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Adsorption of High Chromium Concentrations from Industrial Wastewater Using Different Agricultural Residuals

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Abstract

Hexavalent chromium Cr (VI) is a toxic material used in many industries such as tanneries and electroplating industries. Most of the previous researches studied the removal of chromium at lower concentrations up to 600 mg/L but did not tackle the behavior at higher concentrations, which resemble the real concentration of studied tanneries effluents. The present research is a comparative study of different agricultural low cost adsorbents in the removal of high Chromium concentration from industrial wastewater up to 1000 mg/L, compared to a commercial activated carbon. The tested adsorbents are (Banana Waste (BW), Sawdust (SD), Phragmites Australis (PA), Sugarcane Bagasse (SCB), Pea pod peels (PPP) and Rice straw (RS)). The materials were chemically pretreated with acid-alkali except BW was treated with acid only, to improve adsorbent metal binding capacity. Batch experiments were conducted to study the effect of pH, adsorbent dosage, contact time, initial Chromium concentration and temperature on the removal efficiency of Chromium from wastewater. The experiments were conducted in two sets, one for lower concentration (25-50-100-200-400) mg/L and the other for higher concentration (600-800-1000) to simulate the concentration of Chromium in tannery industry effluents. At 1000 mg/L initial concentration, BW achieved the optimum removal efficiency of 73.28% at pH = 3, adsorbent dosage = 25 g/L and contact time of 3 hours with the adsorption capacity was 39 mg/g. For SD at pH=2, 3 hours contact time, 10 g/L dosage, and 30°C the removal ratio was 64.83% and the adsorption capacity was 86.30 mg/g. The equilibrium data for various agricultural adsorbents was being tested with various adsorption isotherm models such as Langmuir, Freundlich and Tempkin. At low concentrations, AC, BW, PA and SCB follows Freundlich isotherm model while SD follows Langmuir isotherm model. At higher concentrations, BW, SD, PA follows Langmuir isotherm while SCB follows Tempkin isotherm model. To evaluate the mechanism of Cr adsorption on different adsorbents, Pseudo-first-order and Pseudo-second-order equations were used. The adsorption process follows Pseudo-second-order for all adsorbents, which confirms the chemisorption of Cr (VI) on different adsorbents.

Keywords: Chromium; adsorption; low cost adsorbents; Industrial wastewater; isotherms; kinetics; high concentrations

1 Introduction

A wide range of toxic inorganic and organic chemicals are discharged into the environment as industrial wastes, causing critical pollution problems (1). Water pollution caused by toxic heavy metal ions has become a serious environmental problem. A serious health hazard results from dissolved heavy metals escaping into the environment, which accumulate throughout the food chain in living tissues, multiplying their effects (2). Chromium is an important heavy metal that is released into natural water from various sources, including electronics, electroplating, metallurgical, and leather tanning industries (3) (4). It is found in nature in two different forms as trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)) (5) (6) (7) (8). Chromium (III) is relatively insoluble and useful micronutrient for human, plants, and animals metabolism whereas chromium (VI) is primary contaminant and more toxic, carcinogenic and mutagenic to living organisms than other heavy metals (9) (7). In addition, it also has an effect on human skin, liver, kidney, and respiratory organs (10). Therefore, it is necessary to eliminate Cr (VI) from the environment, in order to prevent the deleterious impact of Cr (VI) on ecosystem and public health (4). According to WHO, the maximum allowable limits for chromium in wastewater is 1.0 mg/L while in drinking water is 0.05 mg/L (5).

The process of tanning using chromium compounds is one of the most common methods of processing the hides. Around 60-70 % of chromium reacts with the hides in this process. In other words, about 30-40% of the chromium remains in the solid and liquid. Hence, the wastewater of tanning process is an important source of chromium pollution. In addition, it is desirable to recover chromium from the wastewater (11) (12). A number of methods are available for the removal of heavy metals from aqueous solution. These methods include chemical precipitation, ion exchange, membrane separation process, electrocoagulation and adsorption (2)(13)(7). Although the chemical precipitation has traditionally been the most used method (14), it suffers from many draw backs like incomplete removal, requirement of sizable quantities of treatment chemicals and production of large amount of toxic sludge. A variety of other treatment technologies were considered and evaluated. Techniques such as the exchange of ions and the adsorption using products from naturally occurring materials

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such as activated carbon have been considered as better alternatives. The exorbitant cost involved with ion exchange makes it prohibitive for wide application (15). Among all these methods, adsorption is the most popular since it is a very simple technique due to its convenience, ease of operation, and versatility (16) (9). This process can minimize or eliminate various types of pollutants and has therefore a wide range of applications in wastewater treatment (13).

The most common used adsorbents are nanomaterials and activated carbon as they have large surface area, adsorption capacity and microporous structure but their cost are high (9). Therefore, it is necessary to look for a cheaper and easily available alternate. Consequently, a large number of available low-cost adsorbents including agro-based material are used to remove Chromium from polluted wastewater. The most popular adsorbents prepared from agricultural wastes are Banana Waste (BW), Sawdust (SD), Sugarcane Bagasse (SCB), Phragmites Australis (PA), Pea Pod Peels (PPP) and Rice straw (RS). Many researchers seek the optimum operating parameters for each of these adsorbents including pH, adsorbent dosage, initial concentration and contact time as well as preparation methods. (17) used 0.1 N NaOH and 0.5 N NaOH as a chemical preparation for Banana Waste (BW) to increase its adsorption capacity. Although the pH is an important parameter; its effect and optimum value is a controversial topic, (18) reported that optimum removal achieved at pH of 1, while (19) and (20) found that optimum pH was at pH 3. On the other hand; (21) concluded that the optimum pH was 7. Different adsorbent dosage ranges were used to find the effect of dosage on Cr (VI) removal. The optimum dosage was 0.4, 4 and 20 gm/L according to (18), (19) and (20). The initial concentration was studied also in a range of 1 to 70 mg/L by (18), (21) and (20) while (19) studied the effect of initial concentration at 100 to 600 mg/L. The contact time also was studied from 10 minutes to 270 minutes. Finally, the effect of temperature was studied in a range from 10 to 70^{o}C.

Different studies were applied on Sawdust for the adsorption of Cr (VI) at a pH range of 1 to 11 and using different dosages from 4 to 24 gm/L, the examined initial concentration ranged from 5 to 500 mg/L and contact time from 10 up to 1100 minutes. The optimum removal efficiency was at lower pH according to (S. Gupta & Babu, 2009, (22). (10) and (9) Whereas (23) found that the optimum removal at pH value of 6 after 1 hour contact time, using 1g/L dosage and 20 mg/L initial concentration. Many researches used raw Sugarcane bagasse (SCB) and modified Sugarcane bagasse for the adsorption of chromium from polluted water. Washed SCB with distilled water is examined at pH range from 1 to 7 for different time intervals at low chromium concentrations ranging from 5 to 120 mg/L (24) (25) (26) (27) (28) (2). Modifications on SCB was done through carbonization under N_2 flow (29) or through chemical modification using H_2SO_4 to increase its surface area and the degree of micro porosity(30). Phragmites Australis is used as a new low cost adsorbent for the removal of COD, BOD,TSS and TDS as it is available around drains and also causes environmental problems (31). Phragmites Australis is also used in constructed wetlands to remove Chromium, Boron, Nitrogen and Phosphorous from tannery industrial wastewater because of its ability to adapt to climatic conditions. The optimum removal efficiency for Cr was 48% at HRT = 3 days when the initial concentration was 0.23 mg/L(32). Biochar was produced using pyrolysis process in the presence of nitrogen gas on Green Pea Pod Peels (GPPP) to be used in Cr (IV) removal under different conditions(4). (4) studied the potential of using biochar from GPPP in a pH rang of (2-7), biochar dosages (0.5 – 5 g/L), initial Cr (VI) concentrations (20-200 g/L) and contact time till 300 min at 30^{o}C. (20) used the modification of PPP with NaOH and HCl to increase the adsorptive characteristics of PPP. Many methods for modification of Rice Straw were done to increase its adsorption of heavy metals. First of all is the biochar production at different temperatures of 300, 500 and 700^{o}C as investigated by (3). (33) modified RS with acid treatment using nitric acid and CaO and alkali treatment using NaOH and urea. Modification with NaOH only is used by (34). (35) modified the rice husk with tartaric acid while (36) used KOH for the production of rice straw carbon (RSC) and rice straw activated carbon (RSAC). Activated Carbon (AC) is considered the best adsorbent for heavy metal because of the large internal surface area, pours availability and high microporous(37). AC is preferred for its very high surface areas, porous sorbent , functional groups, high capacity, high rate of adsorption, great capacity to adsorb a wide range of pollutants, fast kinetics and a high quality treated effluent (38). On the other hand, the main disadvantages of AC are its very expensive cost, requires complexing agents to improve its removal performance and its performance is dependent on the type of carbon (39) (40). Most of the previous studies gave great attention to low concentration for heavy metals(5 – 400 mgL^{-1}) and studied the effect of low cost adsorbents in the removal of such metals but they didn't study the effect of these materials on high concentration. Therefore, the main objective of this study is to investigate the effect of these materials on the removal of Chromium from low and high concentration industrial wastewater up to 1000 mg/L.

2 Material and Methods

2.1 Adsorbents Preparation and Treatment

In the current study, the effectiveness of six low cost adsorbent materials in the removal of Chromium from tannery industrial wastewater compared to the efficiency of charcoal Activated Carbon (AC) was investigated. The materials are BW, SD, SCB, PA, PPP and RS. The utilized materials are solid waste that will increase environmental pollution problems if not properly disposed of. BW, PPP and SCB are collected from fruit sellers and farmhouse while SD is collected from wood workshops; RS from fields and finally PA are collected from El-Agoa canal in Zagazig city, located at the Nile Delta zone of Egypt. Each utilized material was treated as followed: (1) it was dried at sunlight for a week and then washed many times with distilled water to get rid of any dusts, impurities and inorganic materials. (2) Oven dried at 90°C for three days (5 h daily). (3) The material was then grinded and sieved through 100 and 200 mesh (Standard Sieves Dual Manufacturing Co., USA) for uniform size distribution. (4) The powder was then washed several times with distilled water to get rid of lighter materials and other impurities. (5) The adsorbents were then used in one of three ways. First, used directly. Second, dipped in 0.1 N NaOH for 9 hours and washed with distilled water to remove the lignin and then dried again then rinsed separately with double-distilled water two times and dipped into 0.1 N HCl for 9 hours again to remove traces of alkalinity (16). Third, dipped in HCL only for 9 hours. Finally, the treated adsorbents were thoroughly washed with double-distilled water, then dried in a desiccator and stored there.

2.2 Preparation of Chromium Solution

All the chemicals used are of analytical grade (AR). A stock solution of 1000 mg/L of Cr (VI) is prepared by dissolving 2.8287 g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solutions containing 25-50-100-200-400-

600 and 800 mg /L of Cr (VI). pH adjustment is done using 0.5 N HCl and 0.5 N NaOH solutions.

2.3 Adsorption Kinetics

In the adsorption process, it is important to study the kinetics of the adsorption to understand and predict how time affects mobility and retention of heavy metals. In order to define the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption process were studied at different time intervals(6). The Pseudo–first-order and Pseudo–second-order equations are the most popular models used to describe the kinetics of Chromium adsorption. The general expression for Pseudo–first-order equation model is:

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (1)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at any time t and k is the Pseudo–first-order rate constant (hr^{-1}). By applying the boundary conditions after integration of both sides from t = 0 to t = t and q_t = 0 to q_t =q_t, the linear form of the equation becomes:

$$\log(q_e - q_t) = log q_e - \frac{k}{2.303} t \quad (2)$$

The values of q_e and k at different initial concentrations are calculated from the slope and intercept of the plots of log (q_e - q_t) versus t (18). The Pseudo–second-order chemisorption kinetic rate equation is also expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at any time t and k_2 is the Pseudo–second-order rate constant (g/mg/hr). By applying the boundary conditions after integration of both sides from t = 0 to t = t and q_t = 0 to q_t =q_t, the integrated form of the equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad (4)$$

The rate constant k_2 (g/mg/hr)and equilibrium adsorption capacity q_e are calculated from the slope and intercept of the linear plot of t (time) Vs t/q_t (19).

2.4 Adsorption Isotherm Models

In order to understand the distribution of the metal ions in the liquid and solid phases at equilibrium at a certain temperature, there is a need to fit the different isotherm models with the experimental data (23). The most applied isotherm models are; Langmuir, Freundlich and Tempkin models.

2.4.1 Langmuir Isotherm Model

Langmuir equation is based on the assumptions that maximum adsorption occurs on a saturated mono-layer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface(18). The linearized form is:

$$\frac{C_e}{q_e} = \frac{1}{b\, Q_m} + \frac{1}{Q_m} C_e \quad (5)$$

where, Q_m and b are Langmuir constants related to the sorption capacity (the amount of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g)), and sorption energy which quantitatively reflects the affinity between the adsorbent and adsorbate (L/mg) , respectively. C_e is the equilibrium concentration in (mg/L) , and q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g) at equilibrium (21). The plot of C_e versus C_e/q_e gives a linear form if the adsorption equilibrium obeys Langmuir equation. An extended analysis of the Langmuir equation can be made based on a dimensionless equilibrium parameter, R_L, also known as the separation factor,

$$R_L = \frac{1}{1 + b\, C_o} \quad (6)$$

If the value of R_L obtained between 0 and 1, it is a favorable adsorption, while if R_L > 1, this denotes an unfavorable adsorption, and if R_L = 1, this represents the linear adsorption, while the adsorption operation is irreversible if R_L = 0.

2.4.2 Freundlich Isotherm Model

The Freundlich model supposes that the adsorption of metal ions takes place on a non-ideal heterogeneous surface by multilayer adsorption. For adsorption from solution, the Freundlich isotherm is expressed in the linear form as:

$$\log q_e = \log K_F + n_F \log C_e \quad (7)$$

where, K_f ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent; the larger its value, the higher the capacity. and n_F is the adsorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. and is also known as Freundlich coefficient(6). If the value of n is unity, then the partition is independent of their concentration between the two phases. The value of n below unit therefore indicates normal adsorption, while the value of n above one indicates co-operative adsorption(21).

2.4.2 Tempkin Isotherm Model

The Tempkin isotherm explained the nature of adsorption heterogeneous system. The Tempkin isotherm assumes that the adsorption heat linearly decreases with increasing adsorption capacity(9). The linear form of Tempkin equation is given by:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (8)$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant (8.314 J/mol.^{o}K). The constant b_T is related to the heat of adsorption (J/mol), A_T is the equilibrium binding constant (L/g) corresponding to the maximum binding energy. Most of the previous studies are limited to the removal of low initial Cr concentrations (5 – 600 mg/L). The main objective of the present study is to examine the adsorption capacity of different low cost agricultural waste materials at high Cr concentrations (600-1000 mg/L). The above review illustrated that there are many different methods for absorbent preparation. Moreover, extensive studies concerning the operating parameters are recommended. In the present study the optimum operating parameters (including pH, adsorbent dosage, initial concentration and contact time as well as preparation methods) for the six different adsorbents (BW, SD, SCB, PA, PPP and RS) will be assessed. Activated Carbon will be examined as standard and reference adsorbent.

2.5 Batch Experiments

The batch experiments were conducted in 50 ml conical flasks. The amount of adsorbent was added in 20 ml of aqueous Cr (VI) solutions, and then mixed in water bath mechanical shaker at 30ºC. The treated solution is finally filtered before analysis. The main investigated parameters are in Table (1).

The high concentration range was studied in a range of 600 to 1000 mg/L based on the characterization of real samples from El-Robiekey factories for tanning in Badr city-Egypt and Quesna tanneries in Quesna city-Egypt, which ranged from 560 to 970 mg/L.

2.6 Instruments

All measurements were conducted according to standard methods. The concentration of Chromium ions in the influent as well as the effluent was measured using Atomic Absorption Spectrophotometer (ThermoFisher–iCE 3000 series) model with air –acetylene gas and wave length of 357.9 nm in the faculty of Agriculture central laboratory- Zagazig University, Egypt.

3 Results and Discussion

Using observations of the sorption studies to optimize the pH, adsorbent dosage, initial chromium concentration, contact time, and temperature have been plotted to determine the feasibility of sorption system along with its mechanisms through kinetics. The results of batch studies were compared for different adsorbents used in the study. The effect of treatment method for materials also have been studied.

3.1 Effect of Adsorbent Preparation Methods and Treatment

Figure (1) shows the effect of preparation methods on the sorption efficiency. The experiments were performed at pH 3, 50 mg/L initial concentration, 1hr contact time, 5 g/L adsorbent dosage and 30 ^{O}C. The results indicated that the chemical treatment of the adsorbent using NaOH followed by HCl achieved higher removal efficiency. BW was the only adsorbent that shows higher efficiency when treated with HCL only.

Table 1: Various parameters considered during batch experimental study.

	Parameter	Initial Cr (VI) concentration (mg/L)	Adsorbent dosage (g/L)	Contact time (hr)	pH	Temperature (ºC)
At lower concentrations	Initial Cr (VI) concentration	25-400	5	1	3	30
	Adsorbent dosage	50	2-20	1	3	30
	Contact time	50	5	1-5	3	30
	pH	50	5	1	1-6	30
At higher concentrations	Initial Cr (VI) concentration	600-1000	optimum	optimum	optimum	30
	Temperature	1000	optimum	optimum	optimum	30-70

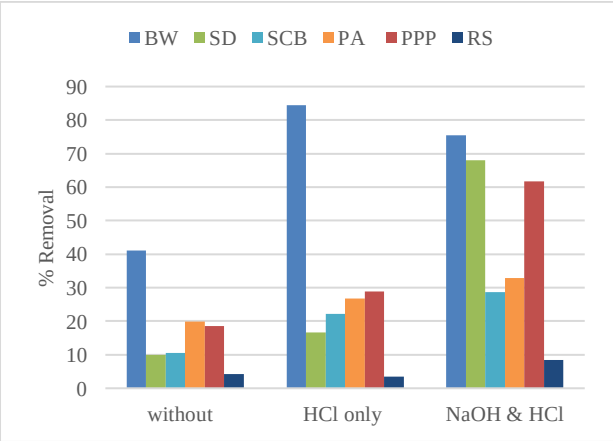

Figure 1: Effect of adsorbent preparation methods

3.2 Effect of pH on Cr adsorption

The pH of a solution is regarded as a significant parameter in the adsorption of Cr ions. The effect of pH on the efficiency of the different adsorbents compared to the activated carbon were investigated at the following conditions initial concentration = 50 mg/L, dosage = 5 g/L, 30ºC and contact time 1 hr. The results revealed that Cr ions adsorption by the materials were highly pH-dependent as shown in Figure (2). Each material has its own behavior at different pH values, most of the examined material show high removal at low pH 2 to 3. BW as well as AC achieved its optimum efficiency at pH 3. It was evident that the most prevalent form of Cr (VI) in aqueous solution was acid chromate ($HCrO^{-}_{4}$), chromate (CrO_4^{-2}), dichromate ($Cr_2O_7^{-2}$) and other oxyanions of Cr. The dominant form of Cr (VI) at initial pH of 2 is acid chromate ($HCrO_4^{-1}$). Increase in pH facilitates the conversion of $HCrO_4^{-1}$ to other forms, CrO_4^{-2} and $Cr_2O_7^{-2}$. At lower pH, the adsorbent has a positive charge because of protonation, and dichromate ion exists as anion and the electrostatic forces developed between

them, resulting in a high adsorption at lower pH. The removal efficiency of Cr (VI) reduced significantly at higher pH due to the competition between OH^- and chromate ions (CrO_4^{-2}), where the former being the dominant species reach the adsorbent surface more quickly than chromium species (18)(41)(42). It is well-known fact that the surface adsorbs anions favorably in low pH range due the presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH values due to the accumulation of (OH^-) ions (16). The highest value obtained was 82.83 % for sawdust at pH=2. Similar observations for best removal efficiency were reported by (19) at pH= 3, (9) at pH = 2 and (7) at pH = 3.

3.3 Effect of Adsorbent Dosage on Cr Adsorption

As shown in Figure (3-a), the percentage chromium removal is directly proportional to adsorbent dose. The effect of adsorbent dosage was studied at pH=3, contact time = 1 hr, initial chromium concentration of 50 mg/L and at 30 °C. Using 5 g/L of BW is sufficient to adsorb about 80% Cr (VI) having 50 mg/L initial concentration within 1.0 h. On further increasing, the adsorbent dose to 20 g/L the removal efficiency was observed to be almost constant. This may be due to some of the adsorption sites remaining unsaturated during the adsorption process. The increase in the adsorbent dosage provides more exchangeable sites or surface area of the adsorbent. Interference among binding sites owing to increased adsorbent dosage cannot be ruled out as this will result in low specific uptake (31).

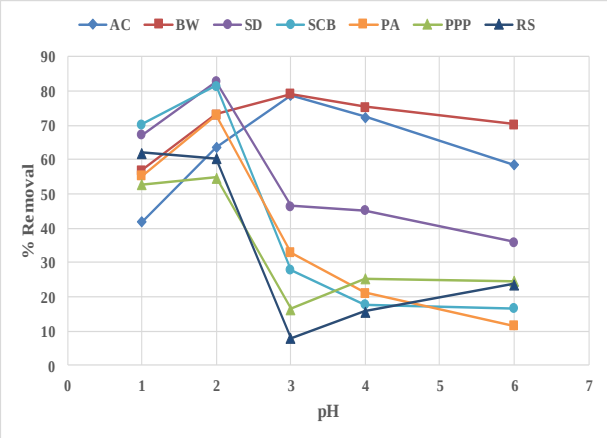

Figure 2: Effect of pH on Cr adsorption efficiency

Similarly, 20 g/L adsorbent dose of sawdust adsorbs more than 60% at pH 3.0; Phragmites Australis adsorbs more than 45% at pH 3.0. Matching trends were also reported by (6), (43) and (2) (44) (26). The increase in Cr (VI) removal with increase in adsorbents amount is due to the increase in surface area and adsorption sites available for adsorption. In contrast, the amount adsorbed for unit mass of adsorbents decreases as the dose of adsorbent increases (Fig. 3-b). At low adsorbent dose, all active adsorbent sites are completely exposed and occupied by the Cr (VI), which is excessive, saturating the surface and yielding the higher q_e, while the decrease in unit adsorption with increased adsorbent dose is mainly due to the unsaturation of adsorption sites during the adsorption phase. The maximum adsorption capacity was 17.6 mg/g achieved by using BW compared to 21 mg/g for AC at 2 g/L dosage. Similar trend was reported by (4), (6) and (45).

3.4 Effect of Contact Time on Cr Adsorption

The effect of contact time on Cr adsorption on the different materials is important to define the time required for Cr (VI) to reach an equilibrium when put in contact with the different adsorbents. Fig. (4) Shows the percentage removal of Cr for different value of contact time ranging from 1 to 5 hours at pH 3, Cr initial concentration = 50 mg/L, adsorbent dosage of 5 g/L and 30°C temperature. Fig. (4) Indicated that increasing the contact time from 1 to 3 hours, increased the percentage removal, because of the large number of active sites available for adsorption and high rate of adsorption at first. After that, the percentage removal of Cr reaches slowly to higher values or remains constant as the active sites is about to be saturated. Hence, the equilibrium time obtained is 3 hours for the Cr adsorption on all adsorbents except for PPP and RS as they gave unsatisfying results so they we refused in further experiments for higher concentrations. These results agree with the trends of (31), (45), (46) and (47) . The optimum Chromium removal percentage obtained at 3 hours equilibrium time was for BW with 80.91% at pH = 3 and 10 g/L dosage followed by 73.79% for SD at the same conditions.

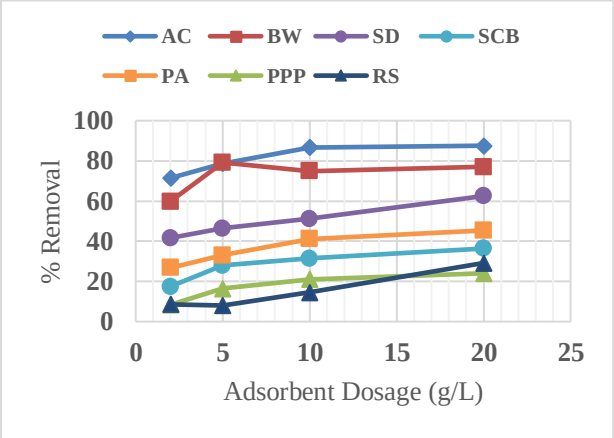

Figure 3-a: Effect of adsorbent dosage on Cr adsorption efficiency

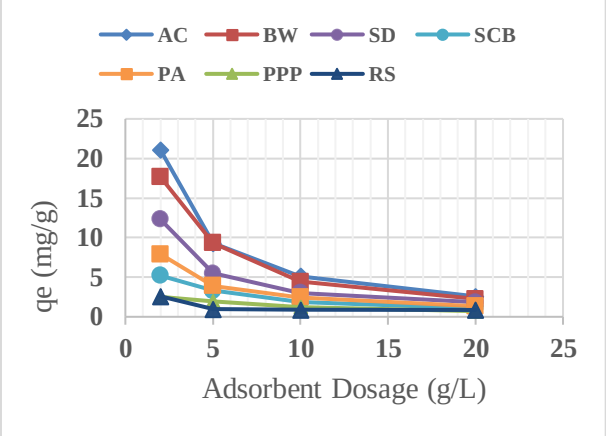

Figure 3-b: Effect of adsorbent dosage on adsorption Capacity (q_e)

3.5 Effect of initial concentration on Cr adsorption

Cr (VI) adsorption is greatly affected by the initial concentration of Cr (VI) in aqueous solutions. In the present study, the adsorption experiments were performed to study the effect of initial Cr (VI) concentration at the following conditions: dosage amount 5 g/L, pH=3, contact time =1hr and at 30°C. Fig. (5-a) shows the effect of initial concentration at low values ranged from 25 to 400 mg/L. The results show that with increase in Cr (VI) concentration from 25 to 400 mg/L, the percentage removal decreases and adsorption capacity increases.

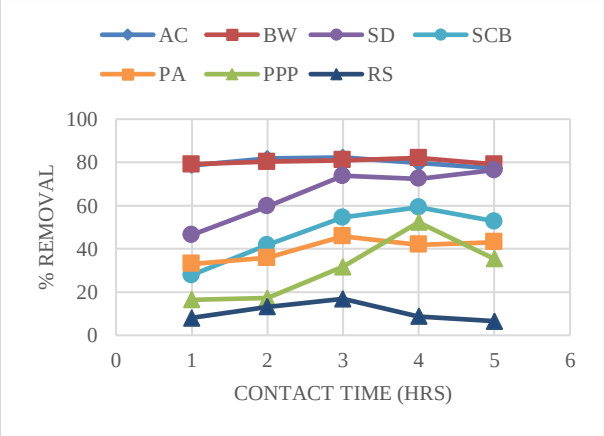

Figure 4: Effect of contact time on Cr adsorption efficiency

The decrease in percentage removal can be illustrated by the fact that all the adsorbents had a fixed number of active sites, which would have become saturated above a certain concentration. The increase in adsorption capacity with increase in Cr (VI) concentration as shown in Fig. (5-b) may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration. Banana waste achieved the optimum removal efficiency of about 84% at Chromium initial concentration of 25 mg/L followed by sawdust with removal efficiency of about 76% then by Phragmites Australis and sugarcane bagasse with removal efficiency of 48%. These results match the trend of (6), (2), (34), (4), (48) and (45). At the highest concentration of 200 mg/L, BW registered the optimum removal efficiency of 60.2%.

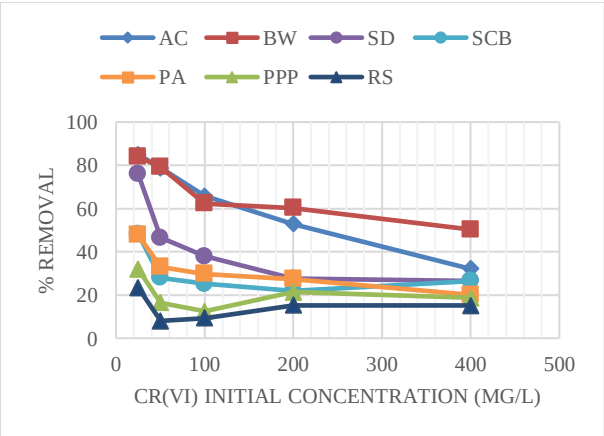

Figure 5-a: Effect of Cr initial concentration on adsorption efficiency

3.6 Effect of high initial concentration on Cr adsorption

The four absorbents achieved higher removal efficiency at 400 mg/L initial concentration (Banana waste (BW), Sawdust (SD), Phragmites Australis (PA) and sugarcane bagasse (SCB)) will be investigated at higher concentration of 600,800 and 1000 mg/L. Figures (6-a), (6-b), (6-c) and (6-d) show the removal efficiencies of the examined adsorbent at high concentrations and their capacities in mg/g. The adsorbents were examined at different three dosages (10-20-25) gm/L. The optimum pH for BW was 3, while it was 2 for the rest and the contact time was 3 hours for all experiments. Fig. (6-a) shows the performance of BW at high concentrations, the dosages changed from 10 to 20 and then 25 gm/L. The optimum removal at 600 mg/L was 77.8% which was decreased to 75.2% at 800 mg/L and finally reached 73.3% at 1000 mg/L using 25 g/L dosage. The decrease in removal efficiency by increasing the initial concentration was due to the occupation of the active sites of adsorbent at higher concentrations.

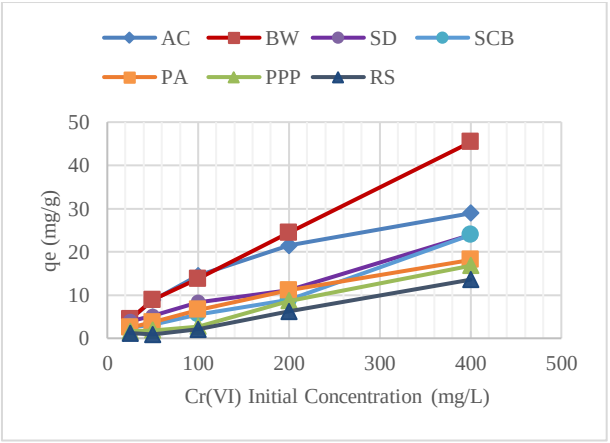

Figure 5-b: Effect of Cr initial concentration on adsorption Capacity

These results agree with (19) results on Grafted Banana Peels(GBP) which study the Cr (VI) for concentration from 100 to 600 mg/L. However, the adsorption capacity increased by increasing the initial concentration and decreasing the dosage because at higher concentrations the rate of adsorption increased and increasing the dosage from 10 gm/L to 20 gm/L reduces the capacity from about 70 to 40 mg/g. As the dosage decreased, it absorbs most of the Cr (VI) found but increasing the amount of adsorbents about some level can leads to overlapping of adsorbent particles, which make it unsaturated. The optimum removal efficiency at initial concentration of 600 mg/L was 77.8% for (BW) at pH=3, 25 gm/L dosage. The adsorption capacity of 86.3 mg/g for SD using 10 gm/l dosage at 1000 mg/L Cr concentration is the maximum value found followed by 74.78 mg/g for BW of 10 gm/L dosage at 1000 mg/L concentration. The maximum adsorption capacity reported by (6) at 400 mg/L initial Cr (VI) concentration was 41.45 mg/g. The high adsorption capacity for BW and SD at higher concentration is due to the active functional groups on their surface and high fixed carbon content. Carboxylic (–COOH) at about (3400-3650) cm^{-1}, carbonyl at about (1670-1780) cm^{-1} and hydroxyl (–OH) groups at about (1429-1639) cm^{-1} are the most common found groups on agricultural waste surface which are responsible for binding Cr(VI) from aqueous solution as shown in Fig. (7) and (8) for BW and SD from literature respectively (13). BW contains about 65 % of fixed carbon which enhance its Cr(VI) adsorption capacity(49). Scanning electron microscopy (SEM) is also a measure for surface morphology of an adsorbent which can be an indication for the surface area and pores size of it. The surface of adsorbent before adsorption showed irregular heterogeneous structure which became flattened after adsorption as a result of metal ion adsorption. Fig (9) and (10) shows the SEM for BW and raw sawdust (R-SD) and modified sawdust (MSD) from literature.

3.7 Effect of Temperature on Cr Adsorption

The effect of temperature on Chromium adsorption was tested on the four adsorbent achieved high efficiency. The pH, dosage and contact time for BW, SD, SCB and PA were 3,2,2,2 and 25,10,10,10 gm/l and 3,5,5,3 hours respectively. The initial concentration was maintained constant at 1000 ppm. As shown in Fig. (7), it is observed that the percentage removal of

Chromium increases by increasing the temperature from 30 to 70ºC for all materials. This increase is due to the increase of the rate of adsorption at higher temperature which indicates that the adsorption process is endothermic(50). The optimum removal was for sawdust at 70ºC by 82% followed 80.7% for banana waste at 60ºC. Similar results were reported by (20), (6) and (27).

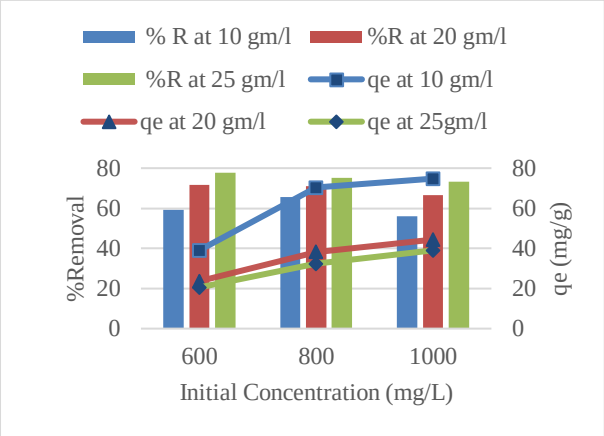

Figure 6-a: performance of BW at high Cr concentrations

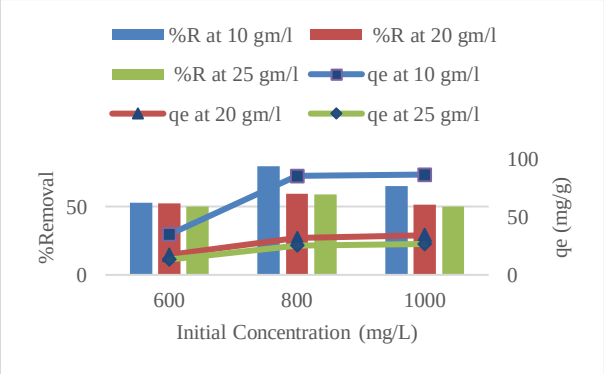

Figure 6-b: Performance of SD at high Cr concentrations

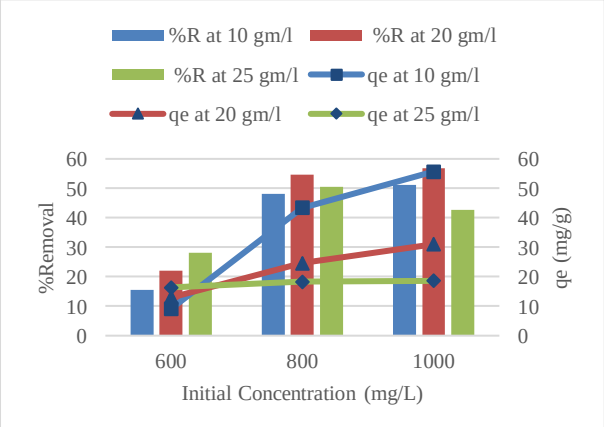

Figure 6-c: Performance of PA at high Cr concentrations

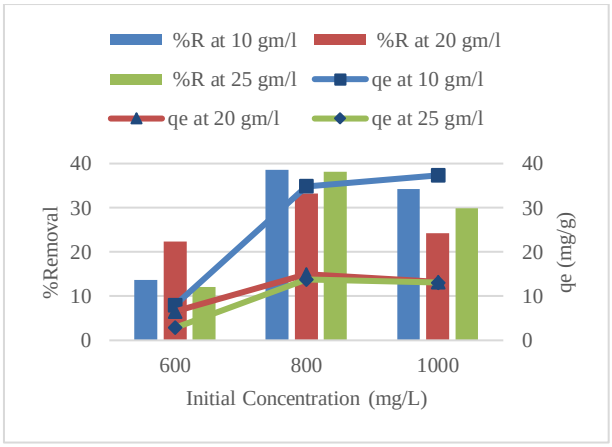

Figure 6-d: Performance of SCB at high Cr concentrations

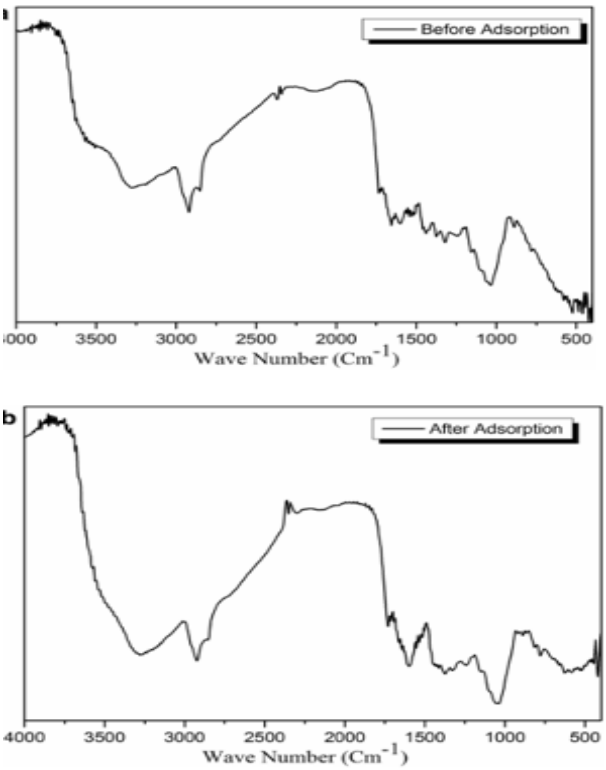

Figure 7: FTIR spectrum of banana peel dust [before and after Cr(VI) adsorption] (18)

3.8 Adsorption Kinetics

In order to understand the kinetic behavior of the adsorption process for Cr (VI) removal using the four tested materials at high concentration (BW, SD, PA and SCB) compared with that of AC, the Pseudo-first- order and Pseudo-second- order models are considered to fit the kinetic experimental data. The different parameters of the two models are calculated and tabulated in Table (2).

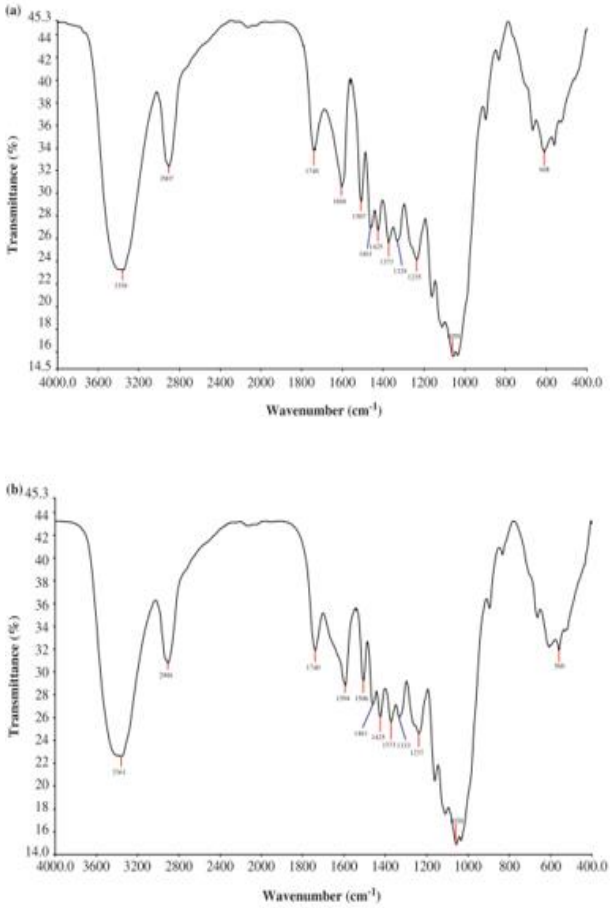

Figure 8: FTIR spectrum of sawdust [before and after Cr(VI) adsorption] (22)

3.8.1 Pseudo-first-order Kinetic Model

The applicability of the Pseudo-first- order kinetic model to the experimental data are tested by plotting the linear form as a graph of log (q_e-q_t) versus time Fig (8). The estimated values of the Pseudo-first- order kinetic parameters, K and q_e along with the regression coefficient (R^2) are in Table (2). The values of (R^2) are estimated as 0.9712, 0.9975, 0.7865, 0.9911 and 0.6318 for the removal of Cr (VI) using AC, BW, SD, PA and SCB respectively. These values indicate the non-agreement of the Pseudo-first- order kinetic model to the experimental data. The experimental value of the adsorption capacities at equilibrium are 9.05, 9.02, 8.41, 5.04 and 6.52 mg/g respectively. The predicted values of adsorption capacities using the Pseudo-first- order kinetic model are 8.26, 0.51, 6.76, 2.24 and 3.83 mg/g respectively. This disagreement between the experimental and predicted adsorption capacities confirms that the Pseudo-first-order kinetic model cannot explain the behavior of Cr (VI) adsorption on the different types of used adsorbents.

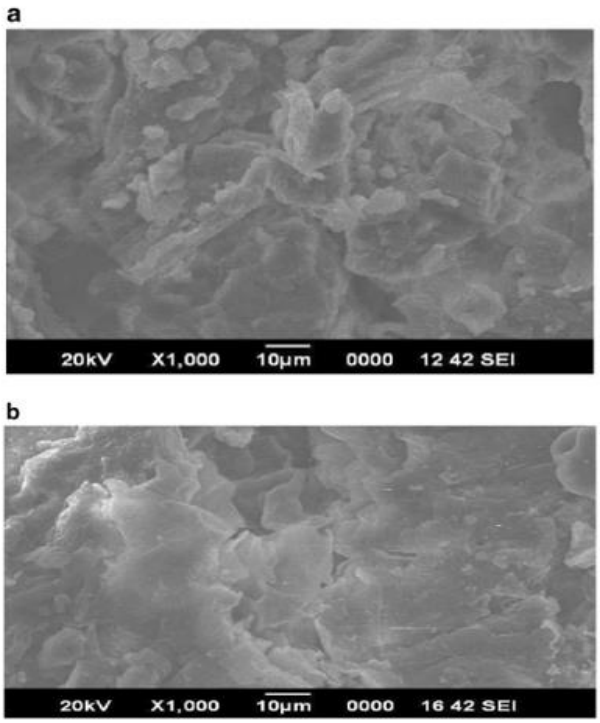

Figure 9: SEM for banana peel (a-before adsorption and b-after adsorption) (18)

3.8.2 Pseudo-second-order Kinetic Model

The kinetic experimental data are also fitted with the Pseudo-second- order kinetic model. The second order kinetic parameters, K_2 and q_e are calculated for different adsorbents using the slope and intercept of the graph of the linear form between t/q_t versus time as shown in Fig. (9). The obtained values of K_2 and q_e and (R^2) for Cr (VI) adsorption using different adsorbents are given in Table (2). The predicted equilibrium adsorption capacities are close to that obtained from the experimental data. The value of K_2 are found to be less than 1 which suggests the higher rate of adsorption at initial stage and further decrease with the lapse of time. High values of R^2 (0.9977, 0.9986, 0.9924, 0.9837 and 0.9352) obtained for the removal of Cr (VI) using AC, BW, SD, PA and SCB respectively, show the agreement between the experimental data and the second order kinetic model.

The predicted values of adsorption capacities using the Pseudo-second- order kinetic model are 8.47, 8.79, 10.05, 5.21 and 7.97 mg/g respectively, which matches the experimental values of adsorption capacities for the mentioned adsorbents. This confirms the applicability of the Pseudo-second- order kinetic model to fit the experimental data and confirms the chemisorption of Cr (VI) on the adsorbents during the adsorption process. In chemisorption (chemical adsorption), the Chromium sticks to the adsorbent surface by forming a chemical bond (usually covalent) and tend to find sites that maximize their coordination number with the surface (44). These results agree with most of the previous studies on adsorbents like, (6), (20), (18), (19), (31), (9) and (22).

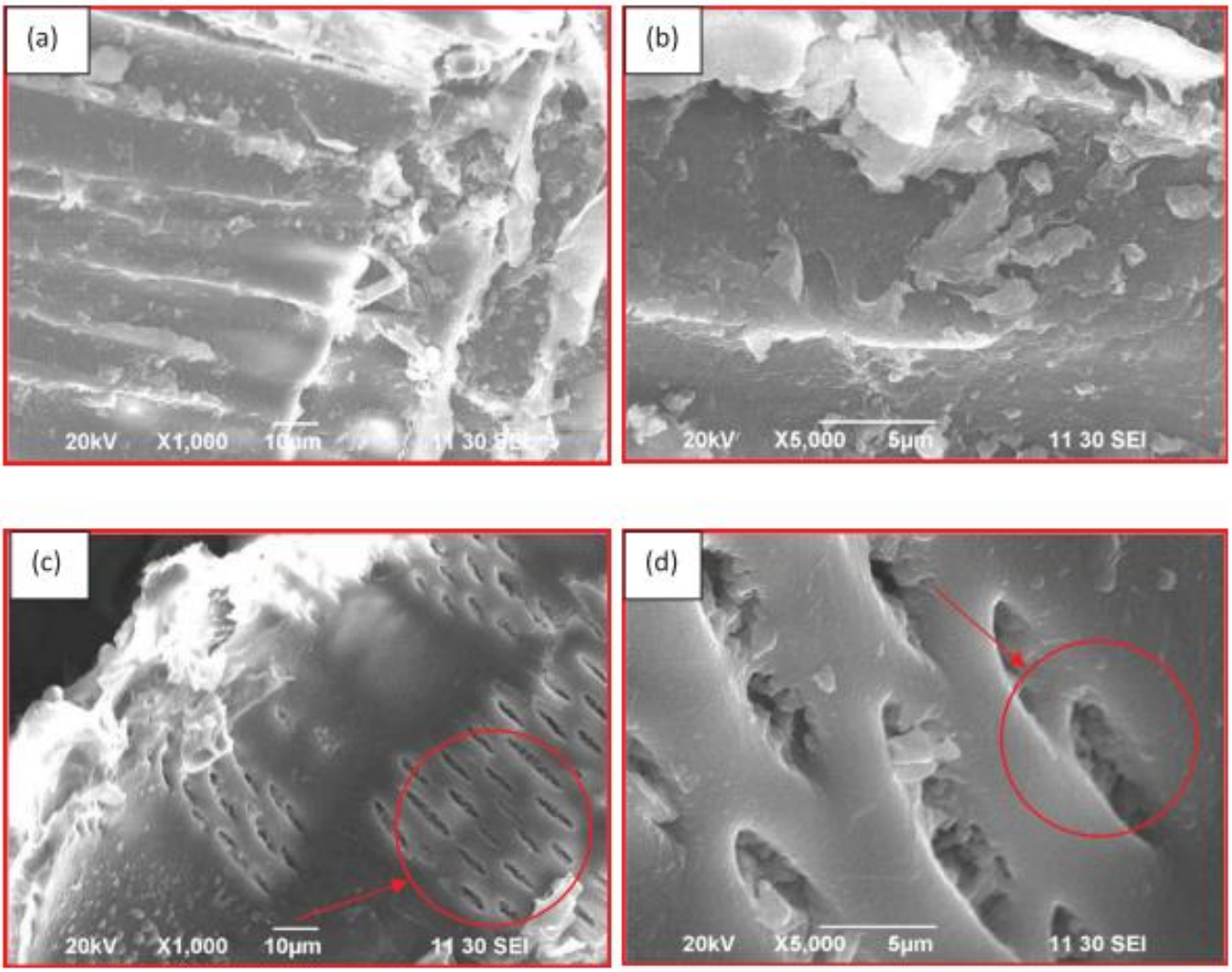

Figure 10: SEM images of (a) R-SD at 1000 magnification, (b) R-SD at 5000 magnification (c) MSD at 1000 magnification, and (d) MSD at 5000 magnification (9)

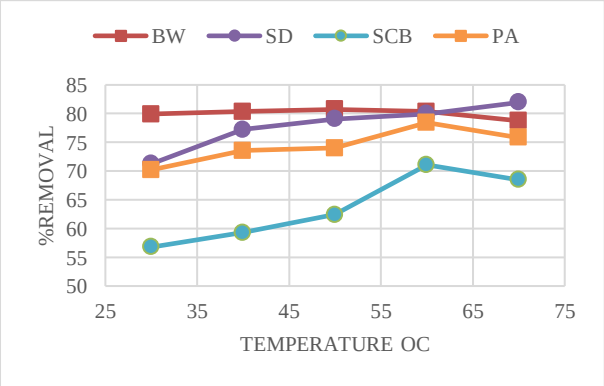

Figure 7: Effect of temperature on Cr adsorption efficiency

3.9 Adsorption Isotherm Study

An adsorption isotherm is characterized by certain constants that express the surface properties and the affinity of the adsorbent towards Cr (VI) adsorption (51). The equilibrium data for the adsorption of Cr (VI) using these adsorbents fits into various isotherm models which results in a suitable model that can be used for the design of an adsorption process. The most used isotherm models in adsorption process are Langmuir, Freundlich and Tempkin isotherm models. Therefore, in the present work, Langmuir, Freundlich and Tempkin isotherm models for different adsorbents are considered and are discussed in the following sections. The various isotherm parameters are estimated and tabulated in Table (3), (4) and (5) respectively.

Table 2: the kinetic constants for Cr removal using different adsorbents

Equation / Material	Pseudo-first-order			Pseudo-second-order			Qe (exp.) (mg/g)
Parameter	K (hr^{-1})	R^2	q_e (cal.) (mg/g)	K_2 (g/mg .hr)	R^2	q_e (cal.) (mg/g)	
Activated Carbon (AC)	2.76	0.9712	8.26	1.24	0.9977	8.473	9.05
Banana waste (BW)	0.481	0.9975	0.51	6.12	0.9987	8.798	9.02
Sawdust (SD)	0.787	0.7866	6.76	0.104	0.9924	10.05	8.41
Phragmites Australis (PA)	0.404	0.9911	2.24	0.435	0.9837	5.21	5.04
Sugarcane Bagasse (SCB)	0.405	0.6318	3.83	0.091	0.9352	7.972	6.52

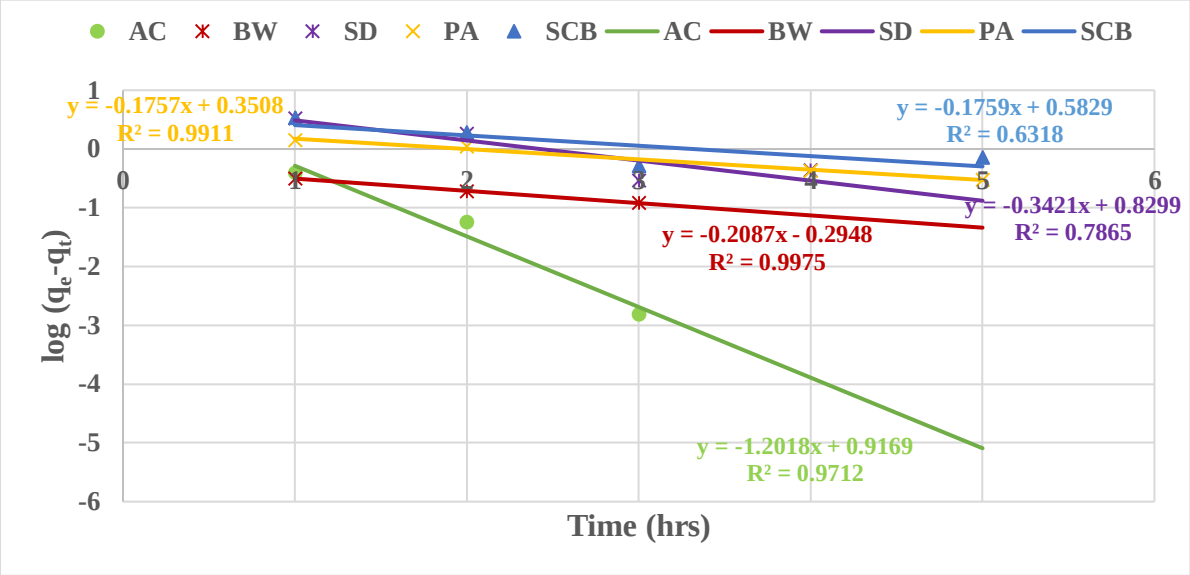

Figure 8: Pseudo-first-order model for different adsorbents

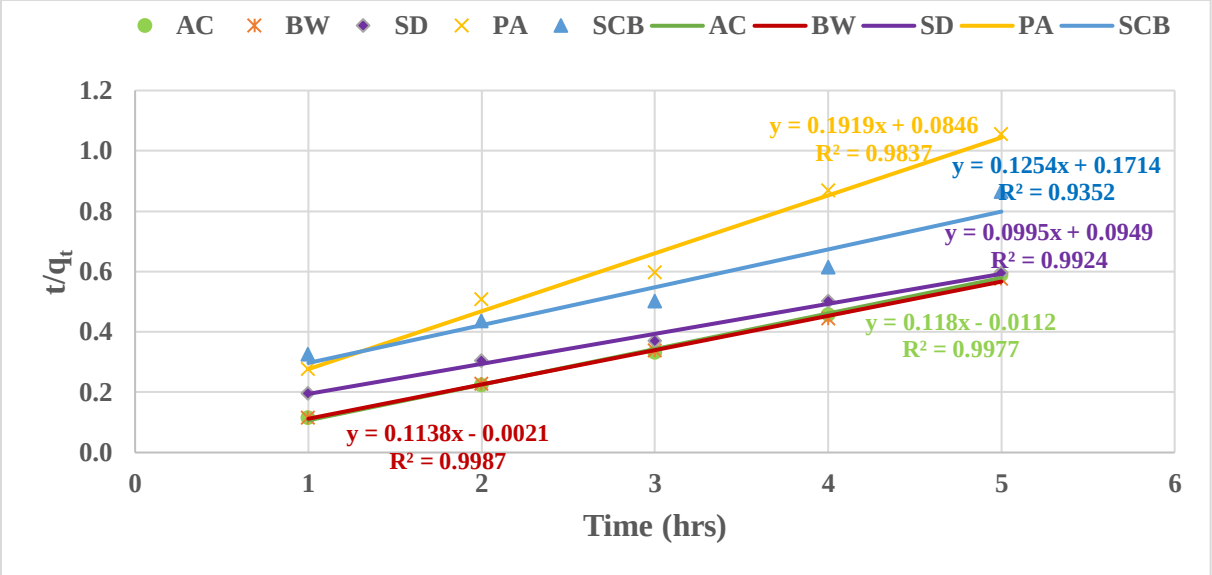

Figure 9: Pseudo-second-order model for different adsorbents

3.9.1 Langmuir Isotherm

The isotherm data has been linearized using the Langmuir equation and is plotted between C_e versus C_e/q_e which is shown in Fig. (10)(a),(b) for low concentrations (25-50-100-200) and for high concentrations (400-600-800-1000) respectively. The Langmuir parameters Q_m, b and R_L are estimated for different adsorbents and are given in Table (3). The Langmuir constant Q_m, which is a measure of the monolayer adsorption capacity of the adsorbents, is obtained as 26.20, 31.51, 13.02, 19.72 and 13.49 mg/g for AC, BW, SD, PA and SCB respectively in the equilibrium pH value of 3 for all adsorbents at low concentrations. At the optimum conditions for the best four materials at high concentration, the increase in Cr (VI) initial concentration to (400-600-800-1000) mg/L increases the monolayer adsorption capacity Q_m to 105.84, 29.86, 19.30 and 73.83 mg/g for AC, BW, SD, PA and SCB respectively. The increase in adsorption capacity with an increase in the Cr (VI) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. The Langmuir constant, b, which denotes adsorption energy, is found to be 0.0424, 0.0301, 0.0327, 0.0076 and 0.0102 L/mg at low concentrations for AC, BW, SD, PA and SCB respectively. Langmuir constant b for low concentration was found 0.0016, 0.0122, 0.0415 and 0.0015 for the last four materials respectively. The value of coefficient of correlation (R^2 = 0.986, 0.8614, 0.9531, 0.7611 and 0.7747) obtained for AC, BW, SD, PA and SCB at low concentrations do not support the monolayer adsorption of Cr (VI) onto the different adsorbents except for sawdust which was 0.9531. On the other hand, it is found that the value of R^2 is very close to unit at higher concentrations for BW,SD and SCB which confirms the monolayer adsorption of Cr(VI) at these adsorbents.

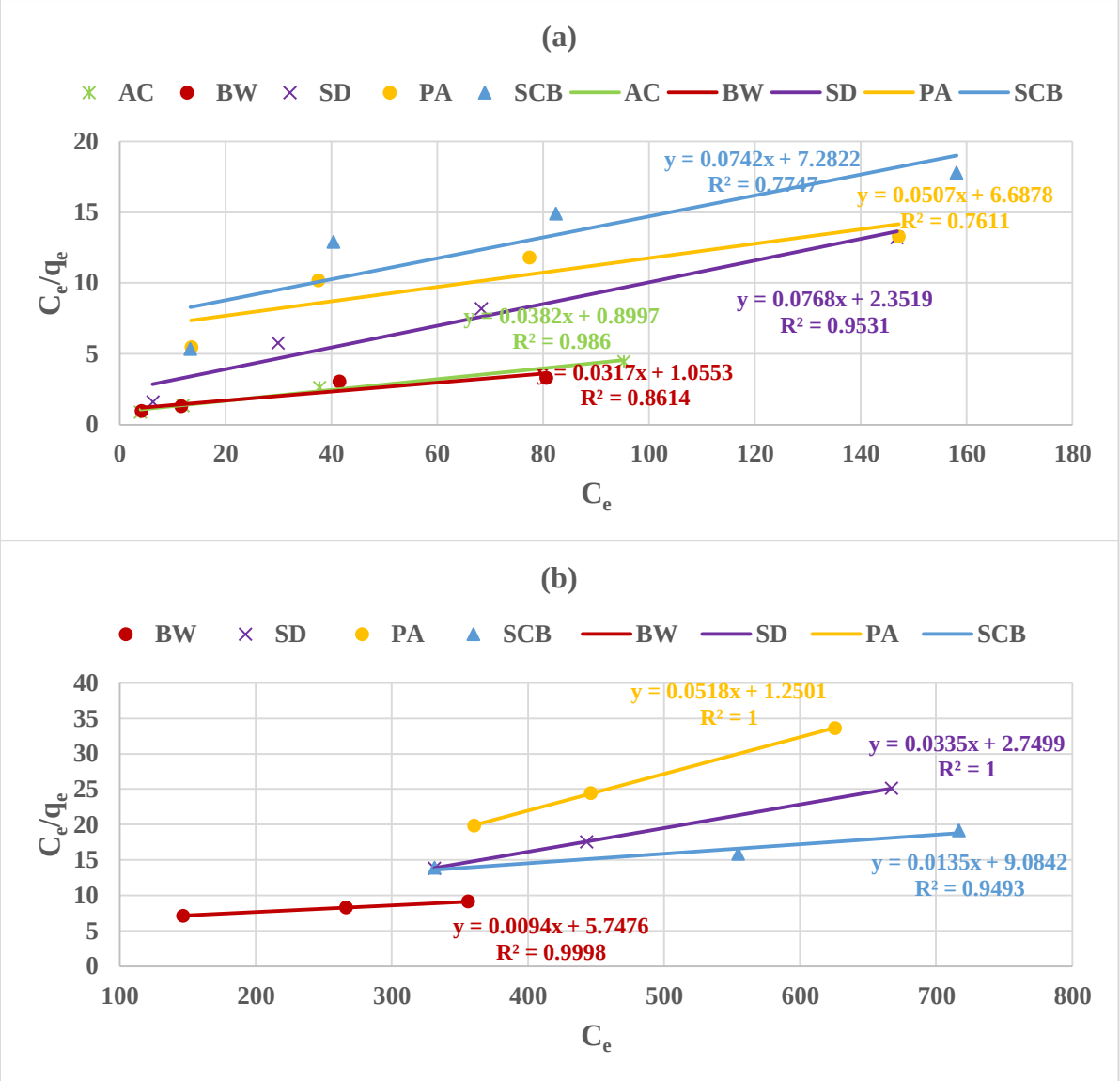

Figure 10: Langmuir isotherm (a) at low conc., (b) at high conc

The dimensionless parameter, R_L, which is a measure of adsorption favorability is found to be in a range of 0.1 to 0.62 ($0 < R_L < 1$) which confirms the favorable adsorption process for Cr (VI) removal using different adsorbents. Though the R^2 value obtained is very high for some adsorbents, in order to find out if a better fit is possible with other isotherms, the results are analyzed with other two isotherms available in the literature.

3.9.2 Freundlich Isotherm

The Freundlich constants, K_f (mg/g) and n are obtained by plotting the graph between log q_e versus log C_e as shown in Fig. (11) (a), (b) for low concentrations (25-50-100-200) mg/L and for high concentrations (400-600-800-1000) mg/L respectively. The values of K_f are 1.46, 1.38, 1.34, 0.70 and 0.78 for AC, BW, SD, PA and SCB at low concentrations respectively and 0.77, 2.72, 3.12 and 0.88 for the last four adsorbents at high concentrations respectively. The values of n_f are 0.49, 0.54, 0.34, 0.63 and 0.52 for AC, BW, SD, PA and SCB at low concentrations respectively and 0.73, 0.15, 0.05 and 0.60 for the last four adsorbents at high concentrations respectively. The obtained values of n_F are less than 1 for both low and high concentrations which supports the chemisorption phenomena during Cr (VI) adsorption on all adsorbents at different conditions (52). It is found that the coefficient of correlation obtained from the Freundlich isotherm model for adsorbents ranges from 0.9405 to 0.9988, which is higher than that for Langmuir isotherm model as given in Table (4). These results support the possibility of heterogeneous adsorption on multi-layers. The obtained result indicates that the equilibrium data is fitted well with the Freundlich isotherm model at low concentrations for all adsorbents except for SD. Similar observations were recorded by (21) when they study the adsorption of Cr (VI) on Banana Trunk Fibers (BTF) and reinforced Chitosan Bio composite (CTB).

Table 3: Langmuir parameters for Cr removal using different adsorbents

At 303 °K	Langmuir Constants for low concentrations				
Adsorbent	Maximum monolayer coverage mg/g (Q_m)	Langmuir constant L/mg (b)	R_L favorable if $0 < R_L < 1$	R^2 Best error distribution	qe (exp.) mg/g
Activated carbon (AC)	26.20	0.0424	0.26	0.986	21.46
Banana waste (BW)	31.51	0.0301	0.33	0.8614	24.38
Sawdust (SD)	13.02	0.0327	0.31	0.9531	11.13
Phragmites Australis (PA)	19.72	0.0076	0.62	0.7611	11.07
Sugarcane bagasse (SCB)	13.49	0.0102	0.56	0.7747	8.88
At 303 °K	Langmuir Constants for high concentrations				
Adsorbent	Maximum monolayer coverage mg/g (Q_m)	Langmuir constant L/mg (b)	R_L favorable if $0 < R_L < 1$	R^2 Best error distribution	qe (exp.)
Banana waste (BW)	105.84	0.0016	0.43	0.9998	39.02
Sawdust (SD)	29.86	0.0122	0.1	1	26.58
Phragmites Australis (PA)	19.30	0.0415	0.03	1	18.59
Sugarcane bagasse (SCB)	73.83	0.0015	0.48	0.9493	37.34

Table 4: Freundlich parameters for Chromium using different adsorbents

At 303 oK	Freundlich Constants for low concentrations		
Adsorbent	Relative adsorption capacity of adsorbent related to the bonding energy (KF)	Heterogeneity factor representing the deviation from linearity of adsorption (nF)	R2 Best error distribution
Activated carbon	1.46	0.49	0.9905
Banana waste	1.38	0.54	0.9755
Sawdust	1.34	0.34	0.9405
Phragmites Australis	0.70	0.63	0.9693
Sugarcane bagasse	0.78	0.52	0.9200
At 303 oK	Freundlich Constants for high concentrations		
Adsorbent	Relative adsorption capacity of adsorbent related to the bonding energy (KF)	Heterogeneity factor representing the deviation from linearity of adsorption (nF)	R2 Best error distribution
Banana waste	0.77	0.73	0.9988
Sawdust	2.72	0.15	0.9891
Phragmites Australis	3.12	0.05	0.9950
Sugarcane bagasse	0.88	0.60	0.9642

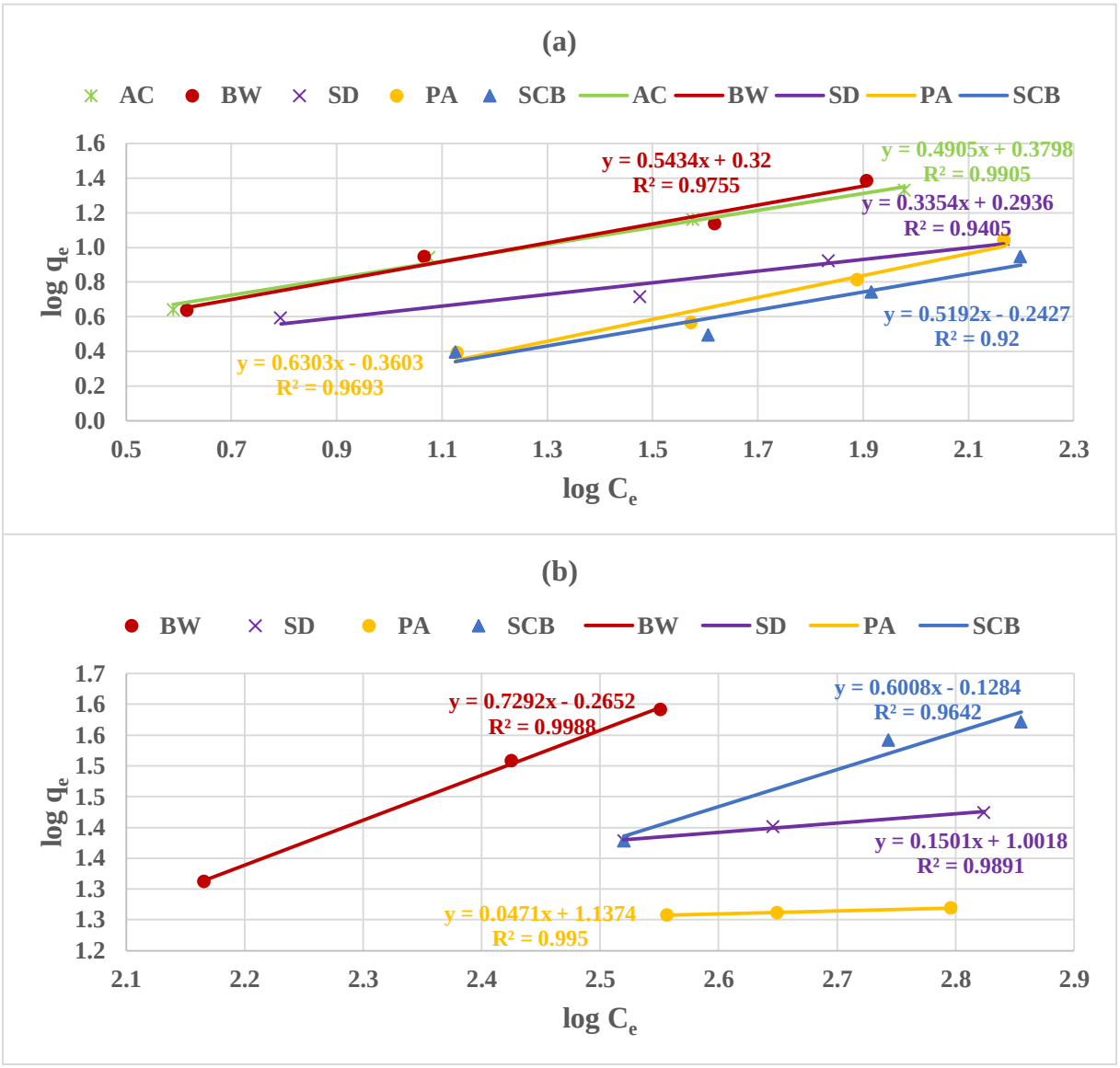

Figure 11: Freundlich isotherm (a) low conc., (b) high conc

3.9.3 Tempkin Isotherm

A plot of q_e versus ln C_e at a constant temperature shown in Fig (12) (a), (b) is used to calculate the Tempkin isotherm constants, A_T and b_T which are tabulated in Table (5) for low and high concentrations respectively. Tempkin isotherm model takes the adsorbent adsorbate interactions in consideration(53). The constant A_T obtained from Tempkin isotherm model are 0.51, 0.40, 0.65, 0.11 and 0.14 L/g for AC, BW, SD, PA and SCB at low concentrations respectively and 0.018, 1.69, 0.005 and 0.012 L/g for the last four materials at high concentrations respectively. The constant b_T obtained for Tempkin isotherm model are 478.69, 409.69, 1116.56, 722.30 and 1002.22 for AC, BW, SD, PA and SCB at low concentrations respectively and 121.79, 664.25, 120.80 and 140.03 for the last four materials at high concentrations respectively. The obtained coefficient of determination (R^2) for Tempkin isotherm model ranges from 0.8442 to 0.9982, which is lower than Langmuir and Freundlich for all adsorbents except for SCB at higher concentrations which was 0.9747 more than the R^2 calculated for the other two isotherm models. The summary of the calculated values of regression coefficient (R^2) and isotherms parameters for the adsorption of Cr (VI) on AC, BW, SD, PA and SCB at both low and high concentrations are tabulated in Table (6). From Table (6), it is clear that AC, BW, PA and SCB follow the multi-layer adsorption theory of Freundlich isotherm that gave the highest R^2 at low concentrations. While SD at low concentration besides BW,SD and PA at high concentrations follow the monolayer adsorption of Langmuir isotherm that gave a R^2 value near or equal to the unit. Finally SCB at higher concentration is the only adsorbent which fits to Tempkin isotherm with R^2 value of 0.9747.

Table 5: Tempkin parameters for Cr removal using different adsorbents

At 303 °K	Tempkin Constants for low concentrations			
Adsorbent	(A_T) (L/g)	(b_T)	(B_T= RT/b_T)	R^2 best error distribution
Activated carbon	0.51	478.69	5.26	0.9799
Banana waste	0.40	409.69	6.15	0.8933
Sawdust	0.65	1116.56	2.26	0.8858
Phragmites Australis	0.11	722.30	3.49	0.8762
Sugarcane bagasse	0.14	1002.22	2.51	0.8442
At 303 °K	Tempkin Constants for high concentrations			
Adsorbent	(A_T) (L/g)	(b_T)	(B_T= RT/b_T)	R^2 best error distribution
Banana waste	0.018	121.79	20.67	0.9982
Sawdust	1.69	664.25	3.79	0.9920
Phragmites Australis	0.005	120.80	20.84	0.9994
Sugarcane bagasse	0.012	140.03	17.98	0.9747

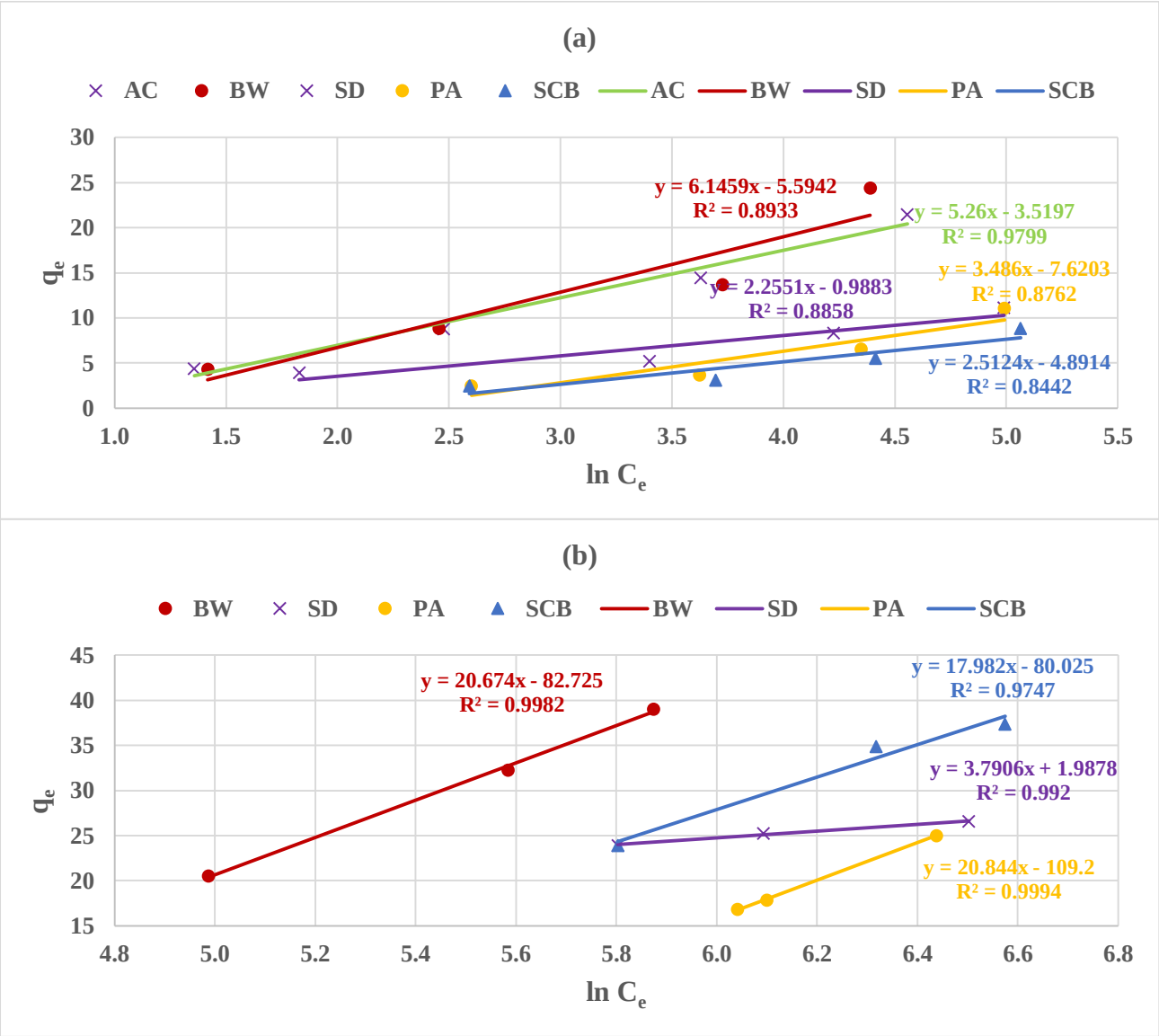

Figure 12: Tempkin isotherm (a) at low conc., (b) at high conc

Table 6: Summary of isotherms constants for different adsorbents at low and high concentrations.

At 303 °K		Langmuir Constants				Freundlich Constants			Tempkin Constants			
For Low Concentrations	Adsorbent	Q_m	b	R_L	R^2	K_F	n_F	R^2	A_T	b_T	B_T	R^2
	Activated carbon	26.20	0.0424	0.26	0.986	1.46	0.49	0.9905	0.51	478.69	5.26	0.9799
	Banana waste	31.51	0.0301	0.33	0.8614	1.38	0.54	0.9755	0.40	409.69	6.15	0.8933
	Sawdust	13.02	0.0327	0.31	0.9531	1.34	0.34	0.9405	0.65	1116.56	2.26	0.8858
	Phragmites Australis	19.72	0.0076	0.62	0.7611	0.70	0.63	0.9693	0.11	722.30	3.49	0.8762
	Sugarcane bagasse	13.49	0.0102	0.56	0.7747	0.78	0.52	0.9200	0.14	1002.22	2.51	0.8442
At 303 °K		**Langmuir Constants**				**Freundlich Constants**			**Tempkin Constants**			
For High Concentrations	Adsorbent	Q_m	b	R_L	R^2	K_F	n_F	R^2	A_T	b_T	B_T	R^2
	Banana waste	105.84	0.0016	0.43	0.9998	0.77	0.73	0.9988	0.018	121.79	20.67	0.9982
	Sawdust	29.86	0.0122	0.1	1	2.72	0.15	0.9891	1.69	664.25	3.79	0.9920
	Phragmites Australis	19.30	0.0415	0.03	1	3.12	0.05	0.9950	0.005	120.80	20.84	0.9994
	Sugarcane bagasse	73.83	0.0015	0.48	0.9493	0.88	0.60	0.9642	0.012	140.03	17.98	0.9747

4 Conclusions

The study reveals that BW and SD are the best adsorbents for the removal of Cr (VI) from industrial wastewater for both low and high concentrations. At higher concentration of 1000 mg/L, (BW) gives the best removal efficiency of about 73% using 25 gm/L dosage, pH= 3 and 3 hours contact time. The maximum adsorption capacity of 86 mg/g at 1000 mg/L was obtained for (SD) at its optimum conditions. Preparation and treatment method has a vital effect on the adsorption characteristics for each adsorbent. BW treated with HCl only shows the best results while other adsorbents give highest removal efficiencies when treated with acid-alkali treatment. The Chromium adsorption capacity of all the investigated materials is highly dependent on pH and achieves high efficiency at low pH 2-3. The Chromium adsorption capacity is highly dependent on dosage, initial concentration, contact time and temperature. In the present study, all adsorbents follow Pseudo-second-order kinetic model with high regression coefficient. The equilibrium isotherm data for AC, BW, PA and SCB at low concentrations were best fitted to Freundlich isotherm while SD at low concentrations and BW, SD and PA at higher concentrations were following Langmuir isotherm. SCB at high concentrations is the only adsorbent fitted to Tempkin isotherm.

Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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