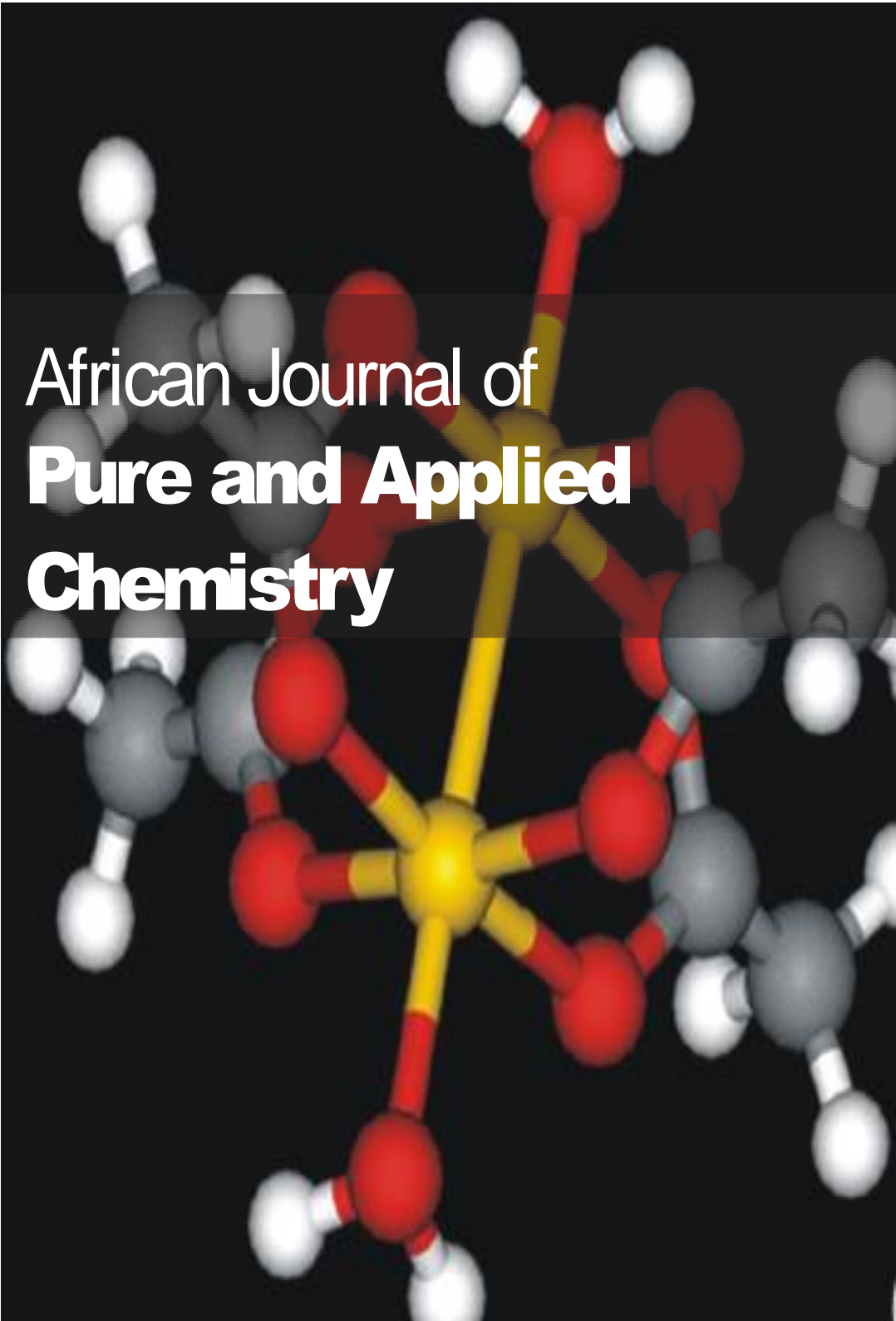


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Full Length Research Paper

Determination of chlorogenic acid content in beans and leaves of *coffea arabica* using UV/Vis spectrometer

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Chlorogenic acid (CGA) is one of the compounds found in coffee beans and other parts of coffee plant. However, its relative content in different coffee plant parts is least researched. Therefore, this study was designed to determine the contents of CGA in coffee leaves and beans. Green coffee beans and leaves were collected from South part of Ethiopia to study the content of CGA using UV/Vis spectrometer with liquid-liquid extraction method in dichloromethane. Results indicated that mean percentage of CGA in green coffee beans and leaves are in the range of 5.96 ± 0.01 to 6.40 ± 0.02 % and 1.94 ± 0.01 to 2.31 ± 0.01 %, respectively. On top of that, the percentage difference of CGA between green coffee beans and leaves was at least about 63%, with beans taking the upper hands. These results showed that there is statistically significant content of CGA in green coffee beans than green coffee leaves.

Keywords: CGA, *Coffea arabica*, coffee leaves, concentration, green coffee beans.

INTRODUCTION

Coffee is one of the most widely consumed beverages throughout the world due to its pleasant taste, aroma, stimulant effect and health benefits (Gebeyehu and Bikila, 2015). Coffee plant is categorized among the medicinal plants because studies on beans and fleshy organs of the coffee plant including leaves have revealed that these organs are found to have generous amounts of secondary metabolites such as phenolic compounds, esters of hydroxycinnamic acids and mangiferin which have high level of antioxidant properties and anti-inflammatory effects on humans (Campa et al., 2012).

Chlorogenic acid (CGA) is one of the compounds found in coffee beans and other parts of coffee plant. CGA is the main phenolic compound in coffee beans and its

concentration is the highest in coffee beans than other coffee parts (Farah et al., 2005). Chlorogenic acids are esters of quinic acid and various class of hydroxycinnamic acids, chiefly caffeic acid (3, 4-dihydroxycinnamic acid), ferulic acid (3-methoxy-4-hydroxycinnamic acid), p-coumaric (4-hydroxycinnamic acid), and sinapic acid (3, 5-dimethoxy-4-hydroxycinnamic acid) (Manach et al., 2004). CGA comprises major class of phenolic compounds. The most abundant are the caffeoylquinic acids (Clifford et al., 2003). They account for approximately 80% of the total chlorogenic acid content (Farah et al., 2005). The total CGA content of green coffee beans varies according to genetic species, degree of maturation and less importantly agricultural practices,

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climate and soil (Farah et al., 2006).

Most of the researches have targeted their journey at studying *Coffea arabica* and *Coffea canephora*. Studies have revealed that the percentage of CGA for green coffee beans on the dry matter varies from 4 to 8.4% for *C. arabica* and 7 to 14.4% for *C. canephora* with some hybrids containing intermediate levels (Farah et al., 2005). Campa et al. (2005) have reported that the CGA level of green coffee beans from Cameroon and Congo is in the range of 0.8 to 11.9% on dry matter basis. However, as reported by Farah et al. (2006b) and Ky et al. (2001), the level of CGA in green coffee beans is about 4 to 8.4% for *C. arabica*. In addition, Perrone et al. (2008) have reported a similar result with a total CGA content of 6.3 and 5.5 g/100 g for *C. arabica* using LC-MS. Budiman et al. (2017) have reported that CGA concentration of Arabica coffee before and after decaffeination has been measured to be 4.16 ± 0.16 and 3.02 ± 0.14 , respectively. As reported by Hall et al. (2018), decaffeinated coffee beans contain 13,005.32 to 46,048.63 mg/kg while caffeinated one possesses 30,171.02 to 49,488.03 mg/kg of CGA content.

Ethiopia is the mother and diversification land of *C. arabica* (Mekuria et al., 2004) with Oromia and Southern Nations, Nationalities and Peoples' Regions are the leading producers. Report from West Ethiopia by Belay and Gholap have indicated that the percentage of chlorogenic acid determined by UV/Vis spectrometry is from (6.05 ± 0.33) - (6.25 ± 0.23) % (Belay and Gholap, 2009). HPLC analysis by Ayelign and Sabally (2013) has unveiled that the CGA concentration of coffee beans collected from different regions of Ethiopia is in the range of 0.981 to 46.155 mg/g. Although chlorogenic acid is found in coffee leaves, researches tilted to coffee beans (Claudine et al., 2012). However, Kristiningrum (2015) reported that concentration percentage of CGA in old and young coffee leaves of *C. arabica* are 2.79 ± 1.87 and 1.89 ± 2.15 , respectively while for *C. canephora* are 1.46 ± 0.83 and 1.05 ± 1.19 , respectively.

The most biologically active compounds exist either in coffee beans or coffee leaves are caffeine and chlorogenic acids (Farah et al., 2006b; Rodrigues et al., 2013). Consumption of coffee beans is common in most part of the world (Pohl et al., 2013). In Ethiopia, besides of coffee beans consumption, coffee leaves have been consumed in different parts of Ethiopia for different reasons since the early times. However, the indigenous knowledge community about leaves is not the same as for beans. Inhabitants of Wolaita in Southern part of Ethiopia cook leaves at matured growing stage to prepare beverages like 'Hytatuke' and drink it with some other spices for usual drink as well as for medicinal purposes. In contrast to the considerable amount of study on green beans, there are relatively few studies concerned with the metabolite content of other parts of coffee plant, such as leaves, the outer fleshy layers of the and other organs. The leaves from the coffee plant which

are suspected to have high medical effects are being undermined by many people. Therefore, this was designed to determine contents of bioactive compound CGA in matured growing stage coffee leaves and green coffee beans for their comparisons.

MATERIALS AND METHODS

Data collection technique

Green coffee beans and matured coffee leaves were taken from the same branches. Simultaneously one coffee bean and coffee leaf samples were collected from each woreda. Samples were collected from Southern part of Ethiopia, Hadiya zone, of five different major coffee growing woredas, specifically, Gibe, Soro, Gombora, Misrak Bedawachew and Mirab Bedawachew. In total, ten samples (five for leaves and five for beans) were collected and analyzed. The coffee samples were collected from the model farmers of the selected woredas by considering their productivity without considering their varieties.

Standard solution preparation

For the standard solutions preparation, a commercially bought pure CGA (Aldrich-Sigma, Germany) of 1000 mg was accurately weighted and dissolved in one liter of de-ionized water to prepare stock standard CGA solution. The solution was uniformly dissolved using magnetic stirrer in dark room to avoid light interaction. Series of standard solutions were prepared from the stock solution (5, 10, 15, 20 and 25) mgL^{-1} for CGA in de-ionized water and all measurements were carried out in short period of time after preparation and absorbance of each series was measured immediately. The series solutions were prepared for method validation against Beer-Lambert's law.

Sample preparations

To prepare CGA samples, the same sample preparation method has been followed for both green coffee beans and coffee leaves. Each sample of green coffee beans and room temperature dried coffee leaves were ground and sieved through 500 μm sieve to get a uniform texture. Accurately weighed 40 mg amount of sieved coffee was dissolved in de-ionized water in a volumetric flask up mark of 30 mL. The solutions were stirred for half an hour using magnetic stirrer and heated gently to increase the solubility of CGA in solution. In addition the solutions were filtered through glass filter to get rid of particles from solution. After filtration, extraction of CGA was done by following liquid-liquid method (Belay et al., 2008).

Liquid-Liquid extraction and absorption measurement procedures

Dichloromethane liquid-liquid extraction was deployed in order to avoid caffeine and CGA spectral overlapping in 200 to 500 nm wavelength range. The same procedure was followed for both beans and leaves samples. The procedure developed by Belay et al. (2008) was deployed to extract caffeine from the solution. Sample solutions prepared above (30 mL solution) were mixed with 30 mL dichloromethane giving total of 60 mL solution of samples. The solution was stirred for 10 min where a layer was formed with

Table 1. Mean concentration of CGA content in green coffee beans (n = 3).

Woredas	Total sample volume (mL)	Measured sample volume (mL)	^a CGA content (mg)	CGA content (mg/g)	^b CGA content (% w/w)
Gombora	60	28	2.48	62.10±0.13 ^D	6.21±0.01
Gibe	60	28	2.38	59.58±0.12 ^E	5.96±0.01
Misrak Bedawacho	60	28	2.53	63.25±0.09 ^B	6.33±0.01
Mirab Bedawacho	60	28	2.49	62.33±0.15 ^C	6.233±0.02
Soro	60	28	2.56	64.04±0.17 ^A	6.40±0.02

Means with the same letter in the fifth column are not statistically significantly different.

^aEquation (1) was used.

^bEquation (2) was used.

caffeine making upper layer and CGA making the lower layer. Caffeine was extracted from coffee solution. After caffeine extraction from the solution the remaining residue of CGA containing solution of the sample were collected and measured to get measured volume (28 mL) of the sample. This process was repeated three times to exhaustively extract caffeine. Either of the extraction of beans or leaves, samples at each round were stored in separate volumetric flasks. All glass wares and curette were thoroughly cleaned, rinsed with de-ionized water and dried before use. From the residue of CGA collected and measured, absorption of CGA were measured using double beam UV/Vis spectrophotometer (spectral 50 analytic Jenna, Germany) with wavelength ranges of 190 to 1100 nm from which CGA concentration were calculated

against the standard solution by Beer Lambert's Law at the maximum wavelength. The same extraction procedure was repeated for all the five areas samples for both beans and leaves of the coffee.

Determination of CGA content

Once the CGA concentration was calculated from the absorbance of the measured sample solution through Beer Lambert's law at maximum wavelength, the CGA contents in coffee beans as well as coffee leaves were calculated using Equation 1 (Zewdu et al., 2016).

$$\text{CGA content (mg)} = \frac{\text{conc (mg L}^{-1}\text{)} * (\text{total sample volume (mL)})^2}{\text{measured sample volume (mL)} * 1000} \quad (1)$$

The percentages of CGA content in the samples analyzed were calculated through Equation 2.

$$\text{Percentage of CGA (w/w \%)} = \frac{\text{calculated mass of CGA (mg)}}{\text{mass of coffee sample measured (mg)}} * 100 \% \quad (2)$$

Statistical analysis

Data entry management and preliminary summaries were done on Microsoft Office Excel spread sheet. Means of data obtained from quantitative measurement of spectrophotometer were determined. One-way analysis of variance (ANOVA) at $p < 0.05$ was used to determine statistically significant differences in the mean concentrations of CGA in leaves and beans as well as across study areas. For comparison of the means, the Fisher's least significant difference (LSD) test was used to check the significance level. Data were presented in mean \pm (SD) as well as in percentages \pm (SD).

RESULTS

Validation of the method was carried out in the linearity property of Beer-Lambert's law from calibration graph correlating the absorption intensity with the corresponding concentration which was constructed for CGA at the highest peak of intensity. The calibration curve facilitated measurement of the content of CGA and validation of the method is displayed in Figure 1. The calibration equation is ($Y = 0.028 + 0.013X$, $R = 0.998$, $S.D = 0.073\%$, $N = 5$) where Y , represents the peak

height at maximum wavelength and X is concentration in mg L^{-1} .

In this research, the percentage of chlorogenic acid determined at maximum wavelength of 324 nm in various green coffee beans collected from five district woredas of Hadiya zone are presented in Table 1. The results in percentage from UV-Vis spectroscopy method range from 5.96 ± 0.01 to 6.40 ± 0.02 %. Relatively the highest percentage of CGA was observed in Soro while the lower one goes to Gibe study area. The average percentage of the five distinctive areas of study was 6.23%. The CGA concentrations of green coffee beans were statistically different when considered in all the study areas.

In the same way, results obtained in this work for green coffee leaves are presented in Table 2. Maximum absorbance was obtained at 322 nm wavelength.

In this study, the percentage of CGA contents in coffee leaves is ranged from 1.94 ± 0.01 to $2.31 \pm 0.01\%$. The highest concentration was found in Gombora while the lowest was identified in Gibe. The average concentration of CGA in coffee leave samples in all the five district areas of study in this Zone was found to be 2.05%.

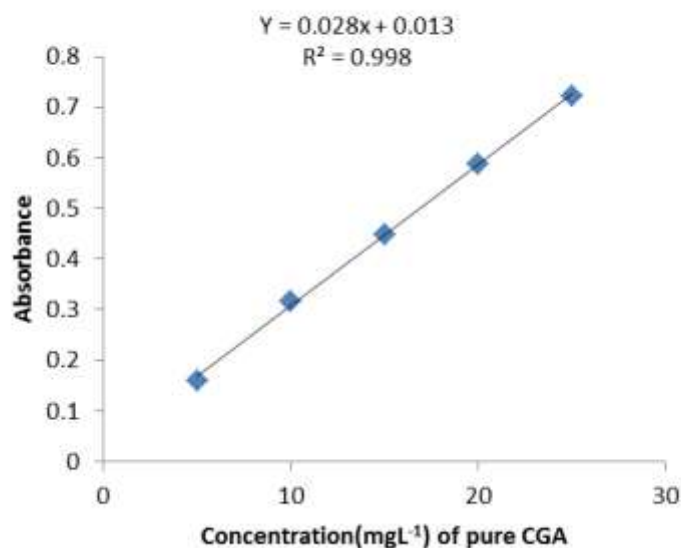


Figure 1. Absorbance versus concentration of pure CGA.

Table 1. Mean concentration of CGA content in green coffee beans (n = 3).

Woredas	Total sample volume (mL)	Measured sample volume (mL)	^a CGA content (mg)	CGA content (mg/g)	^b CGA content (% w/w)
Gombora	60	28	2.48	62.10±0.13 ^D	6.21±0.01
Gibe	60	28	2.38	59.58±0.12 ^E	5.96±0.01
Misrak Bedawacho	60	28	2.53	63.25±0.09 ^B	6.33±0.01
Mirab Bedawacho	60	28	2.49	62.33±0.15 ^C	6.233±0.02
Soro	60	28	2.56	64.04±0.17 ^A	6.40±0.02

Means with the same letter in the fifth column are not statistically significantly different.

^aEquation (1) was used.

^bEquation (2) was used.

Table 2. Mean concentration of CGA in green coffee leaves (n = 3).

Woredas	Total Sample volume(mL)	Measured Sample Volume(mL)	^a CGA content (mg)	CGA content (mg/g)	^b CGA content (% w/w)
Gombora	60	28	0.92	23.08±0.10 ^A	2.31±0.01
Gibe	60	28	0.78	19.40±0.11 ^E	1.94±0.01
Misrak Bedawacho	60	28	0.79	19.75±0.09 ^C	1.98±0.01
Mirab Bedawacho	60	28	0.78	19.51±0.08 ^D	1.95±0.01
Soro	60	28	0.82	20.55±0.14 ^B	2.06±0.01

Means with the same letter in the fifth column are not statistically significantly different.

^aEquation (1) was used.

^bEquation (2) was used.

The analysis of one way ANOVA indicated that CGA concentration of all the studied areas were statistically significant.

CGA contents in green coffee beans and leaves were measured by following the same procedures and by using

the same computational and experimental methods. However, as can be seen from Tables 1 and 2, the contents of CGA in coffee beans and coffee leaves are significantly different. The measured CGA contents in each coffee bean samples were greater than that of

Table 3. Percentage difference of CGA between green coffee beans and leaves (n = 3).

Woredas	CGA content in coffee beans (% w/w)	CGA content in coffee leaves (% w/w)	CGA difference in beans and leaves in percentage
Gombora	6.21±0.01	2.31±0.01	62.85±0.96
Gibe	5.96±0.01	1.94±0.01	67.44±1.03
Misrak Bedawacho	6.33±0.01	1.96±0.01	68.78±1.36
Mirab Bedawacho	6.23±0.02	1.95±0.01	68.68±0.88
Soro	6.40±0.02	2.06±0.01	67.91±1.33

coffee leave samples.

As can be seen from Table 3, the percentage difference of CGA in green coffee beans and leaves in each study area signifies that green coffee beans carry high content of CGA. CGA in green coffee beans was at least 62.85% higher than its counterpart CGA in leaves. Table 3 displays percentage difference of CGA between each green coffee bean and coffee leave samples.

DISCUSSION

Percentage concentration of chlorogenic acid in this work for green coffee beans ranged from 5.96±0.012 to 6.40±0.02 % with average of 6.23%. The level of chlorogenic acid in green coffee beans reported by (Farah et al., 2006b; Ky et al., 2001) were about 4 to 8.4% for Arabica coffee which agrees with results of this work. CAG concentration found in this work also fits in the range of results obtained in Cameroon and Congo (0.8 to 11.9%) (Campa et al, 2005). According to Belay and Gholap (2009), the percentage of CGA in various green coffee beans collected from south west of Ethiopia is in the range of ((6.05± 0.33 to 6.25±0.23) %) which agrees with the results of this work. However CGA results found in this work were found to be slightly lower in the upper range than the one found by Ky et al. (2001) for Arabic coffee (3.5 to 7.5%).

Moreover, concentration of chlorogenic acid in green coffee leaves in matured ages in this study ranged from 1.94±0.01 to 2.317±0.01% with average percentage of 2.05%. Results of the study by Kristiningrum (2015) by validated TLC-Densitometry method showed that CGA concentration percentage of old (aged) and young leaves of Arabica coffee were 2.79±1.87% and 1.89±2.15%, respectively. It can be seen that result of this work is in agreement with results of Kristiningrum (2015) leaves as it falls between the values for young and old (aged) As the age of leaves at matured growing stage is in between young and aged or old (Sujitrat et al., 2017), the percentage of CGA is also in between the two growing stages.

As an be observed in Table 3, high CGA content was recorded in green coffee beans than green coffee leaves at matured growing stage. CGA in beans was at least 63 % greater than in leaves. The minimum mean CGA

concentration in beans was 59.58±0.12 mg/kg recorded in Gibe while the maximum 64.04±0.12 mg/kg which was obtained in Soro. On the other hand the maximum content of CGA in green coffee leaves was 23.08±0.10 mg/kg obtained in Gombora and the minimum values was 19.40±0.11 mg/kg obtained in Gibe study area. For decaffeinated coffee beans, Hall et al. (2018) found CGA of 31,115.23 mg/kg and Budiman et al. (2017) reported that it was 3.02±0.14%. These researches also determined CGA content for caffeinated coffee beans and Hall et al. (2018) reported 38,932.81 mg/kg and Budiman et al. (2017) reported that it was 4.16±0.16%. Current results, as compared to these literatures, are found to be more than both caffeinated and decaffeinated CGA contents of coffee beans reported by Budiman et al. (2017) and Hall et al. (2018). Present results may be linked with work of Fujioka et al. (2008) which reported that diet rich in CGA compounds play a great role in preventing various diseases associated with oxidative stress, as well as cancer, aging, and cardiovascular and neurodegenerative diseases. Thus, intake of more green coffee beans may be recommended for people for such health cases considering other side effects in to account.

Conclusion

We report comparative study on determination of concentration of CGA in green coffee beans and leaves (at matured growing stage) with UV/Vis spectrophotometer though liquid-liquid extraction of dichloromethane solvent. It was observed that more CGA content was present in coffee beans than the leaves in all considered study areas. Percentage of CGA in green coffee beans is at least 63.00% greater than that of green coffee leaves. In order to recommend, intake of more green coffee beans for health benefits like oxidative stress, cancer, aging, and cardiovascular health cases, toxicity study could be recommended. On top of that, the contents of CGA in coffee beans and coffee leaves obtained in this work in agree with results of most literature cited.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interest.

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Full Length Research Paper

Adsorption of chromium by brewers spent grain -g-poly (acrylic acid-co-acryl amide) from electroplating effluent

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Toxic metal ions have lethal effects on all forms of life and these metal ions could enter the food chain when untreated waste effluents are discharged into the environment. In recent years, the use of low-cost adsorbent materials has been widely investigated in search of replacement for the costly methods that are currently used for removing these toxic metal ions from waste streams. In this study, the remediation of chromium ions from electroplating effluent was studied under static conditions using a copolymer material that was derived by grafting polyacrylic acid and polyacrylamide onto the cellulosic backbone of brewers spent grain (BSG). Batch experiments were carried-out using effluents with different concentrations of chromium ions, specifically 25, 50, 75, 100 and 125 mg/L. The results revealed that the optimum sorption of chromium occurs at pH 3.0 and adsorbent-adsorbate contact time of 1.5 h gave maximum adsorption regardless of the metal ion concentration in the effluent. The kinetic data fit the pseudo-second order reaction model, suggesting that chemisorption was the rate limiting step for the sorption of chromium ions onto BSG-g-poly (acrylic acid –co- acryl amide). The isotherm studies showed that the Langmuir model gave the best fit to the experimental data, with q_{max} value of 15.58 mg/g after 5 h of effluent contact with the adsorbent material. The results obtained in this study have shown that BSG-g- poly (acrylic acid –co- acryl amide) has a lot of potentials for application as an alternative adsorbent material for the remediation of chromium ions from electroplating waste streams.

Key words: Adsorption, chromium, electroplating, effluent, brewers spent grain, studies.

INTRODUCTION

The upsurge in industrial development that resulted from population growth necessitated the use of heavy metals in large quantities, thereby creating serious environmental

hazards due to contamination by these metals (Appel and Ma, 2002). Heavy metals are metals with specific gravity greater than five and are toxic (Lakatos et al., 2002).

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Heavy metals such as copper, cobalt, chromium, cadmium, lead, nickel, arsenic and mercury are environmental pollutants. The presence of these metals in aqueous waste streams discharged into the environment from metal plating, metal finishing and mining industries poses a threat to a healthy environment, due to their negative impacts on human health, plant and aquatic life that have been linked with their non-biodegradable nature and bioaccumulative effects (Wan et al., 2010).

Chromium (Cr) is a d-block element and the strong oxidizing nature facilitates its absorption through the skin and rapid movement through the soil and aquatic environment (Zvinowanda et al., 2009). The optimum permissible level of Cr⁶⁺ for potable and surface water are 0.05 and 0.1 mg/L, respectively (Dubey and Krishna, 2007). Effluents (wastewater) and rinses from metal plating, passivation and ferrochrome processing in the electroplating industry constitute the major sources of chromium in the environment (Gupta et al., 1999; Amuda et al., 2007). Respiratory problems (irritation and ulceration of the nasal septum and asthma), skin damage (severe burns and interference of the healing of scalp and cuts) and failure of some vital organs like liver and kidney may result from prolonged exposure to chromium (Singh et al., 2006; Wang et al., 2009; Jusoh et al., 2007).

The eco-toxicity of this metal, the high capital outlay and energy requirements of existing technologies (such as precipitation, ion exchange, electrolytic, membrane processes, osmosis and dialysis methods) and the strict legislation for reduction of heavy metals in industrial effluents (Aldehold et al., 1996) triggered a continuous search for appropriate technologies based on low-cost adsorbent materials for heavy metal remediation in waste streams.

Brewer's spent grain (BSG) is the by-product of the mashing process, which is one of the initial operations in brewery aimed at solubilizing the malt and cereal grains to ensure adequate extraction of the wort (Fillandeau et al., 2006). It primarily consists of grain husks and other residual components that were not converted to fermentable sugars in the mashing process. Traditionally, this material is discarded as an industrial waste (Xiros and Cristakopollos, 2009) and the amount of BSG generated could be about 85% of the total by-products (Tang et al., 2009). Hence, BSG could be a high volume low cost by-product of the brewing industry and may be a valuable resource for industrial exploitation. Besides, the reactive functional groups like hydroxyl, amine and carboxyl that can be activated in BSG are responsible for sorption of heavy metal in aqueous solutions (Li et al., 2008).

In furtherance of the exploitation of Brewer's Spent Grain (BSG) and its derivatives for the remediation of heavy metals from waste streams, this research work was undertaken to investigate the effect of poly (acrylic

acid-co-acryl amide) grafted onto pretreated BSG on the remediation of chromium from electroplating waste effluent.

MATERIALS AND METHODS

Acrylamide, acrylic acid, methanol, sodium hydroxide, hydrochloric acid, potassium chloride, acetone, benzoyl peroxide, ethyl alcohol were all Analar grade procured from Sigma-Aldrich (Germany). Fresh Brewer's Spent Grain (BSG) was kindly supplied by Guinness Nigeria PLC, Ikeja-Nigeria. The BSG obtained was a by-product from the mashing process of lager beer.

Pretreatment of BSG

Prior to chemical treatment, crude BSG was washed with distilled water and dried in an oven at 105°C for 12 h. In order to obtain a material with high surface area, the dried BSG was milled in a ball mill and fractionated using a 100 µm sieve and packaged in polyethylene bags and stored in laboratory cupboard at room temperature.

Preparation of Poly (Acrylic acid-co-Acryl amide) grafted BSG (BSG-g-Ac-co-Am)

The adsorbent material was prepared in a 1000-ml three-neck round bottom flask equipped with a mechanical stirrer, thermometer and nitrogen gas inlet. Precisely 20.0 g of pretreated BSG was placed in the reaction flask and 30.0 ml of toluene was added into the flask. The flask was then fitted and placed in an oil-bath. The content of the flask was stirred at 250 rpm for 30 min at 50°C. Accurately weighed 0.01 g of benzoyl peroxide was added to the flask and stirred at 250 rpm for 20 min at 120°C. At this point, 2.0 ml of acrylic acid and 2.0 g of acryl amide were added simultaneously to the reaction flask. The content of the flask was then stirred at 500 rpm under nitrogen gas for 45 min at 120°C. The flask was then allowed to cool to ambient temperature. The gelled copolymer was precipitated in excess acetone and then washed in methanol. The co-polymer adsorbent material was subsequently dried in a hot air oven at 50°C for 6 h. The dried mass was then ball milled and sieved through a 50 µm mesh to obtain particles ≤ 50 µm, which was stored in a polyethylene bag before experimentation.

Collection of electroplating wastewater effluent

Electroplating rinse wastewater was obtained from the electroplating workshop or laboratory of the Federal Institute of Industrial Research, Oshodi-Lagos, Nigeria. Effluent samples were obtained from three suction points connecting the effluent reservoir tank. They were properly mixed in a 1000-ml Erlenmeyer flask to give a representative sample. This sample was used to prepare effluents with varying chromium ion concentrations of 25, 50, 75, 100 and 125 mg/L.

Batch sorption studies

The sorption of chromium by (BSG-g-Ac-co-Am) was studied in a batch system at room temperature using effluent samples with the range of concentrations of 25 to 125 mg/L. From each effluent stock solution, 50 ml was measured into a 200-ml conical flask and 2.0 g of adsorbent material was weighed into each flask. The pH of the

mixture contained in each flask was adjusted to 4.0 using 1.0 M HCl solution. The experimental mixture was allowed to equilibrate (shaking with a flask shaker at 100 rpm for 20 h). Experimental flasks were withdrawn at 0.5, 1.0, 1.5, 2.0, 5.0, 10.0, 15.0 and 20.0 h intervals and each mixture was filtered using a Whatman #40 filter paper. The filtrate was analyzed for residual chromium ion using an atomic adsorption spectrophotometer (SHIMADZU GFA 7000A). The same procedure was carried for all effluent concentrations and the amount of chromium sorbed per unit mass of BSG-g-Ac-co-Am for each investigation was evaluated using the equations below (Farooq et al., 2010; Meng-Wei et al., 2013);

$$q_e = \frac{(C_o - C_e)v}{w} \quad (1)$$

$$\% \text{ Adsorption} = \frac{(C_o - C_e)100}{C_o} \quad (2)$$

Where C_o , C_e , v and w are the initial concentration of metallic ion (mg/L), final (equilibrium) concentration of adsorbate ion (mg/L), volume of effluent solution in liters (L) and weight of adsorbent (g), respectively.

Effect of initial effluent metal ion concentration and contact time

The sorption capacity of BSG-g-Ac-co-Am for the removal of chromium ion was studied using the effluent concentrations 25, 50, 75, 100 and 125 mg/L. The milligram of chromate ion sorbed per g of BSG-g-Ac-co-Am was evaluated at the equilibration time intervals of 0.5, 1.0, 1.5, 2.0, 5.0, 10.0, 15.0 and 20.0 h. The solution after equilibration in a shaker at a speed of 100 rpm under ambient temperature was filtered (Whatman #40) and the filtrate was analyzed for adsorbate metal concentration. Sorption capacity was expressed as percentage adsorption using Equation 1 as earlier stated.

Effect of pH on adsorbate sorption by BSG-g-Ac-co-Am

The pH range used for this study was 2-9. Exactly 50 ml of 25 mg/L effluent solution was measured into a conical flask, 2.0 g of adsorbent was weighed into the flask, and 1.0 M HCl and 1.0 M NaOH were used to adjust the pH to the required values. The flask was equilibrated in a shaker at a speed of 100 rpm for 20 h. The solution was filtered and aspirated into an atomic adsorption spectrophotometer (SHIMADZU GFA 7000A) for analysis of residual adsorbate ion content. The same protocol was carried-out for all effluent concentrations.

Determination of adsorption kinetics and isotherms

A representative effluent solution for study was prepared by mixing equal volumes of five different effluent solutions with concentrations of 25, 50, 75, 100 and 125 mg/L. From this effluent solution, 50 ml was measured into eight 200-ml Erlenmeyer flasks and 2.0 g of adsorbent was added to each flask and equilibrated in a flask shaker at 100 rpm under ambient temperature. The flasks were withdrawn at the intervals of 0.5, 1.0, 1.5, 2.0, 5.0, 10.0, 15.0 and 20.0 h, respectively, filtered and analyzed for residual adsorbate ions. The values of q_e and C_e were obtained for each investigation, thereafter data obtained were processed with MATLAB software (version 4.0).

The pseudo first and second kinetic orders are often used for the scale-up of sorption systems. The pseudo-first order kinetic can be expressed as (Farooq et al., 2010).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

A plot of $\ln(q_e - q_t)$ vs t gives a straight line graph. The pseudo-second order kinetic was evaluated using the following kinetic equation (Farooq et al., 2010). Similarly, a plot of t/q_t vs t gives a straight line graph.

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

The Isotherm models are widely used to investigate the quantity of metal ions sorbed by a certain adsorbent material. The distribution of metal ions between aqueous solution and adsorbent surface is a measure of the position equilibrium and can be expressed by monolayer adsorption developed by Langmuir and by multilayer adsorption by Freundlich isotherm.

The expression used for Langmuir isotherm is given by the following equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b} (q_{max}) \quad (5)$$

$$q_{max} = \frac{k_L}{b} \quad (6)$$

A plot of $\frac{C_e}{q_e}$ vs C_e gives a straight line wherein the q_{max} and b are obtained from the slope and the intercept, respectively. The Freundlich model on the other hand is suitable for the non-ideal sorption on heterogeneous surfaces in a multilayer way; and the linear form of Freundlich equation used for this study was:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

A plot of $\ln q_e$ vs $\ln C_e$ gives a straight line and the values for n and k_F are obtained from the slope ($1/n$) and the intercept $\ln k_F$, respectively.

RESULTS AND DISCUSSION

Effect of initial concentration of effluent solution and contact time

Figure 1 shows that the uptake of chromate ions from the solution (amount of chromate ions in mg adsorbed per g of BSG-g-Ac-co-Am) with time increases with increase in the initial concentration of chromate ion in the effluent solution. This can be adduced to the fact that the concentration gradient of chromate ions is directly proportional to the initial concentration and the increase in transfer of chromate ion from the solution to the adsorbent material was due to the increase in driving force (Meng-Wei et al., 2013).

Percentage sorption of chromate ion on BSG-g-Ac-co-Am

Figure 2 shows the percentage of chromate ions in the effluent solutions sorbed by BSG-g-Ac-co-Am with changes in time for the various initial concentrations. Interestingly, higher sorption rates were shown at the

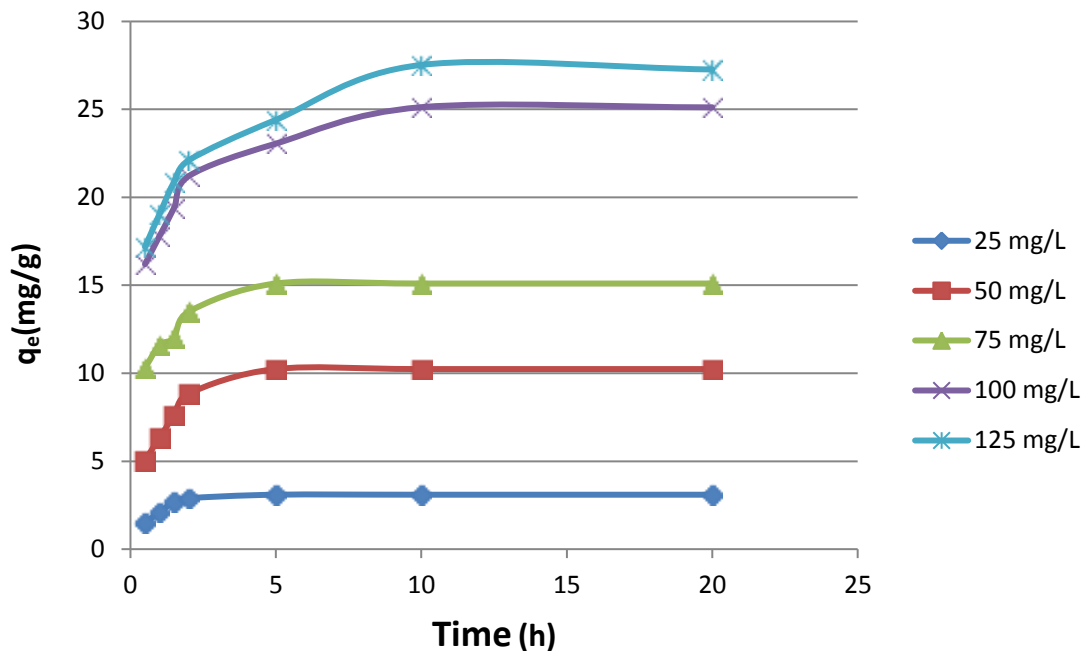


Figure 1. Effect of initial concentration of chromate ion in the effluent and contact time on the quantity of adsorbate sorbed.

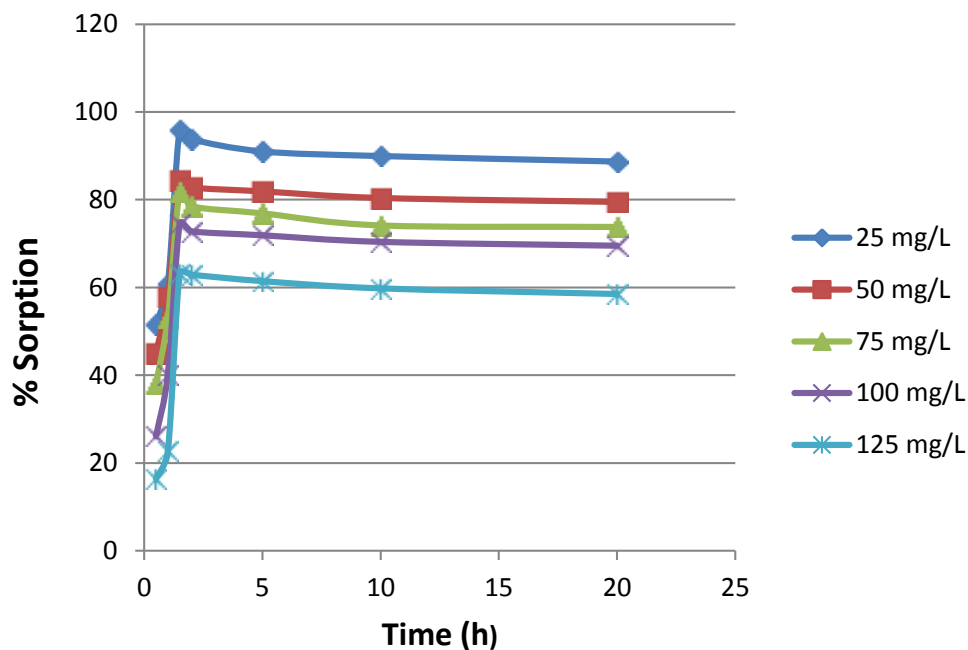


Figure 2. The percentage of chromate ions in effluent solution sorbed by BSG-g-Ac-co-Am.

onset of the experiment. The sorption equilibrium was slowly attained as demonstrated by the plateau shown in each curve. An inverse relationship between the percentage adsorbed and the initial adsorbate concentrations was clearly observed. The maximum

exposure time used was 20 h during the batch equilibrium studies.

BSG-g-Ac-co-Am sorbed more than 60% of adsorbate after 1.5 h regardless of the initial chromate ions concentration in the effluent solutions. As chromate ions

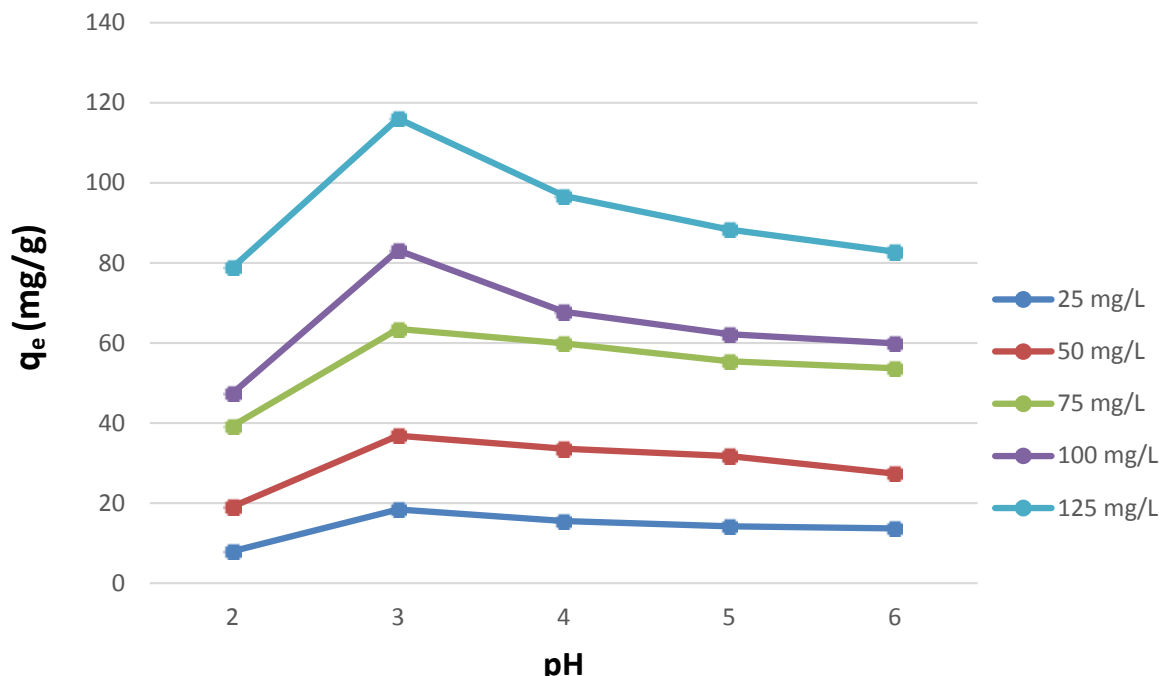


Figure 3. Effect of pH on the sorption of chromate ions.

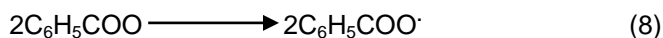
concentration in the effluent solutions increases, binding capacity of BSG-g-Ac-co-Am attained saturation instantaneously, resulting in decrease in the overall percentage of adsorbate (Aydin et al., 2008; Meng-Wei et al., 2013).

Effect of pH

The pH of a solution has been found to be the most important parameter that influences the speciation of adsorbate ions and the charges on the adsorbent sites (Lee et al., 1998; Marques et al., 2000). Thus, the effect of pH on the sorption of chromate ions from solution by BSG-g-Ac-co-Am largely depicts the inter-play between metal solution chemistry and the ionic state of the functional groups on BSG-g-Ac-co-Am within the range pH of values used for this study.

Figure 3 shows a plot of the amount of chromate ions sorbed per g of adsorbent material with respect to pH values of the effluent solutions. Owing to the high reductive potential of Cr^{6+} , it is readily hydrolyzed to various forms of oxo-anions, which includes $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} and HCrO_4^- at low pH values (Mohan and Pittman, 2006; Zvinowanda et al., 2009). The speciation of chromate ion in these oxo-anion states may have facilitated their removal as they readily bind to the positively charged adsorbent sites to form a copolymer-metal complex (Suksabye et al., 2007; Ofomaja and Ho, 2007). Moreover, the reactions which occur during the initiation of polymerization using benzoyl peroxide as

initiator, led to the formation of a highly reactive benzoylperoxy radical, which subsequently combined with the abstracted hydrogen from allylic centers present in Brewers Spent Grain to yield benzoic acid during the grafting process (Penczek et al., 2005) as shown in Equations 8 and 9.



The formation of benzoic acid *in situ* decreases the point of zero charge pH (Kumari et al., 2006; Farooq et al., 2010). This decrease led to the protonation of the amine, hydroxyl, carboxyl and sulphhydryl groups on the surface of BSG-g-Ac-co-Am. These groups then behave as positively charged moieties, thereby sequestering and coordinating the chromium oxo-anions into the copolymer matrix at an optimum pH value of 3.0. A greenish colour was observed on the surface of the adsorbent indicating the presence of Cr^{3+} (Farooq et al., 2010).

Although, Cr^{6+} are reduced to Cr^{3+} at acidic conditions (low pH), the amount of Cr^{6+} and Cr^{3+} at low pH is approximately equal (Kumari et al., 2006; Gupta and Rastogia, 2008). This suggests that at the optimum pH 3.0, the competitive binding of protons with the oxo-anions decreased and the oxidation of Cr^{3+} to oxo-anions outranked the complementary reductive reaction. Hence, more chromate ions were sorbed by the adsorbent at this point. At the extreme pH values of 1.0 to 2.0, the competitive binding of protons with the oxo-anions could

Table 1. Pseudo-first order kinetics studies of adsorbate onto BSG-g-Ac-co-Am.

Effluent Concentration (mg/L)	q_e (mg/g)	$\kappa_1 \times 10^4$	R^2
25	3.11	6.10	0.2241
50	8.24	6.80	0.3951
75	14.02	12.40	0.6224
100	17.55	15.30	0.7002
125	20.14	18.80	0.7194

Table 2. Pseudo-second order kinetics studies of adsorbate onto BSG-g-Ac-co-Am.

Effluent Concentration (mg/L)	q_e (mg/g)	q_e^2	$\kappa_2 \times 10^1$	R^2
25	2.16	4.67	1.92	0.9889
50	10.04	100.80	2.14	0.9978
75	18.41	338.93	4.71	0.9997
100	29.98	898.80	0.99	0.9888
125	100.52	10104.27	2.66	0.9979

lead to the neutralization of the charges of chromate ions, making them unavailable to co-ordinate with the positively charged adsorbent sites. This may account for the low adsorbate-adsorbent interaction at these low pH values. As the pH value increases, the positive character of the adsorbent surface gradually changes to negative charge, a phenomenon that brings about the repulsion of oxo-anions and the 'winner' is the co-metal ions with higher reductive potentials than chromium ions present in the electroplating effluent.

Sorption kinetic studies

From Equation 3, a plot of $\ln(q_e - q_t)$ vs t generated a straight line. The amount of metal ion sorbed per g of adsorbent at equilibrium q_e was determined from the intercept $\ln q_e$ and the slope gave the rate constant k_1 as shown in Table 1.

Similarly, from Equation 4, a plot of t/q_t vs t generated a straight line. The values of $(q_e)^2$, q_e and k_2 were obtained from the intercept $\frac{1(q_e)^2}{k_2}$ and slope $1/q_e$ respectively. The values are presented in Table 2.

From Table 1, it is evident that the pseudo-first order kinetic model did not largely fit the data obtained in the study, resulting in very low linear correlation coefficients (R^2) of 0.2241-0.7194. Comparing these values to that of the second-order kinetic data, the high linear correlation coefficient (0.9889-0.9979) suggests that there was coordination of chromate ions by BSG-g-Ac-co-Am matrix. This observation is in agreement with the sorption of Cr^{6+} onto wheat bran (Singh et al., 2009) and Cr^{3+} onto wheat straw (Chojnack, 2006). The sorption rate $k_2(q_e - q_t)^2$ for a second order kinetics is directly proportional to

dq_t/dt the result as shown in Table 2 indicates a fast adsorption rate in a short equilibrium time (Meng-Wei et al., 2013). The results for q_e and $(q_e)^2$ have shown that there was attainment of equilibrium at a very short time, with very high adsorption of chromate ions. This observation gave credence to the high degree of affinity between the reactive moieties on the adsorbent material and chromate ions in the effluent stream. Therefore, the overall sorption process is controlled chemically (chemisorptions) which involved sharing of electron covalently between the oxo-anoin ions of chromium and coordinating ligand on the copolymer.

Table 3 shows the results from Langmuir and Freundlich isotherms studies conducted on the adsorption of chromate ions by BSG-g-Ac-co-Am. The high regression coefficient shows good linearity of the data obtained, which follows that chromium ion adsorption fits the two isotherms.

The Langmuir isotherm gave higher correlation (99%), which exceeds 98% for Farooq et al. (2010). Thus, it depicts a better fit to the experimental data than the Freundlich isotherm where the R^2 values were within the range of 93 to 96%. The higher correlation coefficient of the Langmuir isotherm is a confirmation that the adsorbate-adsorbent interaction in the study occurred through chemisorption since monolayer adsorption implies that chromate ions formed a strong chemical bond with charged moieties on the BSG-g-Ac-co-Am surface. As no additional chromate ions can be chemisorbed once the surface sites are saturated or covered, the good correlation observed for the Freundlich isotherm for multilayer adsorption suggests that there could be some physisorption onto the chemisorbed chromate ions under extended incubation, since this interaction requires just weakly van der Waals forces

Table 3. Isotherm studies of adsorbate onto BSG-g-Ac-co-Am.

Contact time (h)	Langmuir			Freundlich			
	b	k _l	q _{Max} (mg/g)	R ²	k _F	n	R ²
0.5	0.042	0.461	10.98	0.9964	0.5974	1.35	0.9634
1.0	0.049	0.562	11.46	0.9953	0.7943	1.46	0.9544
1.5	0.051	0.613	12.01	0.9990	0.9953	1.54	0.9348
2.0	0.061	0.766	12.55	0.9982	1.2354	2.14	0.9608
5.0	0.052	0.810	15.58	0.9996	1.4552	2.26	0.9504
10.0	0.078	1.073	13.75	0.9985	1.6244	1.94	0.9328
20.0	0.105	1.475	14.04	0.9991	1.9345	2.08	0.9559

(Davis and Davis, 2003). The Freundlich isotherm model data gave n values greater than 1, which revealed that there was favourable adsorption of chromate ions by BSG-g-Ac-co-Am.

The q_{max} value of 15.58 mg/g was attained after 5 h. This indicates that a preponderance of adsorption sites on the copolymer presents the same proactive attraction of chromate ions from the effluent stream onto the adsorbent material. The higher adsorption time of 5 h obtained in this study when compared to 2 h for adsorption of Cu²⁺ onto chitosan-coated sludge (Meng-Wei et al., 2013) can be attributed to a number of factors. The competitive adsorption of co-metal ions with higher reductive potential than chromium that was present in the electroplating effluent might have negatively influenced the rate of coordination of chromate ions. Moreover, the formation of free homopolymer chains of polyacrylamide and polyacrylic acid during the grafting reaction and perhaps, detachment of poorly grafted chains from the polymer backbone into the effluent solution due to mechanical agitation, may be adduced for the extended time.

Conclusion

The application of Poly (acrylic acid –co- acryl amide) grafted Brewers Spent Grain as an adsorbent material for the remediation of chromium ions from electroplating effluent was investigated. The increase in quantity of chromate ions sorbed per gram of adsorbent that corresponded with the increase in the initial effluent concentration showed that the rate of sorption increases with initial effluent concentration. Over 60% of adsorbate ions were sorbed from all effluents within 1.5 h of commencement of incubation, suggesting that the initial rate of sorption is highest regardless of the initial chromate ions concentration in the effluents. Optimum adsorption of chromate ions by BSG-g-Ac-co-Am occurs at pH 3.0 irrespective of the concentrations of chromium ions in the effluents. The lower sorption observed at extreme acidic pH 1-2 can be adduced to the neutralization of chromate oxo-anions, being inundated

by oppositely charged protons at such pH. Isotherm studies using Langmuir and Freundlich models revealed that the mode of adsorption is chemisorption as the Langmuir model gave the best fit to the data, with 99% correlation. Kinetic plots followed the second order kinetic model with linear correlation coefficient of 0.9889 to 0.9979, and thus is the most suitable model describing the controlling mechanism of the adsorption. The occurrence of chemisorption owing to chemical bond formation between chromate oxo-anions and positively charged moieties on the surfaces of the adsorbent material and the subsequent physiosorption of chromate layer onto the chemisorbed layer offer a greater advantage of using BSG-g-Ac-co-Am as a novel adsorbent material for remediation of chromium from effluent.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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