

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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Received 14 August, 2017; Accepted 18 September, 2017

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

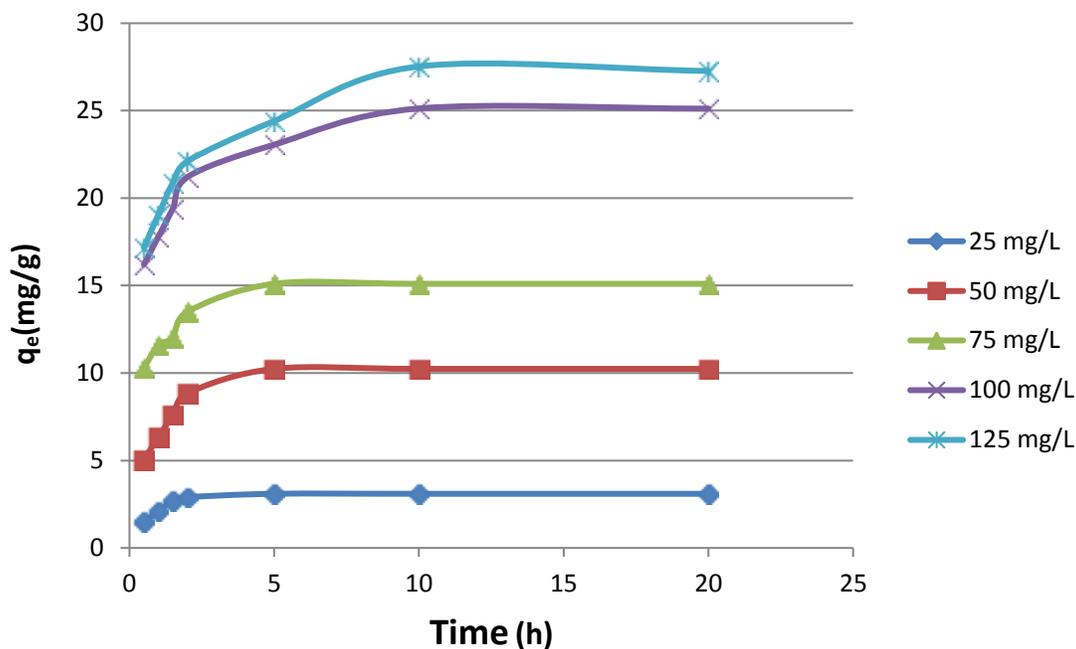


Figure 1. Effect of initial concentration of chromate ion in the effluent and contact time on the quantity of adsorbate sorbed.

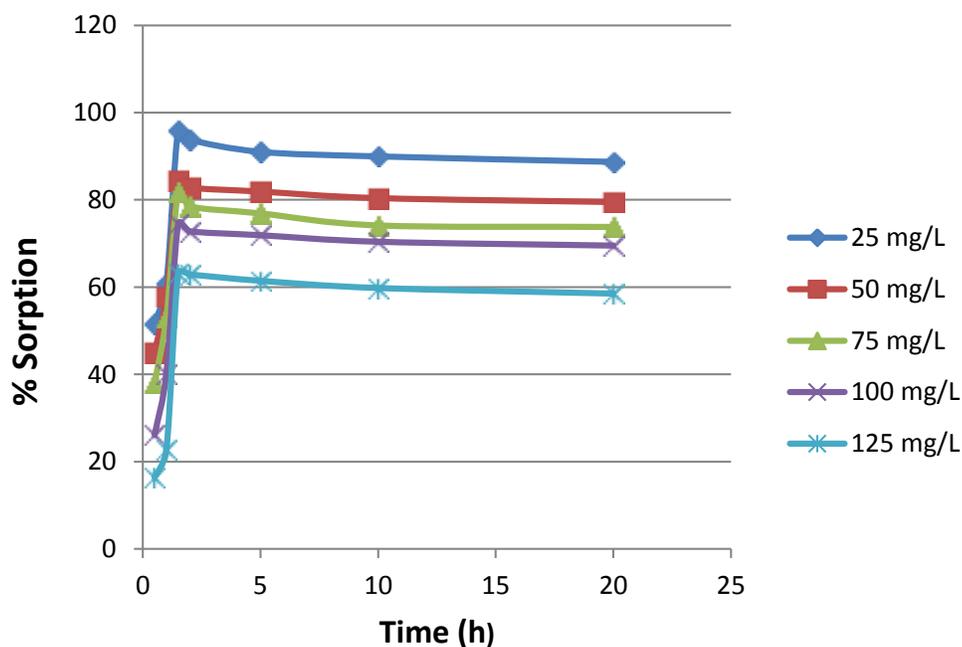


Figure 2. The percentage of chromate ions in effluent solution sorbed by BSG-g-Ac-co-Am.

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

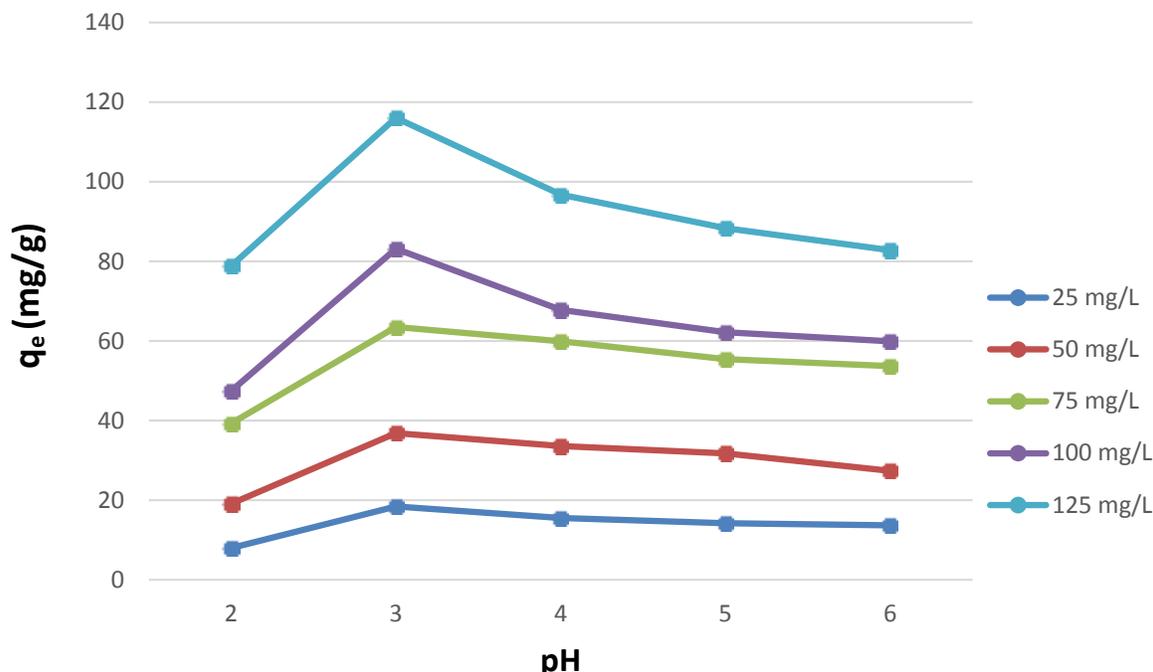


Figure 3. Effect of pH on the sorption of chromate ions.

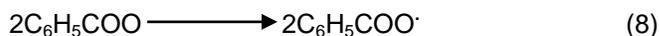
concentration in the effluent solutions increases, binding capacity of BSG-g-Ac-co-Am attained saturation instantaneously, resulting in decrease in the overall percentage of adsorbate (Aydin et al., 2008; Meng-Wei et al., 2013).

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.

REFERENCES

- Aldehold D, Williams JC, Edyvean JBR (1996). The removal of heavy metal ions by seaweeds and their derivatives. *Bioresource Technology* 58:1-6.
- Amuda OS, Giwa AA, Bello IA (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochem. Engineering Journal* 36:174-181.
- Appel C, Ma L (2002). Heavy metals in the environment concentration, pH and surface charge effects on Cd and Pb sorption in three tropical soils. *Journal of Environmental Quality* 21:581-589.
- Aydin H, Bulut Y, Yerlikaya C (2008). Removal of Copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Economics and Management* 87:37-45.
- Chojnack K (2006). Biosorption of Cr (III) ions by wheat straw and grass: a systematic characterization of new biosorbents. *Polish Journal of Environmental Studies* 15:845-852.
- Davis ME, Davis RJ (2003). *Fundamentals of chemical reaction engineering*. McGraw-Hill Higher Education, New York. pp.133-183.
- Dubey SP, Krishna G (2007). Adsorption of chromium (VI) on low cost adsorbents derived from agricultural waste material. *Journal of Hazardous Materials* 145:465-470.
- Farooq U, Kozinki JA, Khan MA, Athar M (2010). Biosorption of heavy metal ions using wheat based biosorbents-A review of recent literature. *Bioresource Technology* 101:5043-5053.

- Fillandeau L, Blanpain-Avet P, Daufin G (2006). Water, Wastewater and Waste Management in Brewing Industries. *Journal of Cleaner Production* 14:463-471.
- Gupta VK, Rastogia A (2008). Biosorption of lead from aqueous solutions by green algae *Spirogyra species*: Kinetics and equilibrium studies. *Journal of Hazardous Materials* 152:407-414.
- Gupta VK, Mohan D, Sharma S, Park KT (1999). Removal of chromium (VI) from electroplating industry wastewater using bagasse fly ash- a sugar industry waste material. *The Environmentalist* 19:129-136.
- Jusoh A, Shiung LS, Ali N, Noor MJMM (2007). A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination* 206:9-16.
- Kumari P, Sharma P, Srivastava S, Srivastava MM (2006). Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: Removal and recovery of arsenic from aqueous system. *International Journal of Mineral Processing* 78:131-139.
- Lakatos J, Brown SD, Snape CE (2002). Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams. *Fuel* 81:691-698.
- Lee SH, Jung CH, Chung H, Lee MY, Yang JW (1998). Removal of heavy metals from aqueous solution by apple residues. *Process Biochemistry* 33:205-211.
- Li X, Tang Y, Cao X, Lu D, Luo F, Shao W (2008). Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. *Colloids and Surfaces A* 317(3):512-521.
- Marques PASS, Rosa MF, Pinheiro HM (2000). pH effects on the removal of Cu^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution by waste brewery biomass. *Bioprocess Engineering* 23:135-141.
- Meng-Wei W, Chan-Ching W, Chien-Min C (2013). The Adsorption Study of Copper Removal by Chitosan-Coated Sludge Derived from Water Treatment Plant. *Journal of Environmental Management* 4:545-551.
- Mohan D, Pitman CU (2006). Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. *Journal of Hazardous Materials* 137(2):762-811.
- Ofomaja AE, Ho YS (2007). Effect of pH on cadmium biosorption by coconut copra meal. *Journal of Hazardous Materials* 139:356-362.
- Penczek P, Czub P, Pielichowski J (2005). Unsaturated polyester resin: Chemistry and technology in crosslinking. *Material Science*, Ameduri. B. Ed. Springer-Verlag, Berlin 184:1-95.
- Singh KK, Hasan HS, Talat M, Singh VK, Gangwar SK (2009). Removal of Cr (VI) from aqueous solution using wheat bran. *Chemical Engineering Journal* 151:113-121.
- Singh KK, Singh AK, Hasan SH (2006). Low cost bio-sorbent 'wheat bran' for the removal of cadmium from wastewater: Kinetic and equilibrium studies. *Bioresource Technology* 97:994-1001.
- Suksabye P, Thiravetyan P, Nakbanpote W, Chayabutra S (2007). Chromium removal from electroplating wastewater by coir pith. *Journal of Hazardous Materials* 141:637-644.
- Tang D, Yin G, He Y, Hu S, Li B, Li L, Liang H, Borthakur D (2009). Recovery of protein from Brewer's Spent Grain by Ultrafiltration. *Biochemical Engineering Journal* 48:1-5.
- Wan WM, Kan CC, Rogel BD, Dalida MP (2010). Adsorption of Copper (II) and Lead (II) ions from Aqueous Solution on Chitosan-Coated Sand. *Carbohydrate Polymers* 80:891-899.
- Wang XS, Li ZZ, Sun C (2009). A comparative study of removal of Cu (II) from aqueous solutions by locally low-cost materials: marine macro algae and agricultural by-products. *Desalination* 235:146-159.
- Xiros C, Cristakopollos P (2009). Enhanced ethanol production from brewer's spent grain by a *Fusarium oxysporum* consolidated system. *Biotechnol. Biofuels* 2:4-6.
- Zvinowanda CM, Okonkwo JO, Shabalala PN, Agyei NM (2009). A novel adsorbent for heavy metal remediation in aqueous environments. *International Journal of Environmental Science and Technology* 6:425-434.