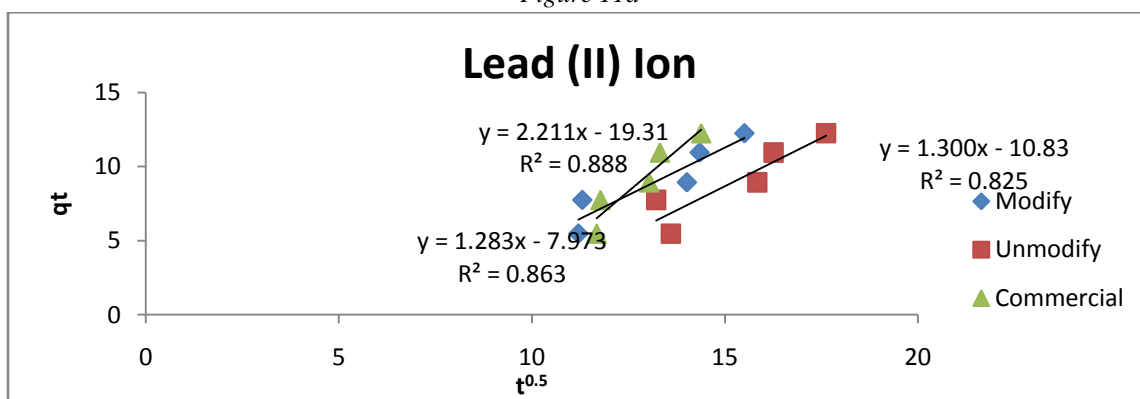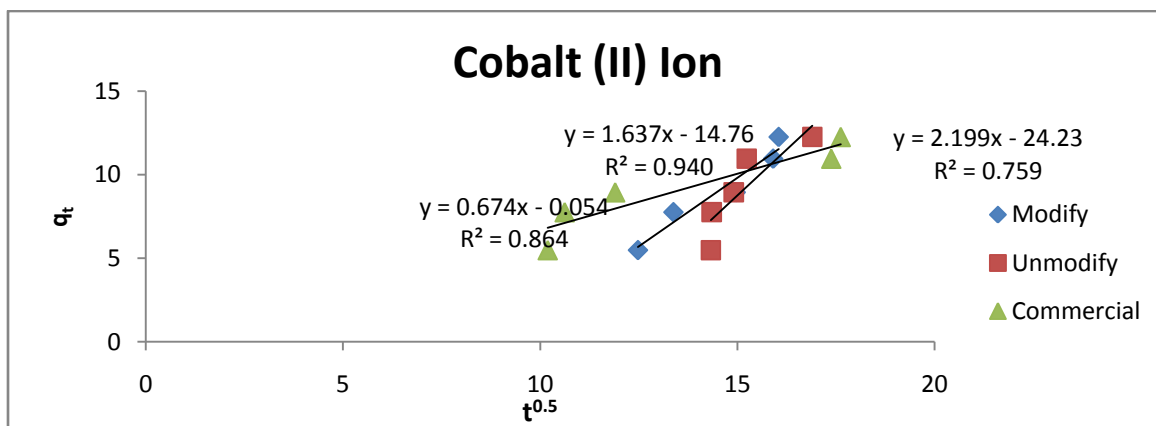

Figure 11a

Figure 11b

Figure 11c

Figure 11a, 11b, 11c: Plot of qt against $t^{0.5}$ for Weber and Morris intra-particle diffusion for biosorption of Cr, Pb and Co by activated carbons derived from lemon peel

Table 3: Pseudo-First-Order Model, Pseudo-Second-Order Model, Elovich Model and Intra-Particle Diffusion Model

Sample	Pseudo-First-Order Model			Pseudo-Second-Order Model			Elovich Model			Intra-Particle Diffusion Model		
	q_e	K_1	R^2	q_e	K_2	R^2	A	B	R^2	K_i	C	R^2
Chromium												
Modify	2.430	37.593	0.537	1.296	6.016	0.885	1.842	6.309	0.604	1.281	0.071	0.727
Unmodify	5.465	101.122	0.605	1.472	9.232	0.968	1.132	3.102	0.815	2.766	2.121	0.819
Commercial	4.300	141.026	0.771	3.101	3.565	0.909	0.978	2.659	0.881	0.719	2.095	0.239
Lead (II)												
Modify	1.370	117.007	0.875	6.568	7.994	0.914	1.216	3.371	0.833	2.211	0.355	0.864
Unmodify	4.680	253.225	0.879	1.711	19.901	0.928	1.105	3.018	0.832	1.300	0.767	0.826
Commercial	2.210	35.694	0.915	1.360	11.683	0914	2.999	20.080	0.826	1.284	3.141	0.888
Cobalt (II)												
Modify	355.471	59.005	0.915	3.308	12.731	0.987	0.958	2.606	0.938	1.637	1.202	0.941
Unmodify	3.557	119.385	0.928	7.687	6.666	0.909	0.599	1.822	0.699	2.199	3.499	0.759
Commercial	5.468	107.614	0.971	3.206	12.094	0.921	1.896	6.658	0.780	0.674	2.291	0.865

3.7 Thermodynamics study

The equilibrium constant [22] at various temperatures and thermodynamic parameters of biosorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{3.10}$$

$$\Delta G^0 = -RT \ln K_c \tag{3.11}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3.12}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{3.13}$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration of Cr^{+6}, Pb^{+2}, and Co^{+2} in solution (mg/L) and C_{Ae} is the Cr^{+6}, Pb^{+2}, and Co^{+2} concentration biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). G^0, H^0 and S^0 are changes in standard, Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K), T is the temperature (Kelvin). The values of H^0 and S^0 were

determined from the slope (H^0/R) and the intercept (S^0/R) from the plot of ln Kc versus 1/T (Fig. 13(a), 13(b), and 13(c)). The values of equilibrium constant (K_c), standard Gibbs free energy change (G^0), standard enthalpy change (H^0) and standard entropy change (S^0) calculated in this work were presented in Table 4. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intraparticle diffusion. The standard Gibbs free energy change (G^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of G^0 were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The positive values of H^0, indicating the endothermic nature of the biosorption Cr^{+6}, Pb^{+2}, and Co^{+2} onto Lemon peel. The positive values of S0, shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.
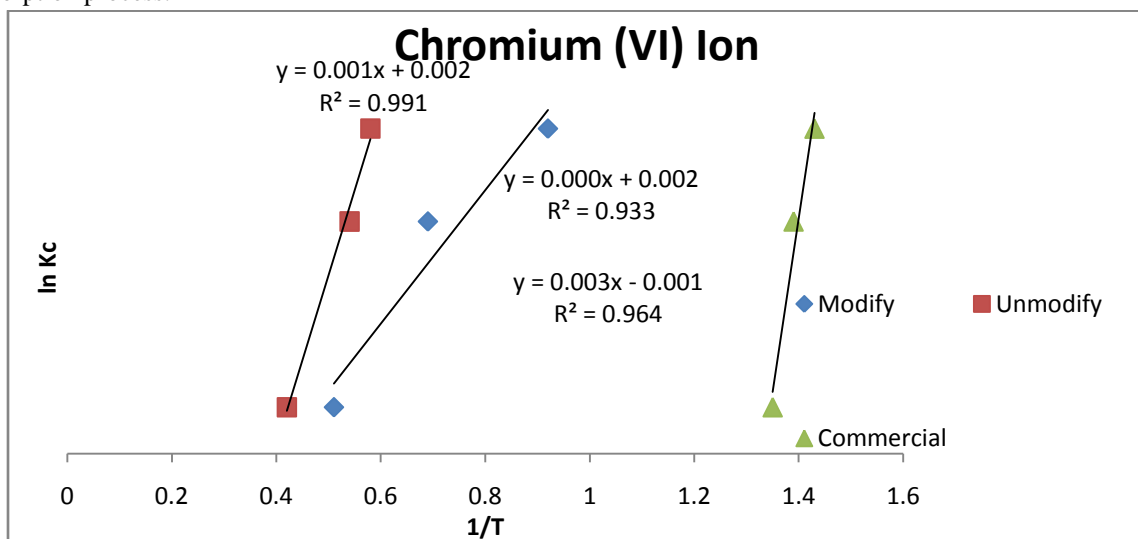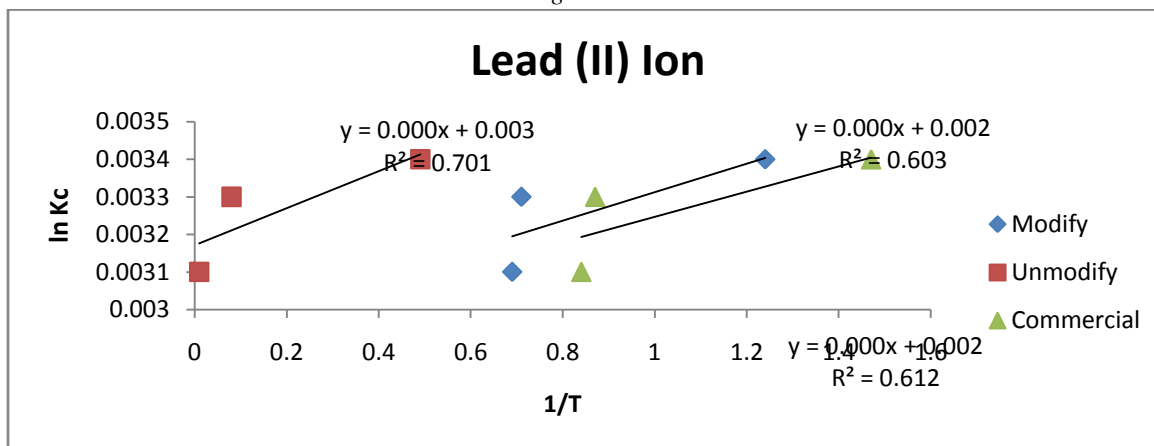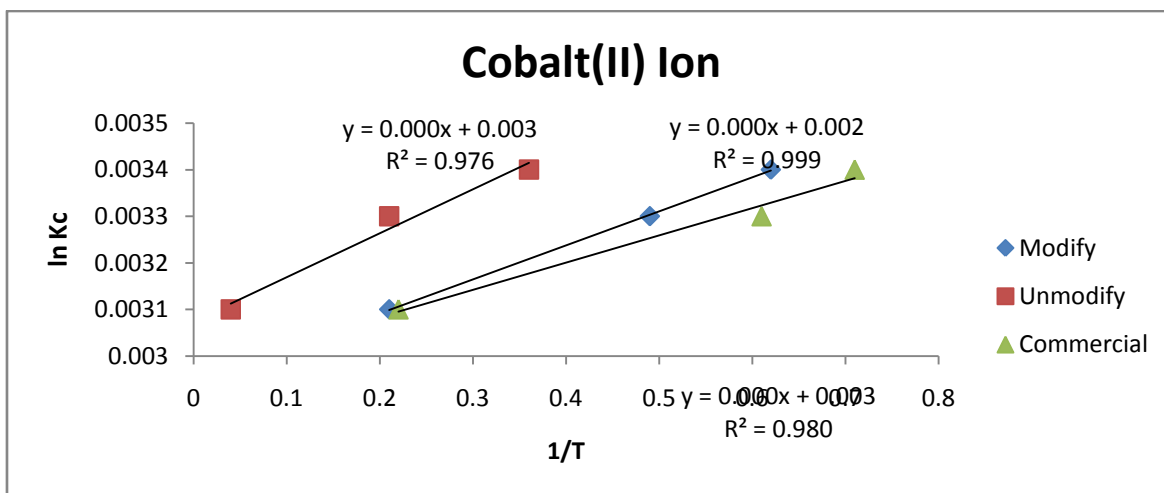

Figure 12a

Figure 12b

Cobalt(II) Ion

y = 0.000x + 0.003
R² = 0.976

y = 0.000x + 0.002
R² = 0.999

y = 0.000x + 0.003
R² = 0.980

Figure 12c

Figure 12a, 12b, 12c: Plot of ln Kc against 1/T for the determination of thermodynamic parameters for bioabsorption of Cr, Pb and Co by activated carbons derived from lemon peel.

Table 4: Entropy, Enthalpy, Gibbs free energy and equilibrium constant

Sample	T(K)	Kc	$-\Delta G^O$ (KJ/mol)	ΔH^O (J/mol/K)	$-\Delta S^O$ (J/mol/K)
Chromium (VI)					
Modify	293	0.069	6.721	0.058	0.023
	303	0.069	6.721	0.058	0.023
	313	0.069	6.721	0.058	0.023
Unmodify	293	0.069	6.721	0.015	0.019
	303	0.069	6.721	0.015	0.019
	313	0.069	6.721	0.015	0.019
Commercial	293	0.069	7.141	0.034	0.016
	303	0.069	7.141	0.034	0.016
	313	0.069	7.141	0.034	0.016
Lead (II)					
Modify	293	0.004	7.029	0.003	0.024
	303	0.004	7.029	0.003	0.024
	313	0.004	7.029	0.003	0.024
Unmodify	293	0.004	7.029	0.004	0.027
	303	0.004	7.029	0.004	0.027
	313	0.004	7.029	0.004	0.027
Commercial	293	0.004	7.987	0.002	0.024
	303	0.004	7.987	0.002	0.024
	313	0.004	7.987	0.002	0.024
Cobalt					
Modify	293	0.007	7.026	0.006	0.024
	303	0.007	7.026	0.006	0.024
	313	0.007	7.026	0.006	0.024
Unmodify	293	0.007	7.026	0.026	0.075
	303	0.007	7.026	0.026	0.075
	313	0.007	7.026	0.026	0.075
Commercial	293	0.007	7.506	0.005	0.025
	303	0.007	7.506	0.005	0.025
	313	0.007	7.506	0.005	0.025

Acknowledgements

4. Conclusion

The present investigation revealed that Lemon peel used as inexpensive, excellent biosorbent for the removal of Cr^{+6}, Pb^{+2}, and Co^{+2} from aqueous solutions. The optimal parameters such as initial Cr (VI) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of Cr^{+6}, Pb^{+2}, and Co^{+2} onto Lemon peel. The biosorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, The maximum Cr^{+6}, Pb^{+2}, and Co^{+2} loading capacity (q_e) of lemon peel determined from Langmuir adsorption isotherm was found to be 0.675 mg g-1. The pseudo- second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of Cr^{+6}, Pb^{+2}, and Co^{+2} onto lemon peel is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that has considerable biosorption capacity, available in abundant, non-hazardous agro material can be used as an effective indigenous material for treatment of wastewater stream containing Cr^{+6}, Pb^{+2}, and Co^{+2}.

This study show that the use of activated carbons derived from lemon peel for metal ion removal is technically feasible eco-friendly and with high efficacy. Besides that, activated carbon derived from lemon peel being agricultural industrial waste makes the study to be relevant in the management of lemon peel waste. The preparation of activated carbon derived from lemon peel is cost-effective. The lemon peel char could be used for waste water treatment.

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