Utilization of Polyacrylamide grafted Brewer Spent Grain (BSG) for Sorption of Cd^{2+}, Cu^{2+} and Pb^{2+} ions in aqueous solution.

Samuel, A.E #1, Olotu, O.O #2, Nwankwo, I.C #3, Odesola O.O #4 and Akinsanya O.O #5

#1, #2, #4 and #5 Federal Institute of Industrial Research, Oshodi (FIIRO) Lagos-Nigeria
#3 Babcock university ilishan--remo, ogun state
Corresponding Author: Materials Development Division, Federal Institute of Industrial Research, Oshodi (FIIRO) Lagos-Nigeria:

Abstract

Adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} using polyacrylamide grafted brewer's spent grain (BSG-g-PAAM) in aqueous solution was investigated. Sorption capacities for Cu^{2+}, Cd^{2+} and Pb^{2+} were found to be 95.12, 87.45 and 84.65% respectively. The uptake of these metal ions were studied with the following parameters; P^H, temperature, initial metal ion concentration, ionic strength and effect of contact time, in order to deduced the optimum condition for practical application of this adsorption material. The outcome indicated that metal ion sorption by BSG-g-PAAM decreased after temperature range of 49-52^oC for these metal ions. Increase in ionic strength led to a decrease in sorption capacity. While increase in initial metal ion concentration showed an increase in adsorbate uptake. Optimal sorption capacity occurred at P^H 4.0, 4.9 and 5.0 for Cu^{2+}, Pb^{2+} and Cd^{2+} respectively. The result from this study demonstrated the ability of BSG-g-PAAM as a resource adsorbent material for the remediation of polluted streams.

Key words: *Adsorption, Sorption capacity, Grafting, Aqueous solution, Remediation*.

INTRODUCTION

Rapid industrialization as a result of development in science and technology created a standard of living which leads to deterioration of the environment. Water contamination occasioned by toxic derivatives, especially heavy metals pose serious environmental dangers owing to their non-biodegradability, toxicity and recalcitrant nature (Fu and Wang, 2011).

Heavy metals are categorized as environmental pollutants as a result of their carcinogenic and mutagenic nature. These metal ions are persistence, and bioaccumulate in food chain through up-take at the primary producer level and through consumption at consumer level (Ghaedi and Mosallanejad, 2013). Heavy metal contamination can originate from natural and anthropogenic sources inter alia; mining and smelting activities, electroplating and metal finishing process and agricultural practice. These metal can be classified into four groups which includes; essential (Cu, Cr, Mn, Fe, Zn and Co), also, referred to as micronutrient, in excess they are toxic (Honda, et al; 1983). Ba, Li and Zr made-up the non-essential group. Sn and Al, Hg, Pb and Cu make-up the less toxic and highly toxic group respectively (Honda, et al; 1983: Parsons, 1999). Heavy metals are also called trace elements due their presence in trace (10mg/kg) or in ultra trace (1µg/kg) quantities in the environmental matrices (Parsons, 1999).

Strict legislation on the discharge of these toxic products makes it absolutely necessary to develop various efficient technologies for the remediation of their contamination from wastewater effluents. Existing technologies for heavy metal removal from effluents includes; advanced oxidation processes (Lee, et al; 2003: Al-momani, et al;2002), chemical and electrochemical technologies (Chen, et al; 2002: Hu, et al; 2003), biological treatment (Ahmady-Asbchin, et al; 2008: Aksu, et al; 2000), membrane processes (Cassano, et al; 2000) and adsorption processes (Okieimen and Okundaye, 1989: Okieimen, et al; 1991).

However, these processes involve high capital outlay, high energy input and instability of the adsorbent in salt and acid conditions (Aldehold, et al; 1996: Barminas, et al; 2005). Besides, these processes are not economically feasible for small scale industries prevalent in developing economies owing to large capital investment (Horsfall and Spiff, 2004). These drawbacks therefore necessitate the continuous search to improve the present technologies or a new technology to replace the present ones.

Brewer's spent grain (BSG) are the by-products 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 compounds not converted to fermentable sugars in the mashing process. Traditionally to a large extent this material is discarded as an industrial waste (Xiros and Cristakopollos, 2009). 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 brewing and may be a valuable resource for industrial exploitation. In addition, the reactive functional groups which includes; Hydroxyl, Amine and Carboxyl that can be activated in BSG are responsible for sorption of heavy metal in aqueous solution (Li et al; 2009).

Currently, reports on the use of BSG or its derivatives are still at the infancy. Hence, an attempt was made by our group by grafting polyacrylamide onto BSG as a sustainable adsorbent material for toxic metal ions (Cd^{2+}, Cu^{2+} and Pb^{2+}) removal from aqueous matrix under different experimental conditions. The batch experimental method was employed to assess the effectiveness of the adsorbent material.

Materials and Methods

Material

Acrylamide, Methanol, Sodium hydroxide, Hydrochloric acid, Potassium chloride, Acetone, Ceric Ammonium Nitrate (CAN), Ethyl alcohol were all analar grade procured from British Drug House. Fresh Brewer's Spent Grain (BSG) was kindly supplied by Guinness Nigeria PLC, Ikeja-Nigeria. The BSG obtain was a by-product from the mashing and lautering process of lager beer.

Pretreatment of BSG

Prior to chemical treatment, crude BSG was washed with water, dried in an oven at 60°C for 12hrs. In order to obtain a material with high surface area, the dried BSG was milled in ball mill, fractionated using a 100µm sieve, packaged in a polyethylene bag and stored in laboratory cupboard at room temperature.

Graft Polymerization of BSG (BSG-g-PAAM)

This was prepared by reacting powdered BSG with acrylamide monomer at 60°C using ceric ammonium nitrate as initiator (Toti and Aminabhavi, 2002). 10% BSG solution was prepared in a 250ml conical flask and stirred for two hours with 0.30 mol. of acrylamide in thermostat oil bath at 60°C. The initiator (2.0×10^{-3} mol. of CAN) was added and stirred using a magnetic stirrer (100rpm) for 8hrs. The copolymer obtained was precipitated in acetone, later washed with 5:2 mixture of water/ethyl alcohol to rip the product of homopolymer. The synthesized copolymer was later dried in an oven at 50°C for 6hrs, and weighed using a chemical balance.

Initial metal ion concentration

The sorption of each adsorbate (Cu^{2+}, Cd^{2+} and Pb^{2+}) were analyzed in a batch system. A 20mg/L solution of each metal ion was prepared with deionized water, 50ml of this solution was measured into a 200ml conical flask and 0.1g of the sorbent (BSG-g-PAAM) was weighed into the flask. The flask was corked and shaken vigorously at room for 24hrs with the aid of a flask shaker. The mixture was filtered using whatmann #40 filter paper. The filtrate was then analyzed for each metal ion with help of an Atomic Adsorption Spectrophotometer (Shimadzu GFA 7000A). These protocols were repeated for other concentrations (40, 60, 80 and 100mg/L).

The quantity (Q_o) of metal ion sorbed by the adsorbent was evaluated as follows;

$$Q_o = (C_i - C_f)V/m \text{-----------------------------------} (1)$$

The sorption capacity of metal ion sorbed was calculated using the relation

$$\text{Sorption capacity (\%)} = [(C_i - C_f)/C_i\ ]100 \text{---------------} (2)$$

Where C_i, C_f are the initial and final (equilibrium) concentration of metal ion in mg/L respectively, V is the volume of solution measured in Liters and m is the weight of the adsorbent in grams (g).

Effect of pH on sorption capacity

The performance of BSG-g-PAAM as adsorbent for Cu^{2+}, Cd^{2+} and Pb^{2+} was studied within the p^H range (1-6) at room temperature (Charmarthy, et al; 2001). A 1.0M HCl and 1.0M NaOH was used to adjust the p^H as required in each case. The flask was equilibrated after 1hr for each determination using a flask shaker.

Temperature effect on sorption capacity

0.1g of BSG-g-PAAM was weight into a 200ml conical flask, 50ml synthetic metal solution was added. The temperature was set at 30°C. The flask was equilibrated for 1hr and then withdrawn from the shaker. The content of the flask was filtered, and the filtrate analyzed for metal ion content. The process was repeated for temperatures between 40-100°C at incremental value of 10°C.

Effect of ionic strength on sorption capacity

In order to establish if the presence of other metal ions most especially (alkali and alkaline earth metals), may affect the performance of the sorbent. Different concentration (0.00M, 0.05M, 0.10M, 0.15M and 0.20M) of KCl was prepared and used to adjust the ionic strength of the synthetic metal ion solution. 0.1g, 50ml and 10ml of sorbent, metal ion solution and Kcl solution respectively, was equilibrated at 25°C for 1hr. The residual metal ion was determined for each case.

Effect of time on sorption capacity

To investigate the kinetics of sorption, ten sets of experimental samples made-up of 0.1g adsorbent and 50ml synthetic metal ion solution were prepared. Simultaneously, all the set-up was agitated in a flask shaker. They were removed at regular intervals of 30 minutes, until the optimum time of 300 minutes (5hrs) was attained. The filtrate from each equilibration was obtained and analyzed for metal ion content.

Results and Discussion

Initial metal ion concentration

Figure 1 below shows the equilibration sorption capacity of the adsorbate (Cu^{2+}, Cd^{2+} and Pb^{2+}) by BSG-g-PAAM. It can be inferred that the adsorbent demonstrated a high capability to take up significant quantities of the adsorbate; 95.12, 87.45 and 84.65% for Cu^{2+}, Cd^{2+} and Pb^{2+} respectively. These values are slightly higher than those reported by similar works (Lee and Lin, 2000: Chamarthy et al; 2001: Osemeahon et al; 2008). The variation observed in the sorption capacities could be adduced to the following; Cu^{2+} is easily bonded than other adsorbate, thus it exhibited the highest complexation reaction with the grafted ligand, the surface reactive sites are more amenable to Cu^{2+} during the covalent bond formation with ligands and Cu^{2+} demonstrated the lowest hydration free energy (Cooper et al; 2002: Osemeahon et al; 2008).

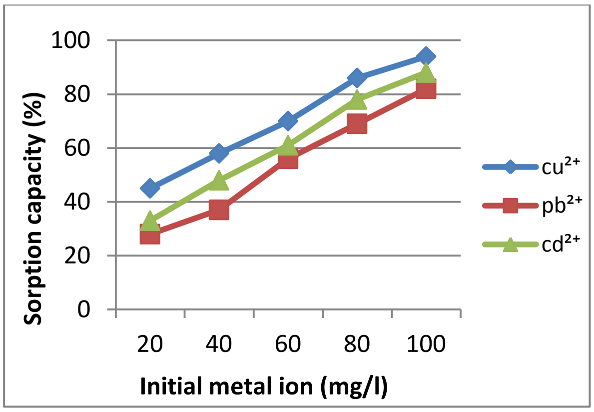

Figure 1: Initial metal ion concentration

Effect of p^H on Sorption Capacity

The effect of p^H on the adsorbate (Cu^{2+}, Cd^{2+} and Pb^{2+}) is presented in figure 2. The p^H reflects the adsorbent-adsorbate physicochemical interactions. A cursory look at the figure indicates that adsorbate sorption increases progressively, it peaks at p^H 4.0, 4.9 and 5.0 for Cu^{2+}, Pb^{2+} and Cd^{2+} respectively. Thus, operation of sorption media at this respective p^H value could bring about optimum sorption capacities. The trend of increasing sorption capacity with increasing p^H is generally explained by increasing dissociation of carboxylic acid group on the cellulosic matrix, which ultimately results in an increasing ion exchange capacity of the adsorbent material. The peak of a typical curve of sorption capacity versus p^H is understood to entail an equilibration point between the soluble hydrated metal ion and corresponding insoluble neutral hydroxide specie (Mohan and Pitman, 2006: Sheng et al; 2007).

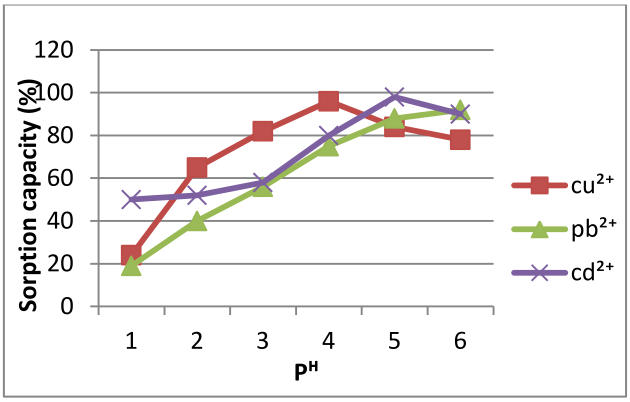

Figure 2: Effect of P^H on sorption capacity

Effect of Temperature on Sorption Capacity

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution by BSG-g-PAAM was studied between 30-100°C as shown in figure 3 below. The adsorption capacity increases as temperature increases. Sorption capacity peaked at 49, 50 and 52°C for Pb^{2+}, Cu^{2+} and Cd^{2+} respectively, and thereafter a gradual, but steady decrease in sorption capacity was observed. These results are comparable with banana stalk grafted PAAM reported by Shibi and Anirudhan (2006) and polyacrylamide grafted konkoli gum reported by Osemeahon et al (2008). Temperature range (49-52°C), seems to present the optimum temperature at which BSG-g-PAAM could be used for practical application for the sorption of these metal ions from aqueous solution. The following factors could suffice, owing to this observations; (i) the inherent fibrous nature the back-bone polymer (BSG) whose pore increases in size as temperature increases (Shibi and Anirudhan, 2006). (ii) Increase in temperature may results in depolymerization of grafted and decrosslinking of polymer chains from the back-bone polymer, resulting in an increase in desorption kinetics of sorbed metal ions (Horike et al; 2002). (iii) The process may be physiosorption. Hence, the adsorption generally increases with a decrease in the temperature owing to the exothermic nature of this process (Ozer et al; 2002).

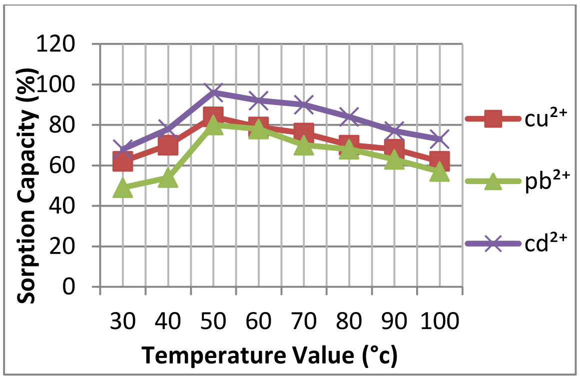

Figure 3: Effect of Temperature on Sorption capacity

Effect of Ionic Strength

Natural waste bodies or industrial wastewater effluents often contain alkali metal ions (Na^+, K^+) and alkaline earth metal ion (Ca^{2+}, Mg^{2+}). Thus, the influence of ionic strength on the adsorption capacity of BSG-g-PAAM on Cu^{2+}, Cd^{2+} and Pb^{2+} was studied adsorption capacity with increasing ionic strength is attributed to the reduction of the difference in ionic osmotic pressure between the adsorbent material (BSG-g-PAAM) and the aqueous solution (Lee and Lin, 2000: Osemeahon et al; 2008). The difference in osmotic pressure between the adsorbent and aqueous solution leads to a decrease in convection transport of metal ion to active sites, owing to competition brought about by population of the external solution with metal ions. This coexistence of metal ions in the aqueous solution occasioned by the presence of K^+ ions interfered with sorption capacity of BSG-g-PAAM. Therefore, we recommend a pretreatment protocol target towards the precipitation of these interfering ions for optimal performance of BSG-g-PAAM.. The effect of ionic strength on BSG-g-PAAM performance is shown in figure 4. The result indicates a reduction in the adsorbate percentage sorbed as ionic strength increases for all metal ions. This trend is in agreement with report for grafted membranes for sorption of Cd^{2+}, Zn^{2+} and Fe^{2+} ions in aqueous solution reported by Osemeahon et al (2008). The decrease in adsorption capacity with increasing ionic strength is attributed to the reduction of the difference in ionic osmotic pressure between the adsorbent material (BSG-g-PAAM) and the aqueous solution (Lee and Lin, 2000: Osemeahon *et al*; 2008). The difference in osmotic pressure between the adsorbent and aqueous solution leads to a decrease in convection transport of metal ion to active sites, owing to competition brought about by population of the external solution with metal ions. This coexistence of metal ions in the aqueous solution occasioned by the presence of K^+ ions interfered with sorption capacity of BSG-g-PAAM. Therefore, we recommend a pretreatment protocol target towards the precipitation of these interfering ions for optimal performance of BSG-g-PAAM.

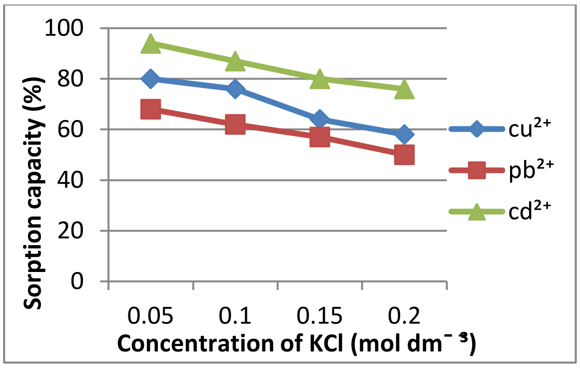

Figure 4:Effect of ionic strength on sorption capacity at 30°c

Effect of time on sorption capacity

Figure 5 below Shows adsorption kinetics plot. Equilibration time of 70 minutes was obtained for both Cu^{2+} and Cd^{2+}, while 95 minutes was recorded for Pb^{2+}. This result compares well with a range of 1-2 hrs for heavy metal equilibration as reported (Garg et al; 2008b: Karnitz et al 2009). The rapid sorption of Cu^{2+} and Cd^{2+} by BSG-g-PAAM could be attributed to the porous nature cellulosic polymer back-bone alongside with attached ligand and their endowment with and/or complex more amenable to metal ions (Bai and Abraham, 2001). This could also be ascribed to loosely held, polarizable outer electrons, so that greater contributions of covalent character can be expected in their interaction with sorption sites (Cheng and Wang, 2010). This is imperative as its presents a positive development in terms of economy as equilibration is reached within a very short time.

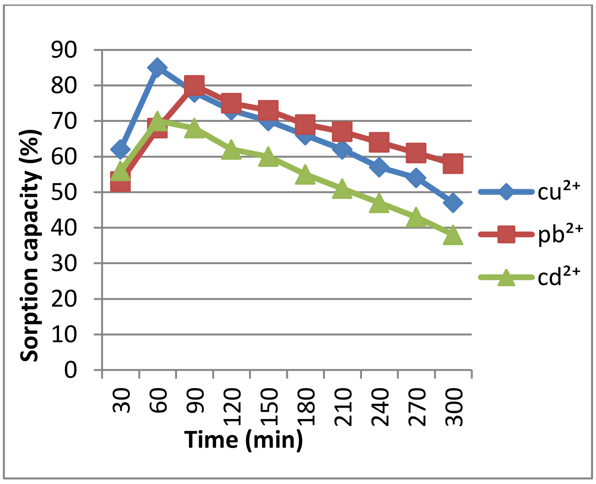

Figure 5: Effect of time on sorption capacity at 30°c

CONCLUSION

This research seek to study the application of chemically modified Brewer's Spent Grain as an adsorbent material for the sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution. The sorption strength depends on initial metal ion concentration, ionic strength, temperature and p^H. The maximum sorption capacities of the adsorbent were 95.12, 87.45 and 84.65% for Cu^{2+}, Cd^{2+} and Pb^{2+} respectively. Equilibration studies also indicated that metal ion sorption decreases with increasing ionic strength and temperatures beyond 49, 50 and 52^{o}C for Pb^{2+}, Cu^{2+} and Cd^{2+} respectively. This study revealed the potential of acrylamide grafted Brewer's Spent Grain as a low cost adsorbent material for remediation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from polluted streams. Therefore, it is recommended that for maximum removal of these metal ions from waste streams during practical application emphasis should be placed on optimization of process parameter for each adsorbate.

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