International Journal of
Mathematical Modelling & Computations
Vol. 11, No. 03, Summer 2021, 1- 19

Review and Modelling of Hexavalent Chromium Removal Efficiency of Bio-Sorption and Activated Carbon for Waste Water Treatment

D. Abdissa[a,*], A. Bekele[a] and T. Abeto[a]

[a]*School of Chemical Engineering, Jimma University / Jimma Technology Institute, Jimma City, Ethiopia.*

Abstract. Hexavalent chromium pollutants in water are the most challenging of human health according to current situations. From many treatment methods, the adsorption method is the best alternatives for hexavalent chromium removal from wastewater. Activated carbon and biosorption are the basic adsorbents in the adsorption process. In these review and model optimization there where many articles reviewed under activated carbons and biosorption without carbonizing. The basic factors for the two adsorbents are adsorbent dose, pH value, and contact time at around room temperature. Maximum removal efficiency allocated at the acidic condition, these show the –OH releasing state is at the acidic condition. According to articles reviewed, the efficiency of bio-sorbent was greater than activated carbon. There were similarity adsorption efficiency of activated carbon and biosorption. As reviewed activated carbon and biosorption preparation, activated carbon preparation was more energy consumption than biosorption preparations. The model optimization also summarised and optimum condition of maximum removal efficiency where specified.

Received: 25 November 2020, Revised: 30 April 2021, Accepted: 28 May 2021.

Keywords: Hexavalent chromium, Activated carbon, Bio adsorbent, Optimizations; Parameters.

Index to information contained in this paper

1. Introduction

In the world, water is the major importance for life (drinking, washing, recreation, irrigation, power generation,) and without water life is impossible. This life needs high standard quality of water, that concerned by WHO. Water pollution is any substance that presents in the water out of standard ranges [18]. Heavy metals like Cr, Zn, As, Pb, Cd, Cu and etc., In less concentration causes high risk on human health [25]. Chromium and Arsenic are highly carcinogenic and can cause cancer of lungs [23], liver, bladder, and skin at lower levels of arsenic exposure can cause nausea and vomiting [24], reduced production of erythrocytes and leukocytes, abnormal heartbeat, pricking sensation in hands and legs, and damage to blood vessels [3]. Long-term exposure can lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease, and diabetes mellitus. Industrial waste constitutes the major source of various kinds of heavy metal pollution in water [29]. The important toxic metals like Ar, Cr, Cd, Cu, Zn, Ni, and Pb finds its way to the water bodies through wastewaters. Heavy metals are major pollutants in marines like the ground water, surface water, spring water, and river water [16]. The

*Corresponding author. Email: abdissa694@gmail.com; desalegn.abdissa@ju.edu.et

http://ijm2c.iauctb.ac.ir

natural heavy metal occurs on earth crust rocks, entering into groundwater bodies through percolation by different causes like climate change, precipitation, and agricultural activities [5]. The other ways that toxic heavy metal enters the water bodies though wastewater releases from industries like leather factories, electroplating factories, mining factories and painting industries to surface water [35].

The removal of these heavy metals from water is not simple treatments, it needs nanotechnology treatment like reverse osmoses, electro dialysis, membrane filtrations, etc. these treatment units are small in treatment capacity and economical cost. Therefore, many scientists and researchers are articulates the ways of these heavy metal removals from water in simple and low cost using locally available materials. Low cost locally available and simple treatment method is adsorption techniques [10]. The treatments methods of adsorption are by biomass activate carbon and bio-sorbents, which are low cost, simple, and locally available.

Varies articles on toxic metal adsorptions are based on isothermal model equations, such as Langmuir, Freundlich, and Temkin, such model regression equations focus only on the best fits [19]. The studies targets to review efficiency competences of biomass activated carbons and bio-sorbents with variable effects, modelling of optimization equations. Evaluation of variables (dose, contact time, and pH) on the hexavalent chromium removal efficiency of different activated carbon and various bio sorption from wastewater. Determining the optimum parameter for maximum hexavalent chromium removal capacity of activated carbon and biosorption using solver excel software and identifying the highest factor variables on adsorption capacity.

2. Adsorption

Adsorption is the process of molecules transfer from liquid to the solid surface of the adsorbent [13]. In the water treatment, adsorption is the process of pollutant transported from a liquid phase to the solid surface by chemical bond energy [31]. Adsorption takes place in between adsorbent and absorber. The adsorbent is a substance that present in water or wastewater in the form of ion pollutant moves to the absorber and attached to the active site of the absorber [31].

The phenomenon of adsorptions is diffusion, the surface chemical reaction using ion-exchange, and surface complex [12]. The diffusion processes are described in terms of pore diffusion, surface diffusion, or combination of surface and Pore diffusions model mechanism [15]. Frequently, an external boundary layer film resistance is incorporated into these models. In the current water and wastewater treatment, adsorption is novel water treatment technology with low cost and locally available material. Large porous adsorbents and good selectivity such as activated carbon have shown excellent ability in the pollutant removal [33].

2.1 *Activated carbon*

The activated carbon (AC) is a type of amorphous carbonaceous materials which contain the highest porosity and high internal surface area [26]. AC can produce from biomass materials and until recently, any high content Carbon material by the carbonizing process that makes the same structural changes in the heating process [2]. Activated carbons are commonly used as adsorbents for water treatments. AC production process is high energy consumption during the carbonizing process and may it not be low-cost adsorbents relative to bio sorbents [9]. In the other ways regenerating activated Carbon is difficult because during the regeneration the porosity and its high surface area may damage and distract [4].

Recently, adsorption onto activated carbon prepared from a wide range of low-cost biomass precursors has been reported. All these studies have found that the produced carbons have comparable and higher adsorption capacities than commercially available varieties [11].

2.2 *Bio adsorbent*

All the carbon-rich biomass can be bio sorbent after taking physical and structural treatment [8]. Biomass with high carbon contents like lignin, hemicellulose, and cellulose has a high adsorption capacity for hexavalent chromium [34].

Also, the technology application of adsorption has developed by using biomass from micro-organisms plant known as Bio-removal [14]. The advantages of using biomass as a bio-removal are require low costs, high efficiency, regenerated, no additional nutrients needed, have an ability to recover metals and produce low result of sludge [17]. From the benefits mentioned, Bio-removal is more effective than ion exchange and reverse osmosis for the sensitivity of the presence of dissolved solids and heavy metals in water treatment [27]. Bio-sorbent also better than precipitation when associated with the ability to simulate any changes in pH and concentration of heavy metals [1]. Low pH industrial wastewater estimated acidic, a basic universal as multiple manufacturers. Increasingly strict environmental management challenge pH, with different contaminants, measured to a specific level before being removed into natural water bodies or the city sewer system [28].

Bio-Sorbents is adsorbents that produced from high Carbone content of organic materials. The process of bio sorbent preparation is the physical treatment of organic carbons and initiating active site of the carboxylic group for bonding with pollutant heavy metal [30]. In the Table 1 all are activated biomass by only physical treatment: n-hexane washing, sodium hydroxide solution, washing by distilled water and etc. are used for physical treatment of biomass for hexavalent chromium removal [22]. The factor that determines the adsorption capacity of adsorbents are: adsorbent dose, contact time, pH, temperature, and the stability of adsorbent material in aqueous. The Figure 1 shows active sites of activating biomass on adsorption of hexavalent Chromium ions without any instability of adsorbent in aqueous solutions. The ability of adsorbent stability used for the regenerating the active site [32]. If the adsorbent does not stable, it is difficult to regenerate. The simple physical treatment of biomass for adsorbent not denatures the natural molecular structure but initiating the functional group adsorption by pH adjustments. Therefore, is not difficult to regenerate adsorbent. The preparation of bio-sorbents is mechanical size reduction, then washing with reagents.

Some examples of bio sorbents articulate in the recent time: avocado seed, moringa seed, agricultural waste composite, and rice straw, avocado seed.

All carbon-rich biomass used as adsorption for heavy toxic metals from the wastewater. Hexavalent chromium is one of the toxic heavy metal releases from industries and natural occurrences. Figure 2 shows how bio-sorbents prepared and remove chromium from water.

Many research articles that determine the efficiency capacity of bio-sorbent on hexavalent chromium removal were done in a different time, by different researchers, Table 1. The basic factor affects the removal efficiency where adsorbent dose, pH and contact time retaining temperature around atmospheric room temperature.

The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive bio sorbent materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration of bio sorbent, no additional nutrient requirement, and the possibility of metal recovery.

2.3 *Activated carbon*

As its name activated carbon is active substances to adsorbed positive ion metal due to hole and -OH group formed during thermal heating, molecular structure expanded. Activated carbon also produces from high carbon-rich biomass, basically from green plants. Activated carbon production needs thermal energy or high concentrated acid, and it is a simple process to produce. Activated carbon is chromium adsorbent, that produced in thermal heat up to 600 for at least 3hrs and a chemical is activating by concentrated acid (sulphuric acid). Activated carbons have advantages and disadvantages in terms of cost, production, adsorption, and area of application.

Activated carbons are**:**

- High adsorption capacity: large pore surface area was produced during the activation process, the metal ion attached on pore area up to saturated or equilibrium reached.
- Produced from locally available materials: can produce from any carbon-rich biomass
- Simple production process: pre-treatment (cutting, washing, size reduction), carbonizing by heat or chemical.

In other way activated carbons:

- High production cost: in the production, carbonizing need high heat supply (600℃ for 3hrs). energy is indirect costs. Or high concentrated acid is cost relative to its application
- Stability: same time activated carbon treated water becomes the black colour that shows the instability of activated carbon in water. And these instabilities of activated carbon prevent regenerations
- Wastes of activated carbon cannot simply degrade cause environmental problems

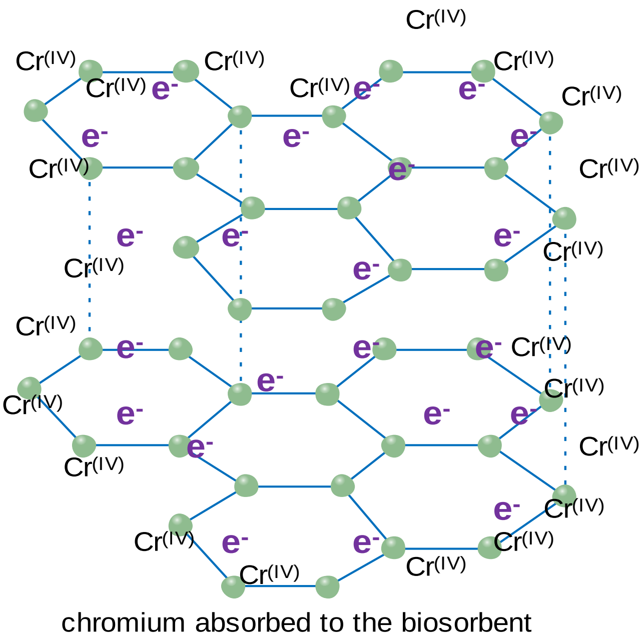

Figure 1. Chromium adsorbed to the bio sorbent.

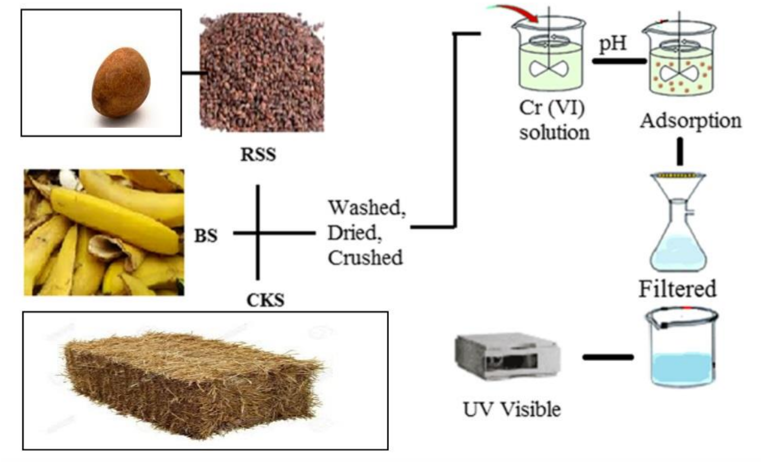

Figure 2. Simple process production of bio-sorbents [21].

Table 1. Review summary of bio-adsorption capacity with the same method and different factor parameter.

Name of adsorbent	Adsorption Method	Adsorbent dose, pH, time, temp	Maximum Adsorption capacity	Year
groundnut hull	Batch	40mg/L, pH 2, 200 min, 30°C	96%	November 2016
tea waste	Batch	6g/L, 3.9pH, 240 min,	96.7%,	2019
Groundnut shell	Batch	2g/L, 10pH, 120 min,	87.6%	15 May 2019
Wheat Straw	Batch	10g/L, pH 1, 50min, 34.85°C	99.9%	December 2, 2016
Rice straw	Batch	80g/L, pH 6, 50 min, 25°C	91 %	Sep 2015
Moringa Seed	Batch	50mg/L, pH 2, 60 min, 20±2°C	99.74 %.	May 2013
Moringa Seed	Batch	10mg /L, pH 5.0, 90 min, 25°C	80%	September 2014.
Mango Seed	Batch	2.5g/L, pH 2, 150 min, 35 °C	100%	December 2016

The negative ion on the surface of activated carbon attracts the positive ion of hexavalent chromium up to saturation condition happen shows Figure 3.

The above Table 2 shows the summary of some articles of biomass activated carbon removal efficiency on hexavalent chromium removal. In the summary of Table 1 shows biomass sorption capacity on hexavalent chromium ion was 94% average from nine article summary and 92.6% average removal efficiency from biomass activated carbon activated in six summaries of articles in Table 2. From this summary, it concludes that the removal efficiency of bio-sorbent is greater than the biomass activated carbon. The preparation of biomass activated carbon also more energy consumption than that of preparing bio-sorbent. In this summary review, bio-sorbent are the best alternatives to remove the hexavalent chromium from wastewater, to fit the WHO standard concentration of wastewater to release at the disposal site. Because biosorption is a low cost, locally available, simple methods, environmental friendly. Finding low-cost high profit and by a simple process, solving community problems is an engineering science discipline.

Table 2. Review summary of activated carbon adsorption capacity with the same method and different factor parameter**.**

Name of adsorbent	Adsorption method	Adsorbent dose, pH, time, temp	Maximum adsorption capacity	Year
Waste Bamboo	Batch	0.1g/L, 2pH, 20 min, 26.85°C	98.28%	February 2014
Teff husk	Batch	20.22g/L, 1.92pH, 124.2min, 25°C	95.597%	December 2019
Parthenium hysterophorus weed	Batch	90 g/L, 2pH, 90 min, 25°C	90.5%	April 2020
Cucumis melo peel	Batch	250mg/L, pH 3.0, 180min	97.95%	February 2018
Algae	Batch	10 g/ L, pH 1, 60 min, 26°C	85%	January 2011
Granular activated carbon	Batch	12mg/L, pH 7, 22.7 h, 20°C	88.3%	November 2014

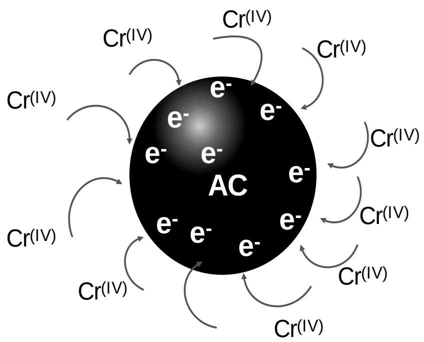

Figure 3. Hexavalent chromium adsorbed on the pore and surface of activated carbon.

3. Hexavalent chromium removal efficiency modelling of biosorption and biomass activated carbon

The modelling hexavalent chromium pollutant removal efficiency of bio sorption and biomass activated carbon varies from original materials produced.

Table 3. Indexed variable optimization for both activated carbon and bio sorption.

Optimization parameter	Variable substitution	unit	Remark
Dose	X_1	g/L	
Contact time	X_2	minute	
pH	X_3		
Removal efficiency	Y_1	%	Constant time & pH
Removal efficiency	Y_2	%	Constant dose & pH
Removal efficiency	Y_3	%	Constant dose & time

4. Modelling of bio-sorption efficiency on hexavalent chromium ion removal

4.1 *Modified groundnut hull adsorption capacity*

The research was done by Samson O. Owalude (2016) on the hexavalent chromium adsorption capacity of modified and unmodified groundnut hull. But in these-modelling equations and optimizations, it is only focused on the modified groundnut hull. The data were generated from the research article and these modelling equations shows the optimum value of variables for maximum yield of adsorption.

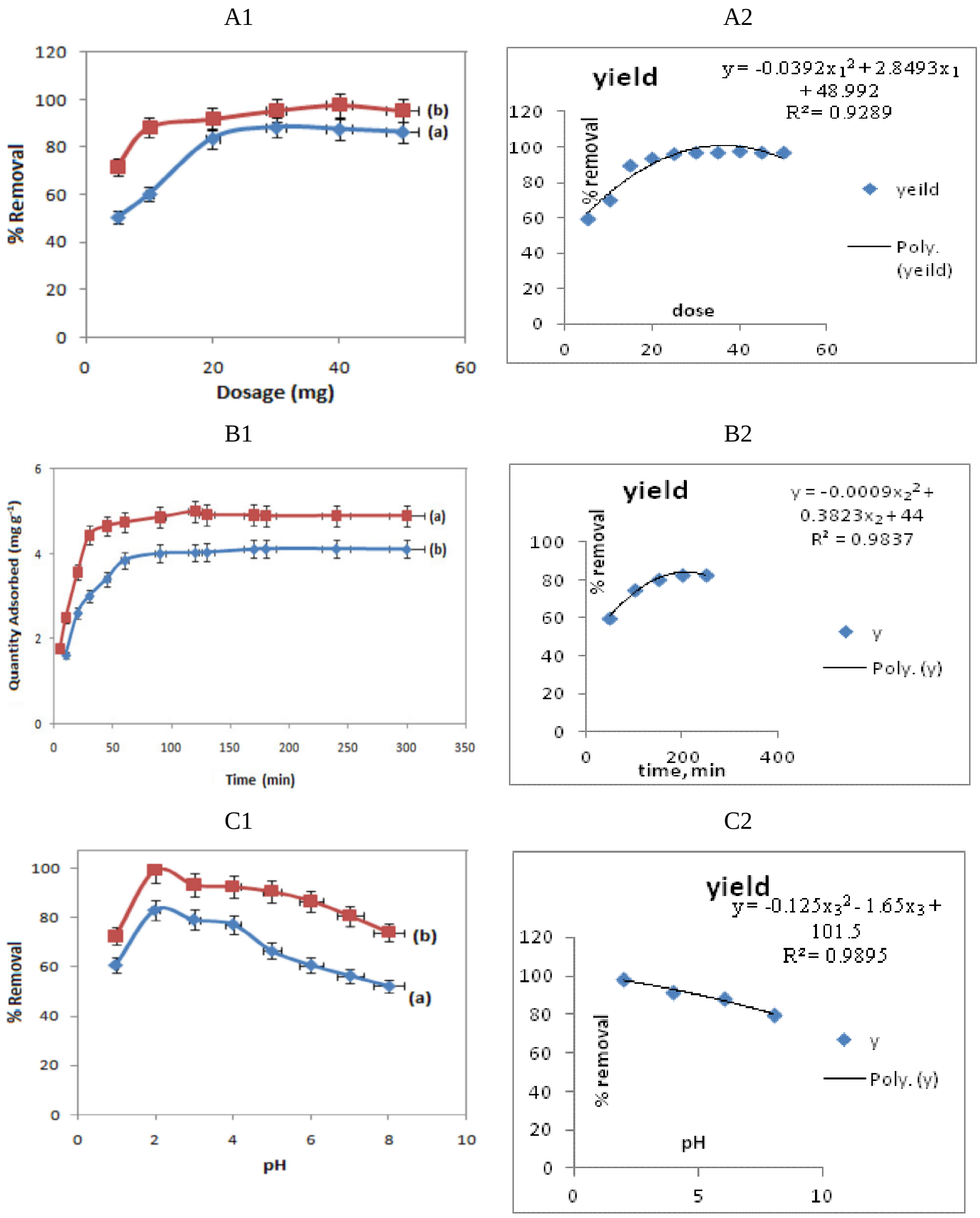

Figure 4. Three-factor variable on adsorptions (A1 and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency modified groundnut hull.

$Y_1 = -0.0392X_1^2 + 2.8493X_1 + 48.992$, at X_2 and X_3 are values of 200 min and 2 pH respectively.
$Y_2 = -0.0009X_2^2 + 0.3823X_2 + 44$, at X_1 and X_3 are optimum values of 40mg/L and 2 pH respectively.
$Y_3 = -0.125X_3^2 - 1.65X_3 + 101.5$, at X_1 and X_2 are optimum values of 40mg/L and 200 min respectively.

$$-0.0392X_1^2 + 2.8493X_1 + 48.992 \cong 98 \tag{1}$$

$$-0.0009X_2^2 + 0.3823X_2 + 44 \cong 98 \tag{2}$$

$$-0.125X_3^2 - 1.65X_3 + 101.5 \cong 98 \tag{3}$$

Where 98, is the maximum removal efficiency of groundnut hull in percent.
The first equation is generated based on adsorbent dose change, at maximum time and pH, equation 2 generates by varying contact time at dose and pH at maximum values and the last equation 3 based on Ph varying and at maximum dose and contact time.

Table 4. Summary and variable optimization of hexavalent chromium removal by modified groundnut hull.

Variables (Optimum point)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency% (Y_i)
Variables	Opt. value				
X_1	31.94393	-0.0392	2.8493	48.992	100
X_2	200	-0.0009	0.3823	44	84.46
X_3	0.853858	-.125	-1.65	101.5	100

According to these regression model equations the maximum removal efficiency of Groundnut hull is 100%, at 31.94393mg/L and at 0.853858 pH. and 84.46% at 200min contact time in Table 4. This table shows that the variables of adsorbent dose and pH values are highly affects of Groundnut hull removal capacity in the model equations. Groundnut hull biomass have high hexavalent chromium removal efficiency characters at acidic condition.

4.2 *Tea waste adsorption capacity*

Research done by Mohit Nigama, Sunil Rajoriyab 2019, tea wastes maximum adsorption capacity on hexavalent chromium ion was 96.7%. In these model equations and optimizations, the maximum removal efficiency depends on the model regression equations.

According to tea waste adsorption analysed from the Figure 5 shows no limitation for contact time, as contact time increase adsorption efficiency also increase. For dose and pH there were limited optimum values. Depending on regression equation below optimum values of all factors were specified with a given ranges in Table 5. From the Figure 5 and experimental data there was equation generates below:
$Y_1 = -1.2083X_1^2 + 19.631X_1 + 17.95$, at X_2 and X_3 are optimum values of 240 min and 3.9pH.
$Y_2 = -0.0008X_2^2 + 0.4659X_2 + 30.821$, at X_1 and X_3 are optimum values of 6g/L and 3.9pH.
$Y_3 = -1.0179X_3^2 + 5.3643X_3 + 86$, at X_1 and X_2 are optimum values of 6g/L and 240min.

$$-1.2083X_1^2 + 19.631X_1 + 17.95 \cong 97 \quad (4)$$

$$-0.0008X_2^2 + 0.4659X_2 + 30.821 \cong 97 \quad (5)$$

$$-1.0179X_3^2 + 5.3643X_3 + 86 \cong 97 \quad (6)$$

The model equations of 4, 5 and 6 with dose, contact time and pH respectively which equating with highest experimental result of 97% of removal efficiency.

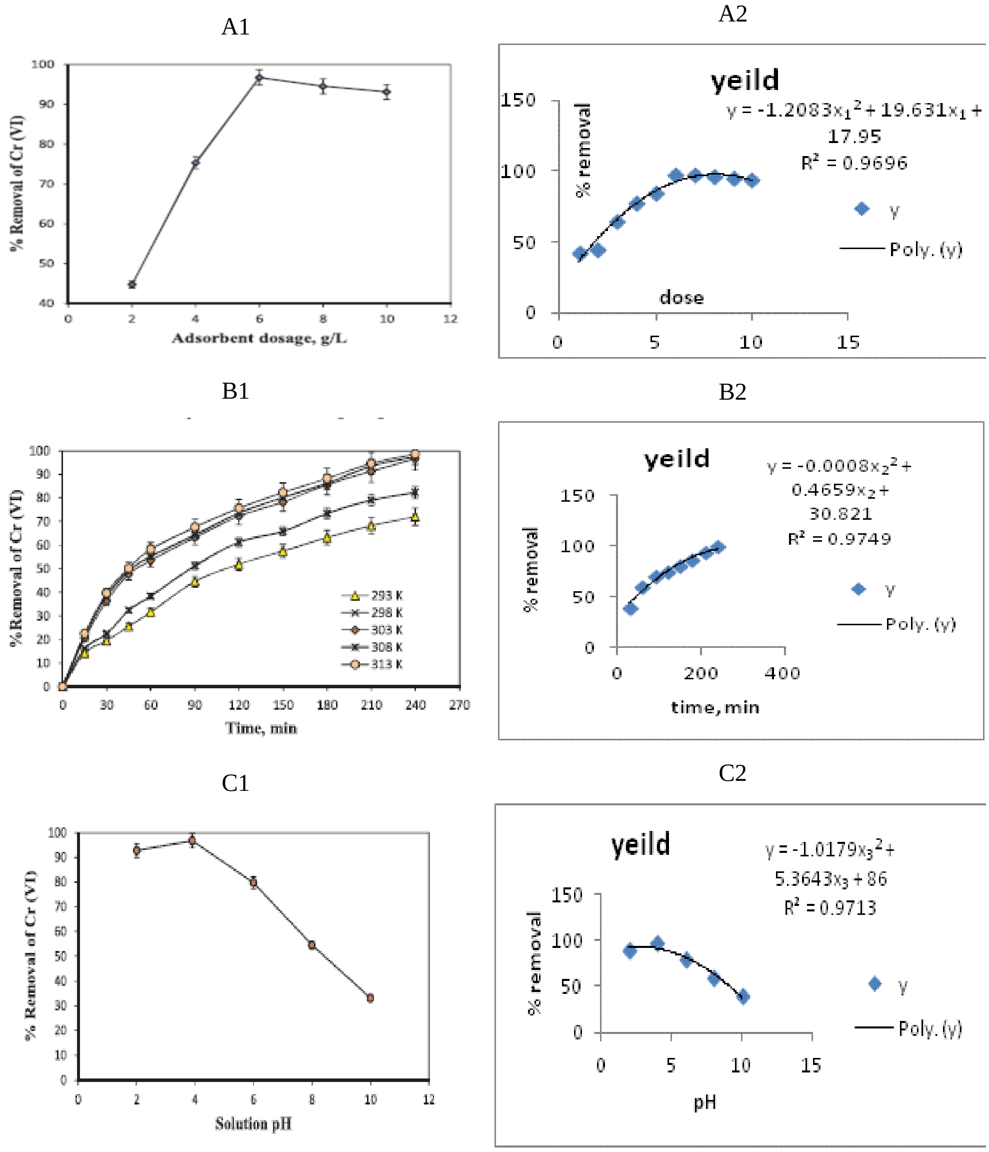

Figure 5. Three-factor variable on adsorption (A1and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency of tea wastes.

Table 5. summary and variable optimization of hexavalent chromium removal by Tea wastes.

Variables (Optimum points)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency (Y_i)
Variables	Opt. value				
X_1	6	-1.2083	19.631	17.95	92.2272
X_2	240	-0.0008	0.4659	30.821	96.557
X_3	2.634984	-1.0179	5.3643	86	93.0742

In these regression model equations, the contact time were the most factors that influences the removal efficiency of tea wastes. The pH was the next factor removal efficiency and adsorbent dose was the last for removal factors. Tea waste bio adsorbent has high removal capacity at acidic condition and high dose shown in Table 5.

4.3 *Groundnut shell adsorption capacities*

Groundnut shells are carbonaceous, fibrous solid agricultural waste that encounters disposal problem but potentially suitable for making low-cost adsorbent for adsorption of heavy metals from water and wastewaters due to its high carbon content.
The present research was conducted to utilize groundnut shell as efficient alternative adsorbent materials to remove chromium (VI) from aqueous solution using three two-parameter isotherm models.
The influence of operating conditions such as contact time, pH, adsorbent dose and initial metal concentrations.

In 2019 Jonas Bayuo articulates the adsorption capacity of groundnut shell for hexavalent chromium and according to experimental results 87.6% removal efficiency by changing the factors adsorbent dose, contact time, and pH values. In Figure 6 shows experimental result and regression model results.

$Y_1 = -9.0286X_1^2 + 38.72X_1 + 40.24$, at X_2 and X_3 are optimum values of 120 min and 10pH.
$Y_2 = -0.001X_2^2 + 0.3385X_2 + 55.636$, at X_1 and X_3 are optimum values of 2m/L and 10pH.
$Y_3 = 0.1205X_3^2 + 4.7982X_3 + 2.1$, at X_1 and X_2 are optimum values of 2m/L and 120min.

$$-9.0286X_1^2 + 38.72X_1 + 40.24 \cong 87.6 \tag{7}$$

$$-0.001X_2^2 + 0.3385X_2 + 55.636 \cong 87.6 \tag{8}$$

$$0.1205X_3^2 + 4.7982X_3 + 2.1 \cong 87.6 \tag{9}$$

According to experimental results equation 7, 8 and 9 were on changes of dose, contact time and pH respectively generated by regression equations model.

In these regression equations model, optimum values were determined for the resulting maximum value of removal efficiency. In this case, Table 6 shows 2g/L, 120min and 10, dose contact time and pH respectively result from 81.5656, 81.856, and 62.132% of removal efficiency. The Groundnut shell removal efficiency characterized that, contact time was the highly effective factor and adsorbent dose the next effective factor that affects the removal capacity. And also, the Groundnut shell was high effective removal capacity in basic conditions.

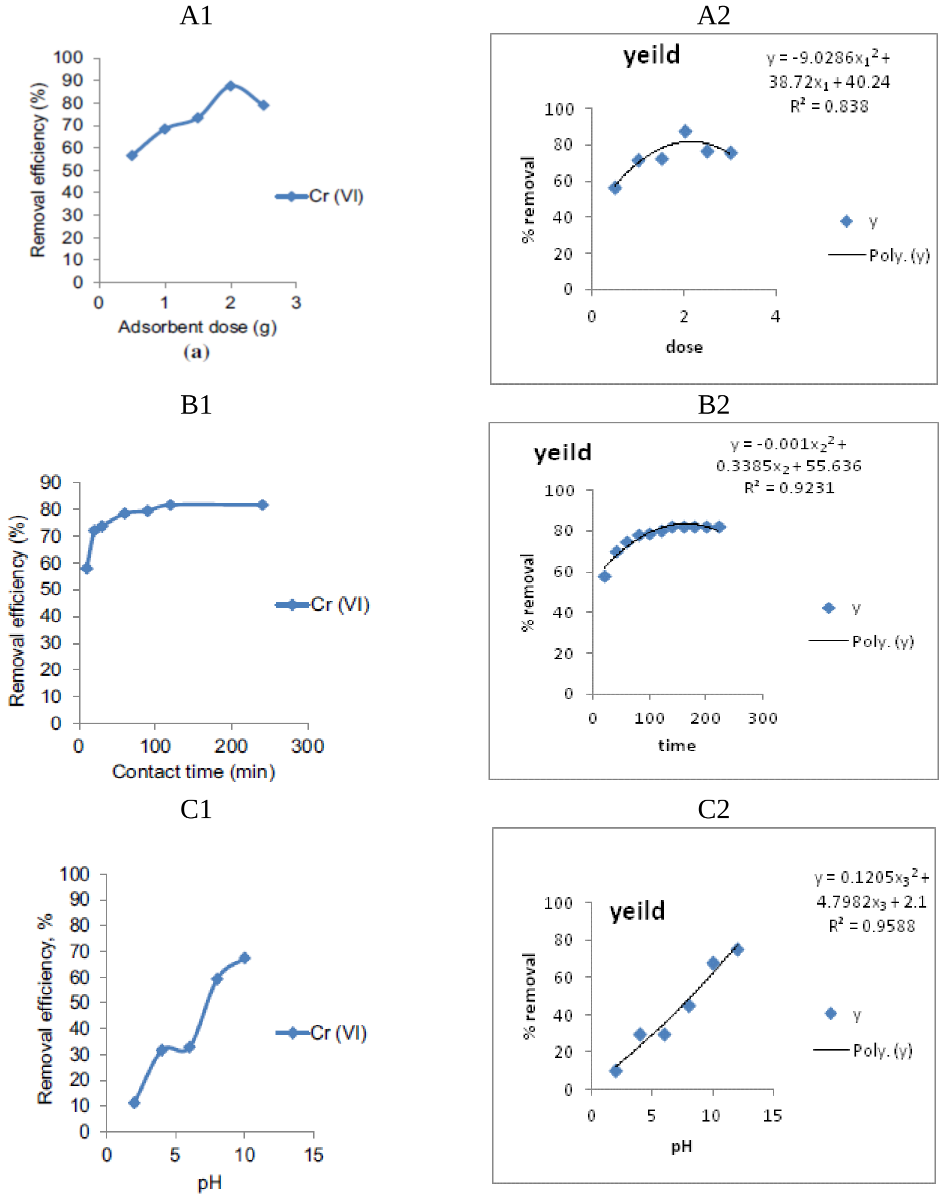

Figure 6. Three-factor variable on adsorptions (A1and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency of groundnut shell.

Table 6. Summary and variable optimization of hexavalent chromium removal by Groundnut shell.

Variables (Optimum points)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency
Variables	Opt. value				
X_1	2	-9.0286	38.72	40.24	81.5656
X_2	120	-0.001	0.3385	55.636	81.856
X_3	10	0.1205	4.7982	2.1	62.132

The method of this optimization model was generating model equation, using excel software and maximizing the removal capacity by optimizing the factor variable using solvers. The solver software is the powerful to solve any linear and nonlinear equations. The result from this model equations were greater than that of each experimental works. Almost all the recent article are used Freundlich and Langmuir equations method for optimization.

5. Modelling of adsorption efficiency of biomass activated carbon on hexavalent chromium ion removal

5.1 *Adsorption capacity of waste bamboo activated carbon*

In 2014, Tamirat Dula, Khalid Siraj, and Simeles studied on the adsorption capacity of Bamboo Activated carbon, the maximum experimental results were 98.28% by changing the basic factors of adsorbent dose, contact time and pH values. Depending on experimental values regression model equations were done for optimization (Figure 7).

$Y_1 = -34.286X_1^2 + 21.71X_1 + 95.14$, at X_2 and X_3 are optimum values of 20min and 2pH.
$Y_2 = -0.00001X_2^2 + 0.0028X_2 + 97.951$, at X_1 and X_3 are optimum values of 0.1g/L and 2pH.
$Y_3 = -0.0094X_3^2 - 0.1088X_3 + 98.512$, at X_1 and X_2 are optimum values of 0.1g/L and 20min.

$$-34.286X_1^2 + 21.71X_1 + 95.14 \cong 98.28 \tag{10}$$

$$-0.00001X_2^2 + 0.0028X_2 + 97.951 \cong 98.28 \tag{11}$$

$$-0.0094X_3^2 - 0.1088X_3 + 98.512 \cong 98.28 \tag{12}$$

Equation 10, 11 and 12 were dose, contact time and pH changes equations respectively equivalent with experimental removal efficiency. Using those three model equations 10, 11, and 12, excel optimization programming by solver table below summary optimization were done.

In bamboo activated carbon model equation optimized numerical analysis, all variable have similarly effects on the bamboo activated carbon removal efficiency on hexavalent chromium, that 98.56726%, 98.143% and 98.2568% for dose (0.3g/L), contact time (120min) and 2 pH values respectively. The removal capacities were high at acidic condition and also in low adsorbent dose results high removal efficiency that shown optimization in Table 7.

5.2 *Teff husk activated carbon*

Recently research studied on the removal efficiency Teff (Eragrostis teff) husk activated carbon by Tsegaye Adane1 · Daniel Haile1 · Awrajaw Dessie1 · Yohannes Abebe2 · Henok Dagne1 2019, and articulates the maximum removal efficiency 96.04% by changing the basic variables of adsorbent dose, contact time and pH values shows Figure 8.

$Y_1 = -0.1031X_1^2 + 4.3742X_1 + 49.032$, at X_2 and X_3 are optimum values of 124.2min and 1.92pH.
$Y_2 = -0.0039X_2^2 + 1.0007X_2 + 31.142$, at X_1 and X_3 are optimum values of 20.22g/L and 1.92pH.
$Y_3 = -12.868X_3^2 + 75.126X_3 - 10.661$, at X_1 and X_2 are optimum values of 20.22g/L and 124.2min.

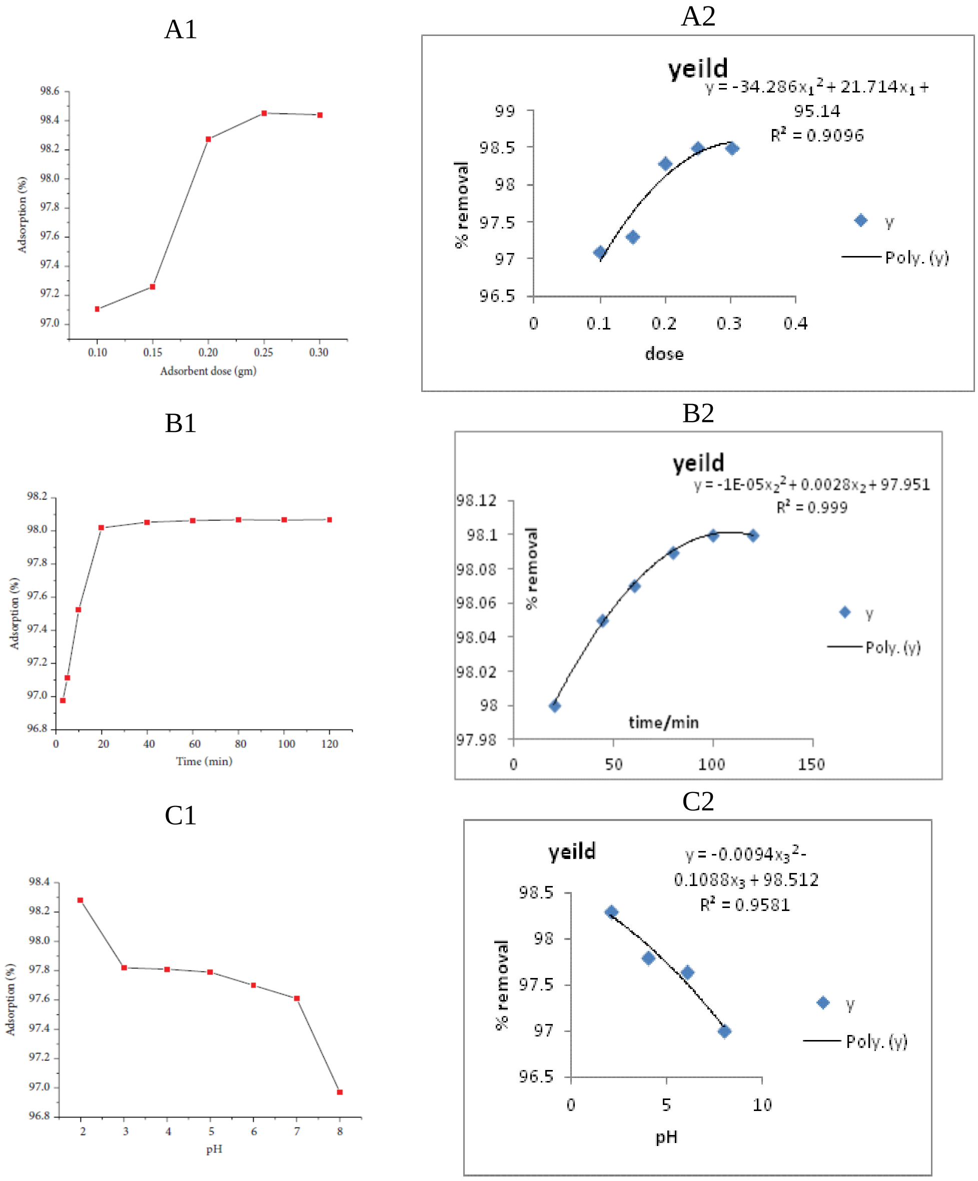

Figure 8. Three-factor variable on adsorption (A1and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency of bamboo activated carbon.

Table 7. Summary of variable optimization for hexavalent chromium removal by Bamboo activated carbon in the regression equation model.

Variables (Optimum points)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency % (Y_i)
Variables	Opt. value				
X_1	0.3	-34.286	21.71	95.14	98.56726
X_2	120	-0.00001	0.0028	97.951	98.143
X_3	2	-0.0094	-0.1088	98.512	98.2568

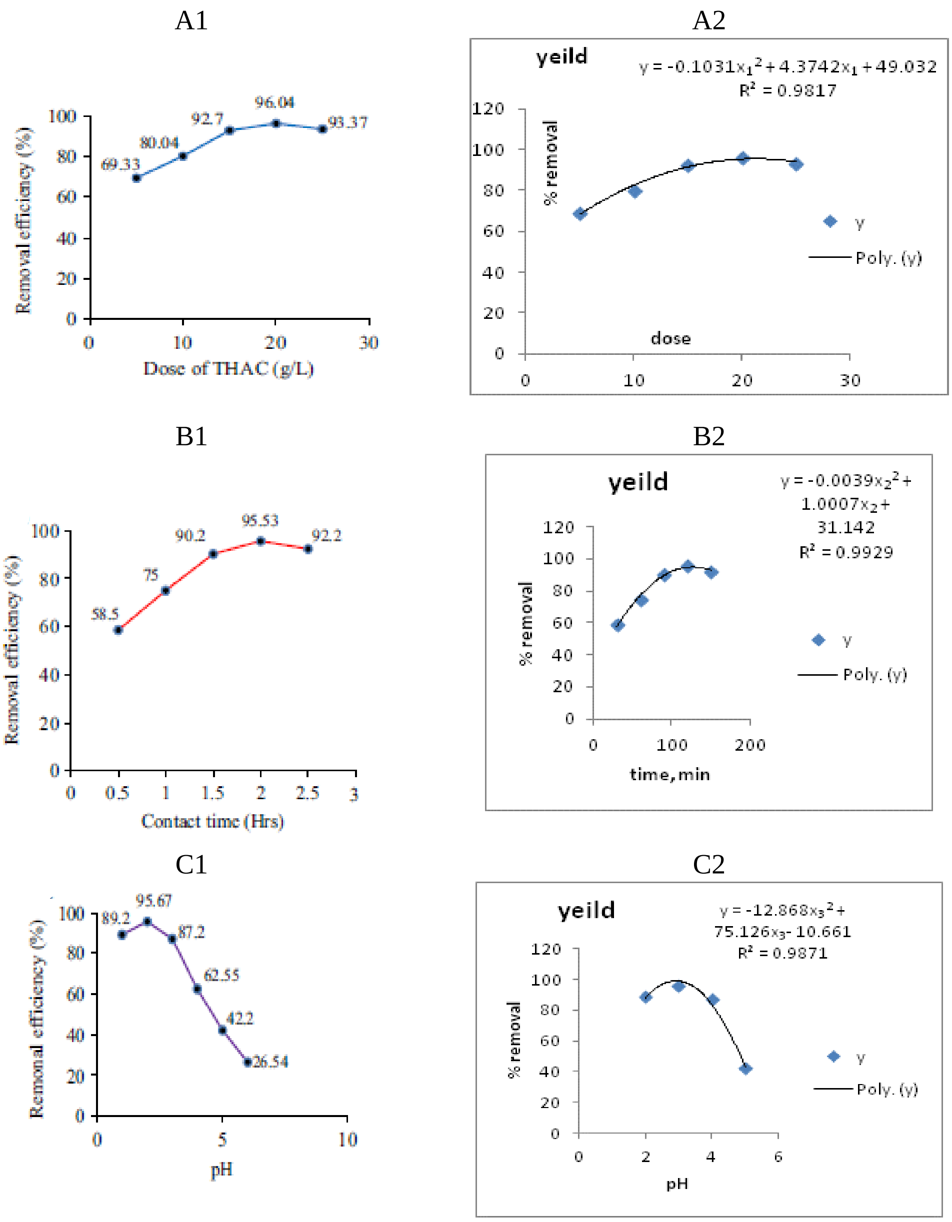

Figure 9. Three-factor variable on adsorption (A1 and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency of Teff Husk activated carbon.

Table 8. Summary of variable optimization for hexavalent chromium removal by Teff Husk activated carbon in the regression equation model.

Variables (Optimum points)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency
Variables	Opt. value				
X_1	21.21	-0.1031	4.3742	49.032	95.43
X_2	128.29	-0.0039	1.0007	31.142	95.33
X_3	2,92	-12.868	75.126	-10.661	98.99

$$-0.1031X_1^2 + 4.3742X_1 + 49.032 \cong 96.04 \quad (13)$$

$$-0.0039X_2^2 + 1.0007X_2 + 31.142 \cong 96.04 \quad (14)$$

$$-12.868X_3^2 + 75.126X_3 - 10.661 \cong 96.04 \quad (15)$$

Equation 13, 14 and 15 where change in dose with removal efficiency, change in contact time with removal efficiency and change in pH with removal efficiency respectively. The model equations were equivalent with experimental removal efficiency. The summery variable optimization for Teff husk activated carbon on chromium removal efficiency were specified using excel solver Table 8.

According to the regression model equation there where a summary of the optimum variable for hexavalent chromium removal efficiency shows in Table 8. 21.21g/L, 128.29min and 2.92 adsorbent dose, contact time and pH value respectively results 95.43%, 95.33%, and 98.99% respectively. In these results pH was the main factor variable that affects chromium removal and contact time were the last factor influence of chromium removal. The Teff husk activated carbon chromium removal capacity at high adsorbent dose and high pH values when compare to bamboo activated carbon.

5.3 *Parthenium hysterophorus weed activated carbon*

Recently research studied on the removal efficiency of *parthenium Hysterophorus* weed activated carbon by Dinaol Bedada, Kenatu Angassa Amare Tiruneh in march 2020, and articulates the maximum removal efficiency 90.5% by changing the basic variables of adsorbent dose, contact time and pH values shows Figure 9.

$Y_1 = 0.01X_1^2 + 0.45X_1 + 85.25$, at X_2 and X_3 are optimum values of 90min and 2pH.
$Y_2 = -0.0007X_2^2 + 0.221X_2 + 77.739$, at X_1 and X_3 are optimum values of 90g/L and 2pH.
$Y_3 = 0.25X_3^2 - 3.55X_3 + 97$, at X_1 and X_2 are optimum values of 90g/L and 90min.

$$0.01X_1^2 + 0.45X_1 + 85.25 \cong 90.5 \quad (16)$$

$$-0.0007X_2^2 + 0.221X_2 + 77.739 \cong 90.5 \quad (17)$$

$$0.25X_3^2 - 3.55X_3 + 97 \cong 90.5 \quad (18)$$

where, equation 16, 17 and 18 are adsorbent dose change with % removal efficiency, contact time change with % removal efficiency and pH change with % of removal efficiency respectively.

Using those three model equations excel optimization programming by solver table below summary optimization was done.

Depending on these regression equations model, Table 9 shows the optimum value of variables and maximum value of removal efficiency. 90g/L, 157.8571min and 2dose, contact time and pH value respectively results 98.25%, 95.18221% and 90.9% removal efficiency. In this modelling, adsorbent dose was the highest factor that affects the *parthenium Hysterophorus* weed activated carbon removal capacity. Contact time was the second factor variable that affects the removal capacity.

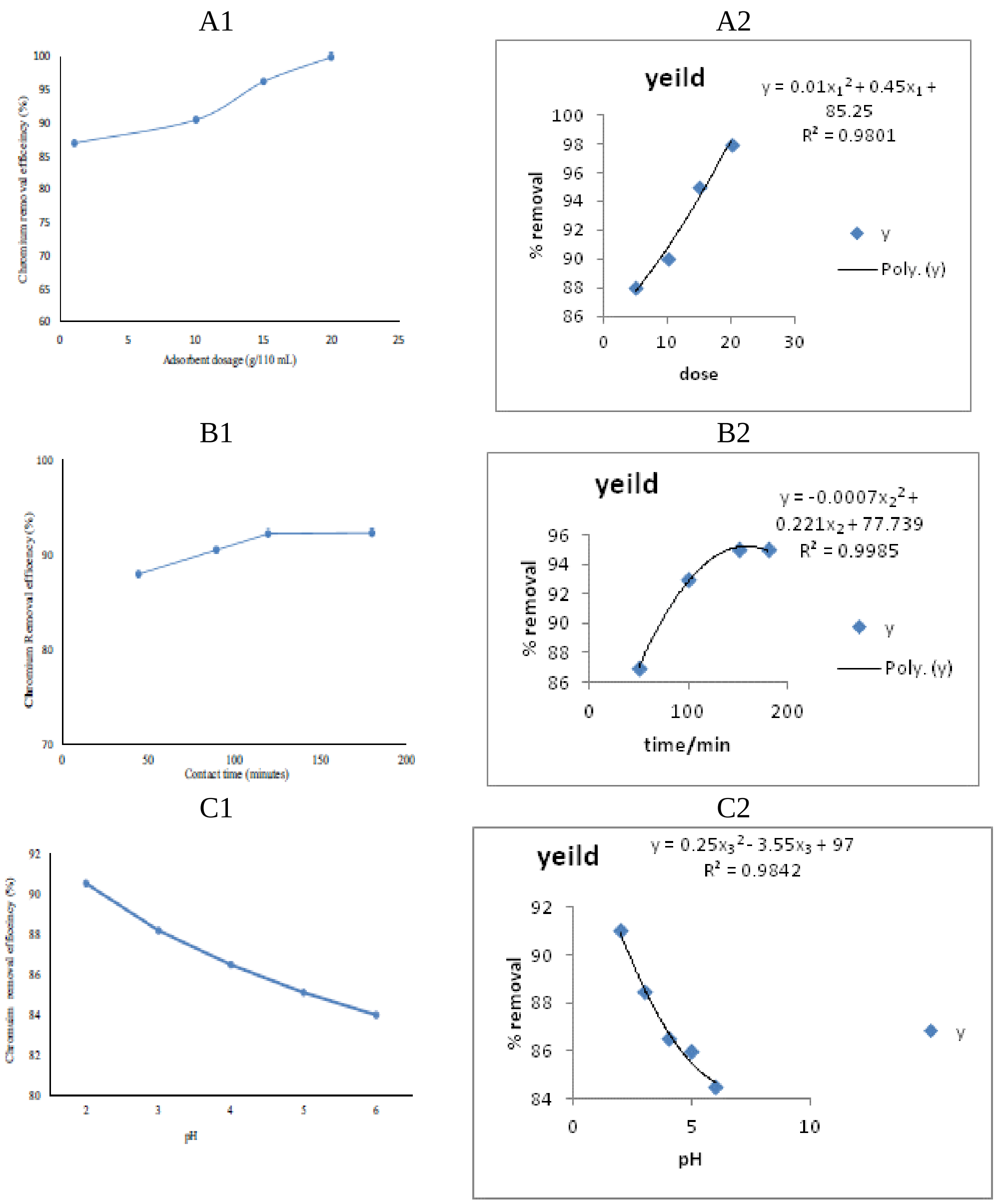

Figure 10. Three-factor variable on adsorptions (A1 and A2 Adsorbent dose from experiment and model respectively, B1 and B2 are contact time from experiment and model respectively, C1 and C2 are pH from experiment and model respectively) on hexavalent chromium removal efficiency of *parthenium Hysterophorus* weed activated.

Table 9. Summary of variable optimization for hexavalent chromium removal by parthenium hysterophorus weed activated in the regression equation model.

Variables (Optimum points)		High order coefficients	Low order coefficients	Intercepts	Maximum removal efficiency
Variables	Opt. value				
X_1	90	-0.01	0.45	85.25	98.25
X_2	157.8571	-0.0007	0.221	77.739	95.18221
X_3	2	0.25	-3.55	97	90.9

In the analysing of Bamboo, Teff husk and Weet activated carbons: bamboo activated carbon has highest removal efficiency at lowest adsorbent dose and adsorbent dose was the highest factor changes of chromium removal capacity in model optimization. Weet activated carbon high adsorption capacity at highest adsorbent dose and adsorbent dose was the highest factor on adsorption capacity according to optimization equations. In teff husk activated carbon analysed the high adsorption capacity at model optimization and pH value was the highest factor of adsorption capacity.

The method of this optimization model was generating model equation, using excel software and maximizing the removal capacity by optimizing the factor variable using solvers. The solver software is the powerful to solve any linear and nonlinear equations. The result from this model equations were greater removal efficiency than that of each experimental works. Almost all the recent article are used **Freundlich** and **Langmuir** equations method for optimization [6, 7, 20].

6. Conclusion

In the comparison hexavalent chromium removal efficiency of biomass activated carbon and bio-sorbent, there was no more difference, in some articles reviewed biosorption removal efficiency was some little amount greater than the biomass activated carbons removal efficiency. To use the bio-sorbent, there was only the physical treatment for active functional groups. In other ways no more energy and cost consumption in the bio-adsorption preparation process. But in activated carbon, there where energy consumption during the carbonization process. Depending on that data experimental specified modelling regression equation and optimization points there were maximum factor influences on each adsorbent capacity.

References

[1] H. A. Abdel-Gawwad, H. S. Hussein and M. S. Mohammed, Bio-removal of Pb, Cu, and Ni from solutions as nano-carbonates using a plant-derived urease enzyme–urea mixture, Environmental Science and Pollution Research International, **27** (2020) 30741–30754, doi:10.1007/s11356-020-09359-y.

[2] Z. Ajmal, A. Muhmood, R. Dong and S. Wu, Probing the efficiency of magnetically modified biomass-derived biochar for effective phosphate removal, Journal of Environmental Management, **235** (2020) 109730, doi:10.1016/j.jenvman.2019.109730.

[3] A. S. Ayangbenro and O. O. Babalola, A new strategy for heavy metal polluted environments: a review of microbial biosorbents, International Journal of Environmental Research and Public Health, **14 (1)** (2017), 94, doi:10.3390/ijerph14010094.

[4] A. Bashir et al., Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods, Environmental Chemistry Letters, **17 (2)** (2019) 729–754, doi:10.1007/s10311-018-00828-y.

[5] A. Baysal, N. Ozbek and S. Akman, Determination of trace metals in waste water and their removal processes, Waste-Water Treatment Technologies and Recent Analytical Developments, **1** (2013) 145–171, doi:10.5772/52025.

[6] D. Bedada, K. Angassa, A. Tiruneh, H. Kloos and J. Fito, Chromium removal from tannery wastewater through activated carbon produced from Parthenium hysterophorus weed, Energy, Ecology and Environment, **5 (3)** (2020) 184–195, doi:10.1007/s40974-020-00160-8.

[7] W. Cai, J. Wei, Z. Li, Y. Liu, J. Zhou and B. Han, Preparation of amino-functionalized magnetic biochar with excellent adsorption performance for Cr (VI) by a mild one-step hydrothermal method from peanut hull, Colloids and Surfaces A: Physicochemical and Engineering Aspects, **563** (2019) 102–111, doi:10.1016/j.colsurfa.2018.11.062.

[8] T. Chen, N. Zhang, Z. Xu, X. Hu and Z. Ding, Integrated comparisons of thorium (IV) adsorption onto alkali-treated duckweed biomass and duckweed-derived hydrothermal and pyrolytic biochar, Environmental Science and Pollution Research, **26 (3)** (2019) 2523–2530, doi:10.1007/s11356-018-3789-x.

[9] L. F. Cusioli, H. B. Quesada, A. T. Baptista, R. G. Gomes and R. Bergamasco, Soybean hulls as a low-cost biosorbent for removal of methylene blue contaminant, Environmental Progress & Sustainable Energy, **39 (2)** (2020) e13328, doi:10.1002/ep.13328.

[10] S. De Gisi, G. Lofrano, M. Grassi and M. Notarnicola, Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review, Sustainable Materials and Technologies, **9** (2016) 10–40, doi:10.1016/j.susmat.2016.06.002.

[11] M. Dizbay-Onat, E. Floyd, U. K. Vaidya and C. T. Lungu. Applicability of industrial sisal fiber waste derived activated carbon for the adsorption of volatile organic compounds (VOCs), Fibers and Polymers, **19 (4)** (2018) 805–811, doi:10.1007/s12221-018-7866-z.

[12] L. Dong, L. Hou, Z. Wang, P. Gu, G. Chen and R. Jiang, A new function of spent activated carbon in BAC process: removing heavy metals by ion exchange mechanism, Journal of Hazardous Materials, **359** (2018) 76–84, doi:10.1016/j.jhazmat.2018.07.030.

[13] G. L. Dotto, N. P. G. Salau, J. S. Piccin, T. R. S. A. Cadaval and L. A. A. de Pinto, Adsorption kinetics in liquid phase: modeling for discontinuous and continuous systems, In Adsorption Processes for Water Treatment and Purification, Springer, (2017) 53–76, doi:10.1007/978-3-319-58136-1_3.

[14] L. Goswami, N. A. Manikandan, K. Pakshirajan and G. Pugazhenthi, Simultaneous heavy metal removal and anthracene biodegradation by the oleaginous bacteria Rhodococcus opacus, 3 Biotech, **7 (1)** (2017), 37, doi:10.1007/s13205-016-0597-1.

[15] M. Kavand, E. Fakoor, S. Mahzoon and M. Soleimani, An improved film–pore–surface diffusion model in the fixed-bed column adsorption for heavy metal ions: single and multi-component systems, Process Safety and Environmental Protection, **113** (2018) 330–342, doi:10.1016/j.psep.2017.11.009.

[16] V. Kumar et al., Global evaluation of heavy metal content in surface water bodies: A meta-analysis using heavy metal pollution indices and multivariate statistical analyses, Chemosphere, **236** (2019) 124364, doi:10.1016/j.chemosphere.2019.124364.

[17] F. Migahed, A. Abdelrazak and G. Fawzy, Batch and continuous removal of heavy metals from industrial effluents using microbial consortia, International Journal of Environmental Science and Technology, **14 (6)** (2017) 1169–1180, doi:10.1007/s13762-016-1229-3.

[18] C. V. Mohod and J. Dhote. Review of heavy metals in drinking water and their effect on human health, International Journal of Innovative Research in Science, Engineering and Technology, **2 (7)** (2013) 2992–2996.

[19] T. C. Nguyen et al., Adsorption ability for toxic chromium (VI) ions in aqueous solution of some modified oyster shell types, Bioinorganic Chemistry and Applications, **2020** (2020), Article ID 2435777, doi:10.1155/2020/2435777.

[20] S. O. Owalude and A. C. Tella, Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull, Beni-Suef University Journal of Basic and Applied Sciences, **5 (4)** (2016) 377–388, doi:10.1016/j.bjbas.2016.11.005.

[21] Ș. Parlayici and E. Pehlivan, Comparative study of Cr (VI) removal by bio-waste adsorbents: equilibrium, kinetics, and thermodynamic, Journal of Analytical Science and Technology, **10 (15)** (2019) 1–8, doi:10.1186/s40543-019-0175-3.

[22] M. Rafatullah, S. Ismail and A. Ahmad, Optimization study for the desorption of methylene blue dye from clay based adsorbent coating, Water, **11 (6)** (2019), 1304, doi:10.3390/w11061304.

[23] J. E. Rager, M. Suh, G. A. Chappell, C. M. Thompson and D. M. Proctor, Review of transcriptomic responses to hexavalent chromium exposure in lung cells supports a role of epigenetic mediators in carcinogenesis, Toxicology Letters, **305** (2019) 40–50, doi:10.1016/j.toxlet.2019.01.011.

[24] C. V. Rao et al., Biological effects and epidemiological consequences of arsenic exposure, and reagents that can ameliorate arsenic damage in vivo, Oncotarget, **8 (34)** (2017) 57605–57621, doi:10.18632/oncotarget.17745.

[25] K. Salnikow and A. Zhitkovich, Genetic and epigenetic mechanisms in metal carcinogenesis and cocarcinogenesis: nickel, arsenic, and chromium, Chemical Research in Toxicology, **21 (1)** (2008) 28–44, doi:10.1021/tx700198a.

[26] K. Sartova, E. Omurzak, G. Kambarova, I. Dzhumaev, B. Borkoev and Z. Abdullaeva, Activated carbon obtained from the cotton processing wastes, Diamond and Related Materials, **91** (2019) 90–97, doi:10.1016/j.diamond.2018.11.011.

[27] S. Sharma, S. Tiwari, A. Hasan, V. Saxena and L. M. Pandey, Recent advances in conventional and contemporary methods for remediation of heavy metal-contaminated soils, 3 Biotech, **8 (4)** (2018), 216, doi:10.1007/s13205-018-1237-8.

[28] M. C. Villarín and S. Merel, Paradigm shifts and current challenges in wastewater management, Journal of Hazardous Materials, **390** (2020) 122139, doi:10.1016/j.jhazmat.2020.122139.

[29] T. Weldeslassie, H. Naz, B. Singh and M. Oves, Chemical contaminants for soil, air and aquatic ecosystem, In Modern Age Environmental Problems and Their Remediation, Springer, (2018) 1–22, doi:10.1007/978-3-319-64501-8_1.

[30] C. Yacou, S. Altenor, B. Carene and S. Gaspard, Chemical structure investigation of tropical Turbinaria turbinata seaweeds and its derived carbon sorbents applied for the removal of hexavalent chromium in water, Algal Research, **34** (2018) 25–36, doi:10.1016/j.algal.2018.06.014.

[31] J. Yang et al., Optimized mesopores enabling enhanced rate performance in novel ultrahigh surface area meso-/microporous carbon for supercapacitors, Nano Energy, **33** (2017) 453–461, doi:10.1016/j.nanoen.2017.02.007.f

[32] Q. Yu, J. P. Delgado, R. Veneman and D. W. Brilman, Stability of a benzyl amine based CO2 capture adsorbent in view of regeneration strategies, Industrial & Engineering Chemistry Research, **56 (12)** (2017) 3259–3269, doi:10.1021/acs.iecr.6b04645.

[33] Y. Yu et al., Fluffy honeycomb-like activated carbon from popcorn with high surface area and well-developed porosity for ultra-high efficiency adsorption of organic dyes, Bioresource technology, **285** (2019) 121340, doi:10.1016/j.biortech.2019.121340.

[34] J. Zhao, L. Yu, H. Ma, F. Zhou, K. Yang and G. Wu, Corn stalk-based activated carbon synthesized by a novel activation method for high-performance adsorption of hexavalent chromium in aqueous solutions, Journal of Colloid and Interface Science, **578** (2020) 650–659, doi:10.1016/j.jcis.2020.06.031.

[35] Y. Zhou, D. Hou, J. Jiang, L. Liu, W. She and J. Yu, Experimental and molecular dynamics studies on the transport and adsorption of chloride ions in the nano-pores of calcium silicate phase: the influence of calcium to silicate ratios, Microporous and Mesoporous Materials, **255** (2018) 23–35, doi:10.1016/j.micromeso.2017.07.024.