

## Amelioration of heavy metals in beverages using eggshell adsorbent: a potential novel approach for improving the quality of beverages

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### ABSTRACT

Available methods of eliminating the heavy metal ions from beverages are either unsuitable or costly. This study was aimed to produce a low-cost eggshell adsorbent for the removal of Pb, Cd and Cr in beverages. Five common beverages: Action Bitters (AB), Coca Cola Coke (CCK), Orijin Bitters (OB), Stout (S) and Challot Blue (CB) were sampled and evaluated for adsorbent dosage and contact time. Optimum adsorbent dose of 0.25 g/25 mL and contact time of 90 minutes were obtained. Beverage samples were wet digested and analysed for Pb, Cd, Cr and phytochemical composition using standard methods. Data were analysed using descriptive statistics and t-test at  $p=0.05$ . Four beverage samples had high Pb and Cr concentrations. Percentage adsorption (%) of Pb and Cr in AB, CCK, OB, S and CB were (4.67; -217.78), (1.69; 95.53), (9.80; 82.79), (85.37; 95.53), and (0.00; -277.78), respectively. Major phytochemicals in treated and original beverages were flavanoids, cardiac glycosides, anthraquinones, terpenoids, steroids, phenol, alkaloids, tannins and saponins. The saponins level in the untreated beverages (0.0920 g) was significantly higher compared to (0.0370 g) in the treated beverage. Eggshell could be a viable low-cost adsorbent for the amelioration of heavy metals in some beverages.

**Keywords:** Beverages, heavy metals, adsorbent, eggshell, phytochemical

### INTRODUCTION

Beverages are drinks that are consumed primarily to quench thirst and can be alcoholic (wine, spirits, and beers) and non-alcoholic (soft drink, candies, chocolates, and milks). In developing nations most especially, regulation of sales, importation and manufacturing of beverages are not subjected to rigorous scrutiny in terms of safety and efficacy as is the case for conventional western medicine. Consequently, heavy metals among other impurities have been reported in some of these beverage products (Barnes, 2003; Zaleska, 2008; Adepoju-Bello *et al.*, 2012; Okareh *et al.*, 2018). These beverages are also noted as accompaniment for intake of herbal medicine which is popular as part of primary healthcare among up to 80% of the world's population according to the World Health Organization (2006). Reports claim that

even minute levels of toxic elements can have negative health consequences which vary according to individual characteristics, nutritional status, metabolic rate, the integrity of detoxification pathways, mode and degree of heavy metal exposure and age (Higgins, 1984).

Heavy metals are natural components of the earth's crust and refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations, including mercury, cadmium, arsenic, chromium, thallium, nickel, copper and lead (Zaleska, 2008; Phillips and Balge, 2007). These metals cannot be degraded or destroyed and could enter human body through food, drinking water, beverage drinks, hot drinks, cigarettes and air. Bioaccumulation of heavy metals constitutes health risk to beverages consumers because they are stored faster than

they are broken down or excreted (Zaleska, 2008; Phillips and Balge, 2007). It has been shown that environmental pollution is the main cause of heavy metal contamination in the food chain. Lead and cadmium are two potentially harmful metals that have stimulated considerable interest. Atmospheric contamination, the excessive use of fertilizers and pesticides and sewage sludge or irrigation with residual water is among the source of contamination of foodstuffs and beverages. As a result of soil, atmosphere, underground and surface water pollution, foods and beverages are contaminated with heavy metals (Adepoju-Bello *et al.*, 2012; Bingol *et al.*, 2010; Demirozu and Saldamli, 2002).

Independent analyses of beverages by various authors have shown traces of heavy metals (Adepoju-Bello *et al.*, 2012; Okareh *et al.*, 2018; Maduabuchi *et al.*, 2008). These heavy metals are not easily excreted from the body and with time, they bioaccumulate, exceed the permissible limits and exhibit toxicity effects on the general systems of the body. The presence of metals in foods and beverages reflects environmental conditions, except for accidental or criminal actions. The concentration of metals in beverages depends on the quality of the water, the raw materials and the processing techniques. In most countries, the concentrations of metals in beverages are determined in order to (a) check compliance with the established regulatory control limits, (b) protect the consumer against contamination, (c) determine regional metal profiles, and (d) perform method development and evaluation of the nutritional status of the beverage (Iwegbwe *et al.*, 2014). The regulatory control limits vary from one country to another and are subject to reviews and revisions from time to time, taking into consideration the changing dietary habits in different populations and countries.

There is urgent need for removal of these heavy metals from beverages prior to package and sale. With the exclusion of wines, methods for overcoming or eliminating the heavy metal ions from food beverages are of relatively recent origin (Kern, 1988). This is due to the ancient origin of wine and the nature of the beverage. One branded method for reducing the heavy metal content of wines is the so-called blue clarification with the aid of potassium hexacyanoferrate, which more or less

selectively removes iron and copper from the beverage. This method of clarification is problematic from the toxicological viewpoint, since in the case of over-clarification of the acid beverage, hydrogen cyanide is created in small amounts and remains in the beverage (Bersvivorgia and Frost, 1958). Additional troubles of this protection type comprise the treatment of the sediment, since the precipitate to be removed partly remains colloiddally dissolved and are poorly filterable. Finally, the separated solids cannot be conveyed to an ordinary landfill, but must ultimately be stored as special waste. All of these make blue clarification challenging and uninviting (Kern, 1988). A similar clarification method is that with Fessler's Compound, which is based on a similar principle. This Fessler's Compound is prepared from iron (II) sulfate and a super equivalent quantity of potassium hexacyanoferrate. The same problems arise in this clarification method as in the case of blue clarification, this complex compound is also unstable on storage (Mannheim *et al.*, 1992). Other attempts to remove heavy metals in wines have exhibited some challenges as they are not selective for heavy metals, but also binds other ions, such as calcium and magnesium ions, which is highly undesirable (Mannheim *et al.*, 1992).

To gain an insight into the potential of eggshells as heavy metal biosorbents in beverages, we have performed a preliminary study on the adsorption behaviour of some heavy metals on an adsorbent produced from eggshell waste. Eggshell waste has been utilized by several authors in the removal of heavy metals in water (Tsai *et al.*, 2006; Carvalho *et al.*, 2011; Zulfikar and Setivanto, 2013; Guru and Dash, 2014). Adsorption using eggshell will offer advantages such as high efficiency, ready availability and low operating cost, and because it is eco-friendly when compared to conventional treatment methods. This method can also be used economically on a large scale and it will provide an option for eggshell waste management. What makes eggshells a striking material to be employed as an adsorbent is its porosity. Eggshells characteristically consist of ceramic materials, the outer surface has the cuticle, the middle layer is made of a spongy (calcareous) layer and finally the inner lamellar layer, organised in a three-layered construction. More than 90% of the material in eggshells is

represented by the mamillary and spongy layers that forms a milieu made up of protein fibres chemically bonded to calcite (calcium carbonate). The numerous pores on the three layers of the eggshell make them a very efficient adsorbent because the pores allow for an increase in the number of binding sites and surface area for the biosorptive process (Zulfikar and Setivanto, 2013; Schwarz and Contescu, 1999).

## **MATERIALS AND METHODS**

### **Preparation of adsorbent**

Eggshell from poultry was used to produce the adsorbent. Boiled poultry eggshell was collected from college canteen and washed several times with distilled water to remove extraneous materials. The eggshell was air-dried, ground and sieved to obtain very fine particle size (0.5 mm) and incubated in hot air oven at 105°C for three hours. The produced adsorbent was stored in an air tight container prior to use and analysed for metal composition using the AOAC (2013) procedure.

### **Procurement of beverage drinks**

Five commonly consumed beverage drinks (Action Bitters, Coca Cola Coke, Orijin Bitters, Stout and Challot Blue) were randomly bought from retail shops and stored in the laboratory at conditions similar to those of retail shops prior to treatment. These drinks were wet digested and Atomic Absorption Spectrophotometer (AAS) was used to determine the initial heavy metal contents.

### **Batch experiments**

Series of tests were conducted to determine the initial heavy metal concentration, the effects of adsorbent contact time on the drinks, and adsorbent dosage of eggshells used as adsorbent materials. These experiments were done at room temperature (25 °C) and the pH of the drinks was not tempered.

### **Initial concentration**

The beverages were subjected to phytochemical analysis to estimate the proportion of the various chemical compounds present. Both qualitative and quantitative phytochemical analyses were done on the beverages. Qualitative analysis was

done using the methods adopted by Edeoga *et al.* (2005), Ayoola *et al.* (2008) and Krishnaiah *et al.* (2009) to establish the presence of the phytochemicals present in the beverages. Quantitative phytochemical analysis was done using the methods of Osuntokun and Oluwafoise (2015) to determine the exact quantity of each of the phytochemicals present in the beverages. The Association of Official Analytical Chemists (AOAC, 2013) method for heavy metal analysis was used, after wet acid digestion, to determine the quantity of heavy metals in the beverages.

### **Contact time determination**

To establish the optimum contact time, 0.5 g of the adsorbent was introduced into a 250 mL flask with 25 mL of the beverage drink. The flasks were placed in an orbital shaker and agitated up to a contact time of 180 minutes at 250 revolutions per minute (250 rpm). Samples were taken at predetermined time intervals (0, 10, 30, 60, 90, 120 and 180 minutes) and then was separated by filtration using filter paper. Then, AOAC (2013) method of analysis for heavy metals determination was carried out on the filtered substrate and the best contact time was determined.

### **Adsorbent dosage determination**

To determine the adsorbent dosage, a contact time of 60 minutes was used. Various adsorbent dosages of 0.1, 0.25, 0.5, 1, 3, and 5 g were introduced into 250 mL flasks with 25 mL beverage drink. They were placed in an orbital shaker and agitated for 60 minutes contact time at 250 revolutions per minute. They were filtered using filter paper and AOAC (2013) method of analysis for heavy metals determination was then carried out on the filtered substrate and the best adsorbent dosage was determined.

### **Efficiency of eggshell**

The optimum contact time and best adsorbent dosage were used in determining the efficiency of the eggshell as an adsorbent. The best dosage (0.25 g) was introduced into 250 mL flasks with 25 mL beverage drink. They were placed in an orbital shaker and agitated for the optimum contact time (90 minutes). They were filtered

using filter paper and were analysed. Phytochemical analyses were done to determine the effect of the treatment on the chemical components of the respective beverage drinks. The efficiency of adsorption (%) was calculated following equation 1 (Pan *et al.*, 2007).

$$R = [(Co - Ce) / Co] \times 100 \dots \text{Eq. 1}$$

Where;

$Co$  and  $Ce$  are the initial and the final heavy metal concentrations respectively.

$R$  is the removal efficiency (%).

### Statistical analysis

Data was processed for statistical analysis using the Statistical Package for Social Sciences (SPSS) for Windows software version 20.0. The results obtained from the quantitative phytochemical analysis were analysed using Paired sample T-test and level of significance was set at  $p < 0.05$ .

## RESULTS

### Baseline heavy metal content in the selected beverages

**Table 1:** Baseline heavy metal content of the selected beverages

Beverage type	Lead (mg/L)	Cadmiu m (mg/L)	Chromiu m (mg/L)
Action Bitters	0.075	ND	0.089
Coca Cola Coke	0.0295	ND	0.1705
Orijin Bitters	0.0255	ND	0.122
Stout Beer	0.0615	ND	0.0895
Challot Blue	ND	ND	0.018
WHO limit	0.01	0.03	0.05
USEPA limit	0.015	0.05	0.08

**Table 2:** Metal content of the produced adsorbent

Metal	Concentration (mg/L)
Calcium	9530.00
Manganese	0.02
Iron	13.00
Copper	0.232
Zinc	2.850
Lead	0.069
Cadmium	0.090
Nickel	0.975
Chromium	0.038
Cobalt	0.091

The initial heavy metals content of the selected beverages used in this study are presented in Table 1. Lead concentration ranged from

0.0255-0.075 mg/L; action bitters had the highest concentration (0.075 mg/L); and Orijin Bitters had the lowest (0.0255 mg/L); Lead was not detected in Challot Blue wine. Cadmium was not detected in all the beverages. Chromium was detected in all the beverages but its highest content was 0.1705 mg/L in Coca Cola Coke and least in Challot Blue wine with a concentration of 0.018 mg/L.

### Prepared adsorbent for the removal of heavy metals in beverages

Quantitative analyses of proximate composition of the eggshell adsorbent indicate that the produced adsorbent was not void of heavy metals as metal analysis of the produced adsorbent shows traces of heavy metals in the produced adsorbent (Table 2).

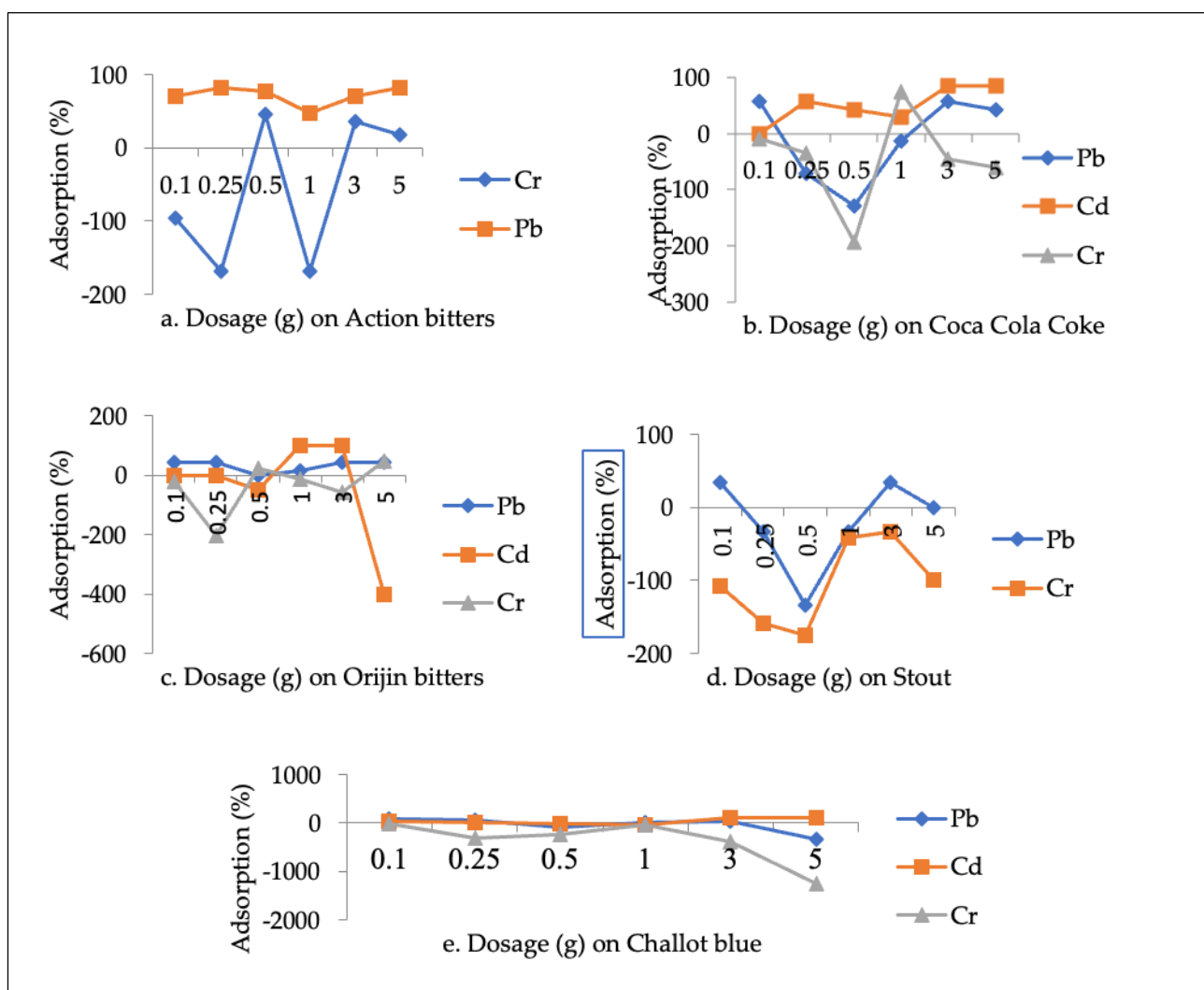
### Effect of dosage on the adsorption of heavy metals in beverages

The effect of dosage on the adsorption capacity of eggshell for Pb, Cd and Cr in “Action bitter drink”, Coca Cola Coke drink, Orijin bitters, Stout and Charlotte Blue wine is represented in Figure 1a, b, c, d, and e, respectively. Lead appeared to be easily adsorbed with its highest efficiency of 82% at a joint dosage of 0.25 and 5 g. The least efficiency of Pb adsorption was at a dosage of 1 g which has an efficiency of 47%. Cadmium was not detected in the drink hence there was nothing to be adsorbed. The adsorption of Chromium from the beverage was highest at a dosage of 0.5 g with a percentage efficiency of 45 while there was notably a negative efficiency at some dosages. For Coca Cola coke drink, the highest adsorption (57%) for lead was at a dosage of both 0.1 and 3.0 g, there was a negative adsorption at 0.25, 0.5 and 1.0 g. For the adsorption of cadmium in the beverage, equilibrium of 86% efficiency was reached at dosage of 3 g. There was positive efficiency across all dosages. The adsorption of chromium from coca cola coke was mostly negative but there was a positive adsorption of 74% at 1.0 g dosage. The effect of dosage on the adsorption capacity of eggshell for Pb, Cd and Cr in “Orijin bitters drink” indicates that lead in the beverage was adsorbed at all dosage except at 0.5 g where there was no change between the level of lead in the beverage before and after the experiment. The highest adsorption of 43% was recorded at dosage of 0.1, 0.25, 3.0 and 5.0 g. The adsorption of cadmium in the beverage recorded a perfect adsorption efficiency of 100% at dosage of 1 and 3g, there was however

a negative adsorption of 400% at 5 g dosage. Chromium adsorption was highest (47%) at a dose of 5 g and there were negative adsorptions at most dosages.

In Stout, there was no detectable cadmium in the beverage. Lead was not effectively adsorbed, recording its highest adsorption percentage as 33%. Chromium level in the beverage increased leading to a negative adsorption across all dosages. In Challot Blue wine, the adsorption of Cadmium attained equilibrium adsorption at

dose of 3 g. Dosages of 0.5 and 1 g gave a negative adsorption while the other two dosages of 0.1 and 0.25 g showed a slight adsorption of Cadmium. The adsorption (94%) of Lead in Challot wine was highest at the lowest dose of 0.1 g, the other doses gave a lesser adsorption capacity and there were two negative adsorptions at 0.5 and 5 g dosage. For Chromium, there was no proper adsorption as a negative result was obtained all through the dosages tested.



**Figure 1:** Effect of dosage on adsorption process of eggshell in five beverages

### Effect of contact time on the adsorption of heavy metals in beverages

The effect of contact time on the adsorption of heavy metals in Action bitters, Coca Cola Coke, Orijin bitters, Stout and Charlotte Blue wine is presented in Figure 2a, b, c, d, and e,

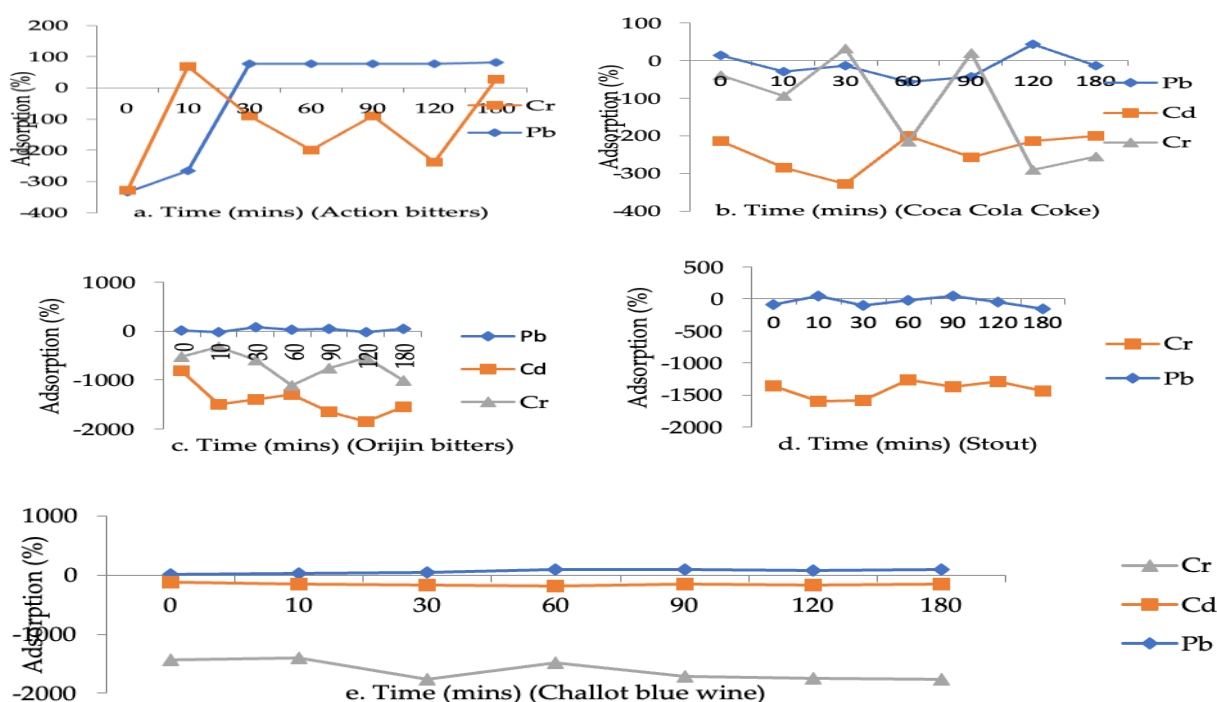
respectively. In Action bitters, there was a plateau (76%) for lead at contact time starting from 30 minutes till 120 minutes and the highest adsorption was recorded to be 82% at a contact time of 180 minutes. It is worthy of note that both contact time of 0 and 10 minutes had a

negative adsorption. There was no detectable level of Cadmium hence it was not adsorbed and all the tested contact time gave a negative result for the adsorption of chromium except 10 (55%) and 180 minutes (36%). The highest adsorption was at 10 minutes of contact time.

There was a general negative trend in the adsorption of all the heavy metals of interest for Coca Cola coke. Cadmium was negatively adsorbed all through the testing. Lead however recorded a positive adsorption at 0 (14%) and 120 minutes (43%) contact time. The highest adsorption of Pb in coca Cola Coke is 43% which was obtained after a contact time of 120 minutes agitation. Chromium adsorption in coca cola coke shows a similar trend to that of Lead. There were only two positive adsorptions of 32% (at 30 minutes) and 19% (at 90 minutes) contact time. The other test group gave a negative adsorption. As for Orijin bitters, Lead was in general positively adsorbed across all tested time, however there were negative adsorption at contact time of 10 and 120 minutes. The highest adsorption was recorded at 30 minutes with an adsorption efficiency of 71%. The adsorption of both Cadmium and Chromium both yielded negative adsorption across all the tested time range. Cadmium was not detected in Stout drink and the adsorption of Chromium was negative all through the tested

contact times. The adsorption of Lead was mostly negative however gave a positive adsorption at contact time of 10 minutes (43%) and 90 minutes (43%) efficiency of adsorption. For Challot Blue wine, there was positive adsorption of Lead. As contact time increases, there was a steady increase in the adsorption capacity of eggshell for Lead until the 60 minutes which recorded the joint highest adsorption efficiency with 180 minutes. The adsorption capacity of eggshell for both Cadmium and Chromium showed a negative adsorption.

Generally, the effect of contact time on the adsorption process of Pb, Cd and Cr in these beverages did not follow any known pattern. All the factors that affect adsorption come together depending on the contact time available for the active sites to be saturated and it is expected to increase progressively until equilibrium saturation is reached. There might be some explanations to this as most literature in this regard uses water unlike the sample used in this study. The difference between ordinary water and beverage might be responsible for the non-conformance of this study. Also, the presence of heavy metals in trace quantity in the produced adsorbent could be responsible for this negative adsorption.



**Figure 2:** Effect of contact time on adsorption process of five beverages

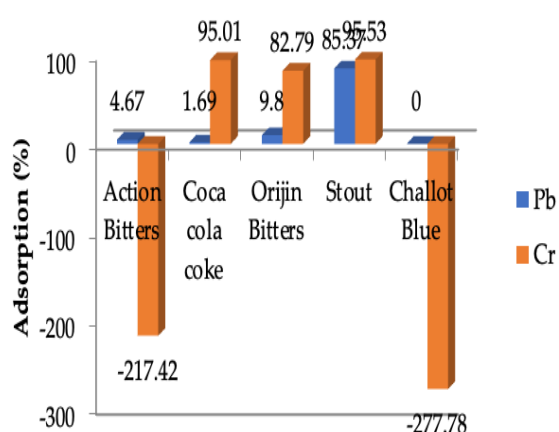


### Adsorption of heavy metals under optimum conditions

The effects of the optimum conditions obtained from the aforementioned results, without alteration to the pH and temperature of the beverages, (dose of 0.25 g and contact time of 90 minutes) in the adsorption of the three individual metals by the eggshell adsorbent are presented in both Table 3 and Figure 3. There was no detectable cadmium in all the treated beverages. In the treatment of action bitters, adsorption efficiency of the eggshell was generally low (4.67% for Pb and -217.42% for Cr). In Coca Cola Coke treatment, the adsorption efficiency of eggshell is higher for Cr with 95% adsorption than for Pb with 1.69% adsorption. Same pattern was found in the treatment of "Orijin Bitters" which adsorbed Cr with 82.79% than for Pb with 9.8%. In the treatment of "Stout" drink under optimum conditions, both Pb and Cr were well adsorbed by the eggshell with adsorption efficiency of 85.37% and 95.53% respectively. At optimum conditions, Lead was not detected in Challot blue hence no adsorption but there was a negative adsorption of -277.78% for Chromium.

**Table 3:** Efficiency of eggshell adsorbent under optimum condition

Beverage	% adsorption of Pb	% adsorption of Cr
Action Bitters	4.67	-217.42
Coca cola coke	1.69	95.01
Orijin Bitters	9.8	82.79
Stout	85.37	95.53
Challot Blue	NA	-277.78



**Figure 3:** Efficiency of eggshell adsorbent under optimum condition

### Phytochemical properties of the selected beverages

The qualitative and quantitative phytochemical analyses of the five beverages before and after treatment is presented in Tables 4 and 5. There was no substantial variation in the phytochemical parameters present in the beverages before and after the treatment. There was no alteration in phytochemical composition in Coca Cola Coke and Orijin Bitters while in Action bitters and Challot blue, Cardiac glycoside was added and Saponins was removed in the beverages respectively after the experiment. Eggshell adsorbent to an extent altered the presence of phytochemicals in Stout as Tannins, Phenol and Alkaloids were all removed from it while the level of Saponin in it was reduced. The results of the quantitative phytochemical analyses show that eggshell adsorbent has no significant effect at  $p = 0.05$  on the phytochemical properties of the beverages except for saponins that showed a significant difference ( $p = 0.022$ ) between the untreated and the treated groups.

### DISCUSSION

Preliminary evaluation of heavy metal content of the beverages shows that Lead and Chromium constituted health risks particularly Lead which exceeded the WHO and USEPA permissible limits in 80% of the beverages. Earlier studies have reported similar findings for Lead and other toxic metals in beverages (Adepoju-Bello *et al.*, 2012; Okareh *et al.*, 2018). Lead toxicity could inhibit calcium-dependent processes and interacts with proteins such as sufhydryl, amine, phosphate and carboxyl groups (WHO 1995). Also, it affects the peripheral and central nervous systems, renal functions, blood cells, and metabolism of vitamin D. It is associated with hypertension, reproductive toxicity, developmental effects and neurological disorders, some of which may be irreversible (Mottet, 1980). The presence of Pb in almost all the sample can be attributed to environmental pollution of which Lead is at their fore front. Lead can enter into the beverage through the raw materials used in the brewing of the drink or through the metallic containers used in preparation of the beverages. The non-

detection of Cadmium could be attributed to inability to reach the detectable limit for Cadmium during the screening. Cadmium interferes with some essential function of Zn, thereby inhibiting enzyme reactions and nutrient utilization. It catalyzes oxidation reactions, generating free-radical which can lead to tissue damage (WHO 1992). The finding in this study is in agreement with the report of Orisakwe and Ajaezi (2014), that cadmium was not detected while the presence of Lead, Chromium, Cobalt and Nickel were found in Nigerian beverages. Some studies have however reported traces of Cadmium in some beverages consumed worldwide (Adepoju-Bello *et al.*, 2012; Zaleska, 2008; Okareh *et al.*, 2018). Chromium is one of the metals of public health concern, its presence in all the beverages shows the extent to which regulating bodies have to intensify efforts in ensuring safer drinks. Chromium is classified as a carcinogen by the International Agency for Research on Cancer-IARC. Hexavalent chromium is more harmful than trivalent chromium (Mohan and Singh, 2006). Chromium can gain access into beverages mostly through the raw materials used as extensive use of chromium compounds in industrial applications have discharged huge amounts of it into the environment and it is in turn taken up.

In this study, eggshell produced adsorbent has carbonate content that reflects adsorptive capability. The presence of inherent metals in the eggshell adsorbent shows the level of heavy metal contamination in the environment and possible accumulation of these metals in the poultry through heavy metals contaminated feeds. Eggshell has been employed widely in the successful removal of heavy metals in wastewater (Tsai *et al.*, 2006; Zulfikar and Setivanto, 2013; Gun and Dash, 2014). The effect of dosage on the adsorption process of Lead, Cadmium and Chromium in beverages yielded results which were not consistent between a sample or even across all samples. This is in disarray with literature as most adsorption parameter experiment showed that as the dosage increases, the adsorption increases until equilibrium is reached. Several studies report the removal of Pb to be influenced by the dose of eggshell, as the effective removal of solutes increased with increasing dose of adsorbent (Schiewer and Volesky, 1997; Eamsiri *et al.*, 2005; Arunlertaree *et al.*, 2007).

Agarwal and Gupta (2014) studied the removal of  $\text{Cu}^{2+}$  and Fe from aqueous solution by using eggshell powder as low cost adsorbent for a period of 24 hours and observed a change in the percentage adsorption of  $\text{Cu}^{2+}$  from 65 to 80 and 95% with the increase in the adsorbent dosage from 0.5 to 1.0 and 1.5 g in 100 ppm concentration. The same pattern was also observed by Agarwal (2013) during the removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solution by using eggshell as an adsorbent. The study reported that the percentage adsorption changed from 72.4 to 95 and 96.3% for  $\text{Cu}^{2+}$  and 60.5 to 78 and 86.4% for  $\text{Pb}^{2+}$  with the increase in the adsorbent dosage from 0.5 to 1.0 and 1.5g in 100 ppm concentration. This therefore suggests that the adsorbent dosage plays a significant role in the removal efficiency of the eggshell. However, the trend has been for the relationship between adsorbent dose and effective adsorption in wastewater studies, this current study did not follow that same pattern. This alteration can be as a result of many factors which may favour the adsorption of heavy metals in water but certainly not in beverages. Beverages have more components when compared to water (hydrogen and oxygen only) and some of these components might be working antagonistically for the effective amelioration of heavy metals in it. Another factor that could have played a role in the unpredictable pattern of adsorption in this study might be the presences of heavy metals in trace quantity in the produced adsorbent which could have filtered into the beverage on contact. The effectiveness of eggshell adsorbent produced in this study to ameliorate Pb, Cd and Cr in beverages were done under the optimum condition; adsorbent dose of 0.25 g and contact time of 90 minutes. The other parameters that play a role in the effective removal of heavy metals in liquids were not under the scope of this study. The results show that on the average, Chromium was adsorbed (95.53%) more than Lead (85.37%) while Cadmium was beyond the detectable limits. The overall effectiveness of this adsorbent was poor when the adsorption of Lead is of paramount importance as adsorption of less than 10 percent (<10%) was recorded in three out of the four samples. This can be due to the fact that only dosage and contact time determination are not enough to effectively establish the efficiency of a particular adsorbent in removing heavy metals.



The results of the qualitative phytochemical analysis denote that eggshell adsorbent does not greatly alter the phytochemical parameters of the beverages. This is breakthrough because one of the setbacks in the amelioration of heavy metals in wine and wine-like beverages is the alteration of the chemical compositions of the said drink (Mannheim *et al.*, 1992). In some cases, there is heavy deletion of important constituents while in some; there is addition of

excess elements. The quantitative result shows that eggshell adsorbent has no significant effect on the phytochemical properties of the beverages except for saponins that showed a significant difference ( $p=0.022$ ) between the untreated and the treated groups. This significant change in the saponin levels can be adjusted for by increasing the saponins source during the production stage.

**Table 4:** Qualitative phytochemical analyses on the selected beverage

Test	Action Bitters Before	Action Bitters After	Coca Cola Before	Coca Cola After	Orijin Bitters Before	Orijin Bitters After	Stout Before	Stout After	Challot Blue Before	Challot Blue After
Saponins	++ve	++ve	+ve	+ve	+ve	+ve	++ve	+ve	+ve	-ve
Tannins	+ve	+ve	-ve	-ve	-ve	-ve	+ve	-ve	+ve	+ve
Flavonoids	+ve	+ve	-ve	-ve	+ve	+ve	+ve	+ve	+ve	+ve
cardiac glycosides	-ve	+ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Anthraquinones	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve
Terpenoids	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve	+ve
Steroids	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Phenol	+ve	+ve	-ve	-ve	-ve	-ve	+ve	-ve	+ve	+ve
Alkaloids	+ve	+ve	+ve	+ve	-ve	-ve	+ve	-ve	+ve	+ve
Remarks	+Cardiac glycosides		No alteration		No alteration		Tannins, phenol and alkaloids were removed while saponins was reduced.		Saponins was removed	

**Table 5:** Quantitative phytochemical result

Test	Action Bitters Before (g)	Action Bitters After (g)	Coca Cola Before (g)	Coca Cola After (g)	Orijin Bitters Before (g)	Orijin Bitters After (g)	Stout Before (g)	Stout After (g)	Challot Blue Before (g)	Challot Blue After (g)
Alkaloids	0.0405	0.0385	0.0405	0.062	ND	ND	0.0265	0.000	0.0465	0.0405
Flavonoids	0.033	0.0255	ND	ND	0.003	0.015	0.035	0.0515	0.038	0.0175
Saponins	0.013	0.005	0.004	0.003	0.0065	0.0035	0.0016	0.007	0.0065	0.000

## CONCLUSIONS

In this study, an eggshell adsorbent for the removal of heavy metals in beverages with no alteration in the phytochemicals properties is developed. The highest adsorption is obtained for stout drink though adsorption percentage of other beverages is low. The phytochemical properties, except saponins, of the beverages were not significantly altered to a great extent. This is an eye opener towards the modification and use of adsorbent produced from eggshell for the removal of heavy metals in beverages. This study concludes that eggshell could be a viable low-cost adsorbent for the amelioration of heavy metals in some beverages.

## Ethics Committee Approval

NHREC/05/01/2008a and UI/EC/19/034

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