



Separation of Lead by Sulfonated and Esterified Gallus Domesticus Shell Powder: A Green Approach

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ABSTRACT

A potential of biosorbent prepared from Gallus Domesticus (Hen) egg shell powder was evaluated for removal of lead from aqueous solutions. To establish the time, dose, initial metal ion concentration and pH profile batch adsorption experiments were conducted at room temperature. Lead was removed 93% within 20 min by employing raw biomass. Sorption studies with esterified and sulfonated biosorbent indicated a loss of 37% binding due to decline of C-O functional group. However, sulfonation improved sorption for Pb considerably due to participation of new peaks and improved sites of carboxyl, carbonyl and phenols. Our results suggest that the hen egg shells biomass can be used for removal of Pb from polluted aqueous effluents.

Keywords: Biosorption; sulfonation; esterification; active sites

1. INTRODUCTION

Lead is one of the hazardous heavy metals in terms of high toxicity to humans, plants and animals (Low et al., 2000) causing a range of health effects, like anemia, learning disabilities, renal damage, seizures and even death (Naseem and Tahir, 2001). The lowest reported lethal dose (LD₅₀) in human is 1470 µg/kg (Sax and Lewis, 2004). Lead was in use and is still in use in many products found in and around our homes. Industrially, it is a vital ingredient in all kinds of glass, pigments, internal combustion engines, explosives, oils and insecticides. Wastewater from battery manufacturing industry contain as high as 0.50-25 mg/L lead (Arunlertaree et al., 2007). Unregulated disposal of effluents in both developing and developed countries has led to the contamination of ground waters. In addition, developing countries pay a high cost to import chemicals

for water treatment. Much research and development of affordable, technologically doable, and efficient procedures are directed towards the remediation and removal of metals from aqueous media in response to environmentalist's objection and to protect human health (Shetty and Rajikumar, 2009).

Despite a number of published laboratory data, there is a need to look for viable non-conventional low-cost adsorbents to meet the growing demand due to the enhanced quantum of heavy metals in the environment. Gallus Domesticus (chicken egg) is the most common food article utilized immensely in daily nutrition, and egg shell weighs 11% of total egg weight (Pundir et al., 2009; Stadelman, 2000). Eggshell and its membranes are considered as an inexpensive and abundant waste material that become a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs (Bailey et al., 1999). In the present study,

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we offer Gallus Domesticus (GDS) shells as green and sustainable biosorbent to remove lead from aqueous solutions. The possible mode of adsorbate-adsorbent interaction is evaluated through surface tailoring with the aim to transform lower-value material to higher-value products (Mulholland et al., 2000).

2. EXPERIMENTAL

2.1 Preparation and characterization of biosorbent

Egg shells of hen, collected from local market were prepared for sorption studies by washing with distilled water to remove the surface dirt. The sample was ground and oven dried at 50°C for 24 hours, followed by sieving through US standard testing to obtain particle size ranges of ground sorbent i.e., 600-250 µm. Surface morphology of untreated, metal treated and modified sorbent was studied through SEM-EDX and FTIR spectrums. Boehm's titration procedure was employed for determination of active sites on sorbent surface (Boehm, 2008). Zero point charge pH (pHpzc) of sorbent was determined following the protocol of (Leo'n et al., 1994; Moreno et al., 2000) with slight modification. Surface area, pore volume and pore diameter of egg shells powder, were determined by multipoint Brunauer, Emmett and Teller (BET) and Barret-Joyner-Halenda (BJH) methods.

2.2 Batch sorption protocol

Biosorption protocol was similar to described elsewhere (Aliya and Uzaira, 2012), briefly it was carried out by agitating at 100 rpm (X) mass of sorbent into 100-mL Erlenmeyer flasks containing 20 mL solution of (Y) metal ions concentration. Sorbent was separated by filtration after predetermined time interval of 1

minute until equilibrium attainment. Each data point was obtained from individual flasks to ensure uniform contact between solid and liquid till equilibrium. Contact time, sorbent dose and sorbate concentration was optimized by this practice for kinetic study. Removal efficiency of modified sorbents was explored by contacting 0.1 g dose in 25 mg/L of initial metal ions concentration.

The standard solution (1000 mg/L) of Pb(II) was prepared from lead nitrate (PbNO₃) procured from Merck. The concentration of Pb (II) ions in the sorption medium was determined using Flame Atomic Absorption Spectrophotometer (Varian AA-220, Australia). Cations uptake by GDS was calculated as percentage removal (% R) of Pb (II) ions by:

$$\%R = \left(\frac{C_i - C_f}{C_i} \right) 100 \quad (1)$$

The biosorption efficiency, q_e (mg/g), was calculated by:

$$q_e = \left(\frac{C_i - C_e}{w} \right) V \quad (2)$$

Where C_i and C_e (mg/L) are metal ions concentration at initial and equilibrium, respectively. V is the volume (L) of the solution and W is the weight (g) of dry sorbent.

2.3 Chemical modification of sorbent surface

The sorbent surface was tailored by adopting procedures reported for esterification (López et al., 2005) and sulfonation (Shin and Roger, 2005) with slight modifications.

2.3.1 Sulfonation with sodium meta bisulfite

Sulfonation of sorbent was carried out under acidic conditions (pH 3.0) with 12.6 g of Na₂S₂O₅ solution in deionized water. The solution was stirred at 70 °C for 1 day.

2.3.2 Esterification with methanol

A known mass of biosorbent was suspended in 633 mL of 99.9% pure methanol and 5.4 mL of concentrated hydrochloric acid, to maintain a final acidic concentration of 0.1 mol/L HCl. The mixture was continuously agitated for 48 hours at 60 °C.

Chemically treated sorbent was drained to separate the solution and reaction was quenched in deionized water till constant pH. The biomass was filtered, dried in oven at 50 °C for 24 hours and stored in desiccator till further analysis.

3. RESULTS AND DISCUSSION

3.1 Egg shell optimization: time dependence

Relationship of sorption capacity of the adsorbent with the metal ions when subjected to different retention time is provided in Figure 1. Generally, the biosorption capacity of biomass and removal efficiency of metal ions became higher with prolonging the contact time. However, in practice, optimization of contact time is necessary for considering the reusability of biomass. It can be seen that a regular increasing trend was followed with maximum removal of 56% at equilibrium by contacting 0.2 g of adsorbent with 50 mg/L concentrated solution of lead at room temperature. The prevailing output of present research was much readily removal of Pb (II) on egg shells in comparison to 15 hours reported for lead sorption (Al-Masri et al., 2010) and 30 min by black gram husk (Saeed et al., 2005).

3.2 Dose dependence

The impact of altering the GDS dosage on adsorption of lead was explored by employing 5 g/L, 10 g/L, and 20 g/L (0.1, 0.2, 0.4 g) against 50 mg/L concentration (Figure 2).

Dose amplification from 5 g/L to 10 g/L showed slight overlapping, while the effect was clearly significant at highest amount. Percentage removal increasing from 41% to 83% within 20 minutes contact time portrays effectiveness of this waste at such a small dose. The number of exchanging ions and available surface area for adsorption depends upon the amount of adsorbent in the biosorption process. Although better removal can be assumed from decreasing residual concentration of Lead from 30 mg/L to 9 mg/L, yet to keep minimum partial aggregation of biomass the effective dose of sorbent was finalized for 10 g/L dose. Similar combination of dose, removal and sorption efficiency was described by Bhattacharya et al. (2006), in Zn (II) adsorption by increasing rice husk ash and neem bark dose.

3.3 Sorbate optimization: concentration dependence

Figure 3 shows the relationship between initial Pb(II) ion concentration (25, 50 and 75 mg/L) and percentage removal at fixed dosage of 0.2 g/20 ml. Batch sorption study at solution pH (4.75) depicted increase in initial concentration decreased lead percentage removal and increased the uptake capacity of GDS. Due to increase in concentration, number of ions competing for the available binding sites increases.

As the sorbent quantity kept fixed the removal was observed decreasing drastically from 93 to 40%. Therefore, more metal ions were left unadsorbed in solution at higher concentrations. The decreases in the adsorption efficiency in perspective of solid liquid ratio can be stated as: higher energy sites are involved for metal ion sorption at low metal ion/adsorbent ratios, whereas the increase in metal ion/adsorbent ratio saturate the higher energy sites and fixing begins on lower energy sites (Kadirvelu and Namasivayam, 2003;

Zouboulis et al., 2002). At lower metal ions concentration, removal rate was faster owing to unequal concentration on two ends i.e., GDS surface and boundary layer. On the other hand, lesser removal at increased sorbate concentration was mainly due to decrease

driving force across boundary layer, thus slower diffusion. Same drift (Wei et al., 2008) was mentioned for tobacco stems removing 94%, 92% and 90% lead ions at 10 mg/L, 30 mg/L and 50 mg/L, respectively.

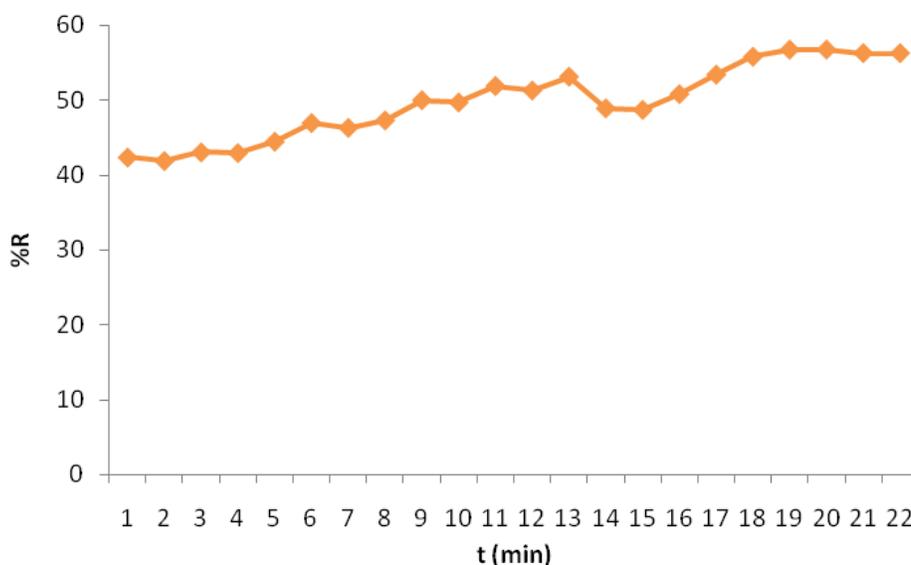


Figure 1 Time Course Studies of Pb by GDS

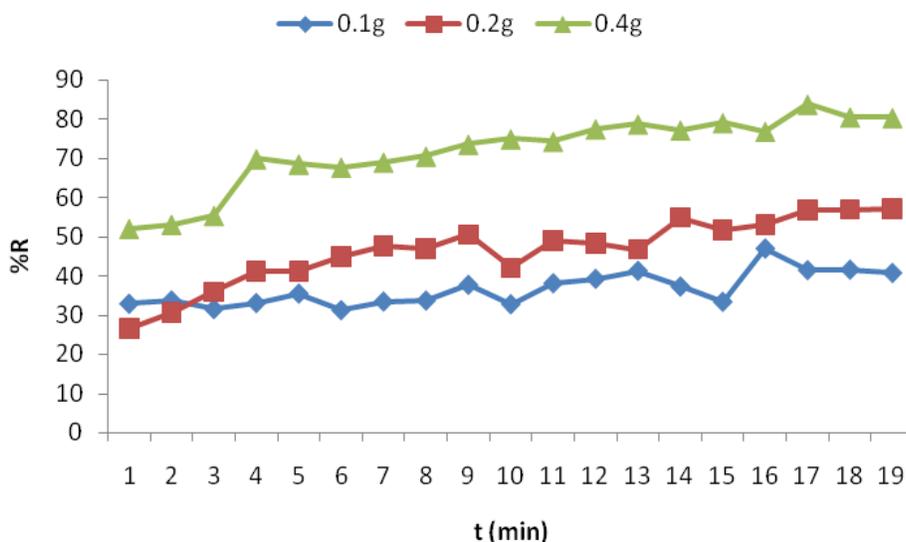


Figure 2 Egg shells dose effect on Pb biosorption affinity

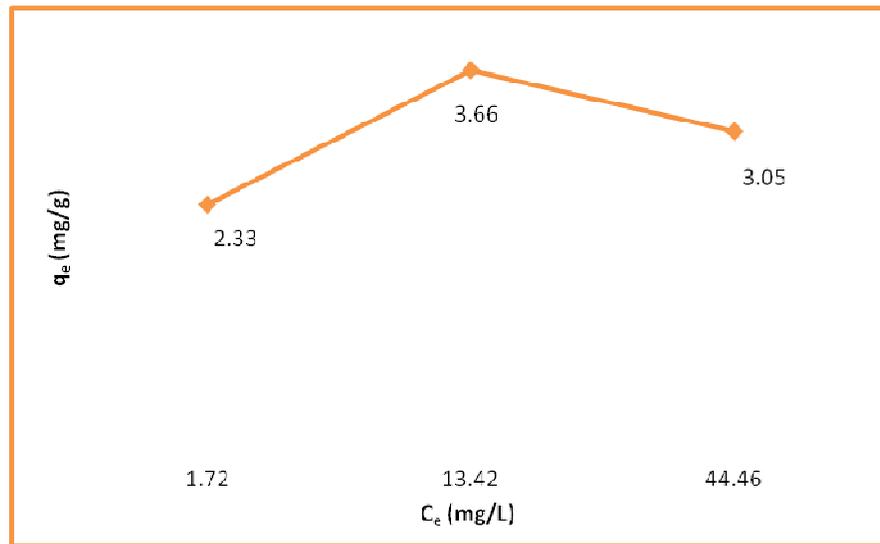


Figure 3 Influence of Initial Metal Concentration on Biosorption Capacity of GDS

3.4 Solution pH dependence

Efficiency of metal ion sorption by biomass was controlled by adjusting initial pH of the reaction mixture from acidic to neutral pH; Results are presented in Figure 4. According to Low et al. (1995), at low pH, surface of adsorbent was closely associated with hydronium ions (H_3O^+) hindering the access of metal ions to functional groups on the surface.

The adsorption of lead (II) ions on the sorbent was found to be highly dependent on initial pH of 50 mg/L concentrated solution. As pH increased, the extent of removal increased, but graph depicts for initial 10 minutes of reaction time that the percentage removal at pH 5 was slightly higher than pH 3, which became comparable beyond this point. The near neutral pH was found to be favorable as maximum uptake is noted at pH 7. Rationale for biosorption being influenced by pH can be deduced from point of zero charge pH_{PZC} and active sites of the adsorbent. pH_{PZC} of GDS suggested the surface to be negative

at pH higher than pH_{PZC} , which is 9.19, found experimentally for GDS. The optimum removal of lead ions could be at pH higher than pH_{PZC} value; conversely above pH 7.00 the Pb^{2+} ions were precipitated as lead hydroxide. Hydroxides of metal ions decreased the concentration of free metal ions, thereby the adsorption did not truly stands for sorption capacity of sorbent.

After acid hydrolysis total acidic and basic sites of GDS decreased from 0.25 meq/g to 0.05 meq/g and 2.61 meq/g to 0.48 meq/g respectively. Thus lesser removal of lead in the acidic pH range can be assumed from less significant accessibility of binding sites. Measurement of solution pH at equilibrium for different induced solution pH showed increase from 3 to 6.72, 5 to 6.89 and 7 to 7.33. The effect was found more pronounced at acidic pH in comparison to neutral, suggesting the possibility of mineral release from egg shells particles in acidic synthetic systems like calcium being noted 48% decreased to 36% after sorption (EDX data).

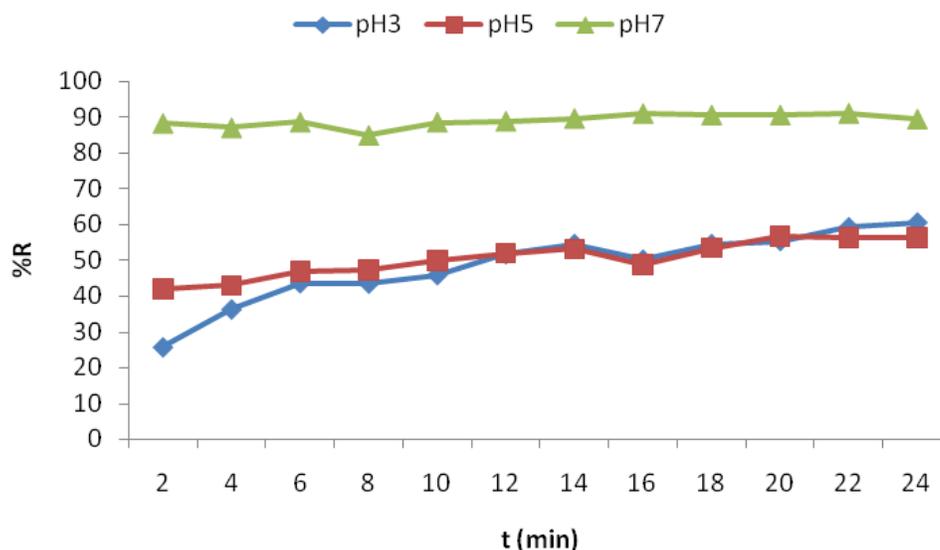


Figure 4 Biosorption Capacities of GDS at Different Initial Solution pH for Pb

3.5 Surface modification

Surface area, pore volume and pore diameter of sorbent determined by BJH method were 44.32 m²/g, 0.08 cc/g and 35.44 Å°, respectively while surface area by BET method was 38.33 m²/g. SEM images revealed considerable change in surface morphology of sorbent after metal sorption to native one, efficient capture of metal ions onto the binding sites was reflected by coverage as visible white encrustations (Figure 5).

Protuberances of egg shell surface became less obvious and thin layer appeared that may be due to deposition of metal ion. Flange on powdered egg shell surface can be related to the presence of calcium. This indication was supported by high percentage of Ca under EDX analysis (Table 1).

GDS was greatly altered by Sulfonation; reflected by radical increase for lactonic and phenolic (acidic) sites and decrease in basic sites from 2.61-0.38 meq/g (Figure 6). FTIR spectrum demonstrated that O-H stretching absorption band at 3404 cm⁻¹ (phenols) and 2515 cm⁻¹(carboxylic) became deep and sharp

with increase surface linkages. Carboxyl oxidation to carbonyl can be assumed due to manifestation of peak at 1629 cm⁻¹ for C=O (amide). The modification can be figured to inception of sharp peaks at 651 cm⁻¹, 520 cm⁻¹, 491 cm⁻¹, 439 cm⁻¹ for stretching vibrations of C-S (aryl thioether) and S-S (di/polysulphides). Sulfonation not only decreased intensity for aromatic phosphates (875 cm⁻¹ band) but dramatically illustrated improved P-O-C binding sites on sorbent surface with broad band emergence at 939 cm⁻¹ - 999 cm⁻¹. This was a clear indication of the fact that sulfonation improved 20% sorption for Pb in comparison to raw biomass in synthetic solutions considerably due to participation of these new peaks and improved sites of carboxyl, carbonyl and phenols (see Figure 8).

Spectrum of methanol esterified GDS revealed depression of transmitted peaks specific to surface carboxyl groups (see Figure 8). The increased absorbance of C-H stretch at 2978 cm⁻¹ and decreased transmission at 1653 cm⁻¹ were due to oxidation of C-O functional site to C=O (amide). It showed accomplishment of attempted treatment to change surface

functionality of biomass. An increase in absorption of peaks at 1425 cm^{-1} and 1797 cm^{-1} may be attributed to carbonate ions. Alteration to stretching vibrations of O-H, C-O, and C=O was verified by comparing spectral results with active site study, quantifying change of 0.10 to 0.56 meq/g for phenols, 0.07 to 0.48 meq/g for lactones, and 0.23 to 0.09 meq/g for carboxyl.

It is well known that metal ions tend to form bonds with functional groups containing

electron-donating atoms (Muthulakshmi and Sakthi, 2010). Furthermore, Pb sorption was portraying the downhill effect with decarboxylated sorbents, thus C-O functional group decline can be related with its 37% lesser removal (see Figure 8). Similarly, reduction of 51% for Cd by spent black tea (Fazal and Rafique, 2012) and 90% for Cu for Pb (Tiemann et al., 1999) showed decarboxylating the sorbent surface.

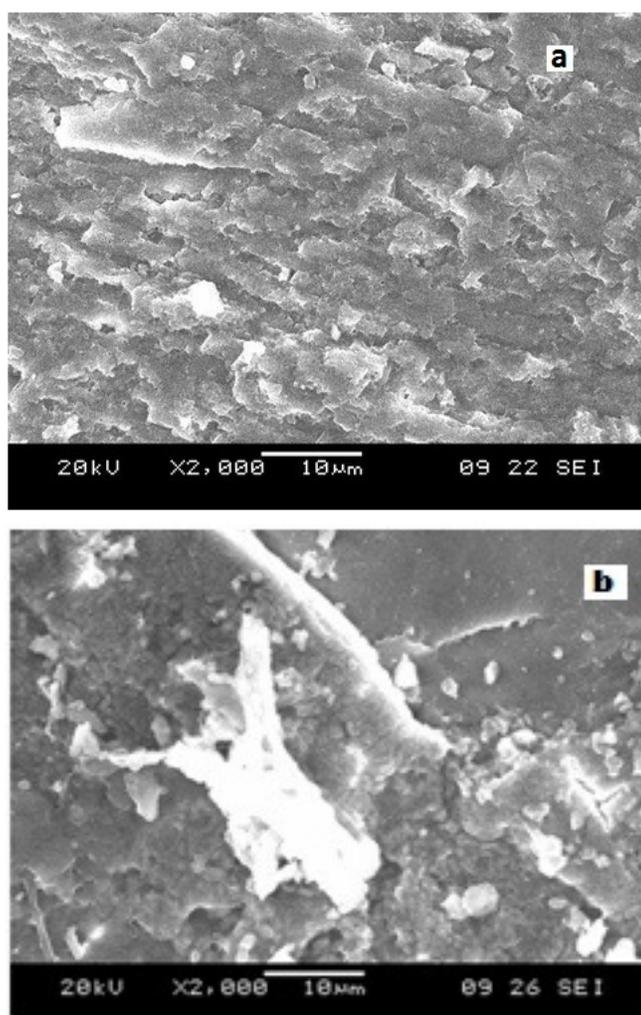


Figure 5 SEM images of GDS before and after Pb sorption

Table 1 EDX Analysis Chart of Egg Shells

Elements (Weight Percent)	<i>C</i>	<i>O</i>	<i>Al</i>	<i>P</i>	<i>S</i>	<i>Mg</i>	<i>Ca</i>	<i>Pb</i>
<i>GDS Native</i>	24.51	31.01	1.99	1.47	1.71	1.47	48.03	-
<i>GDS Pb loaded</i>	30.52	30.48	0.64	-	2.05	0.58	35.86	2.46

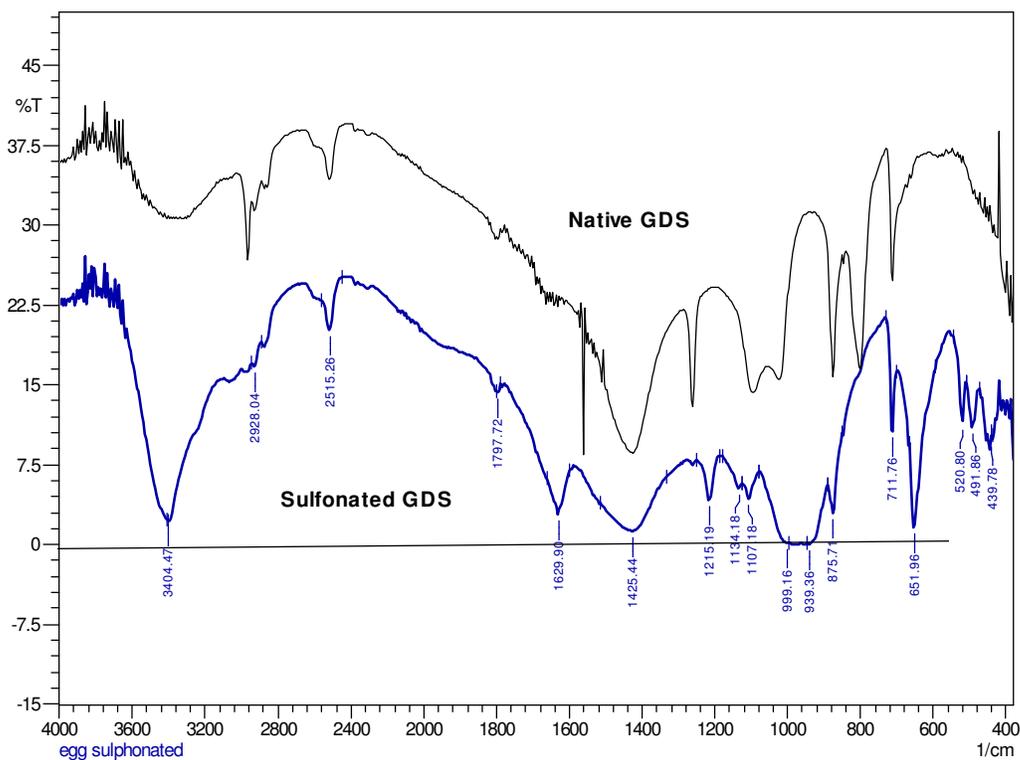


Figure 6 Sodium Meta Bisulfite Sulfonated GDS

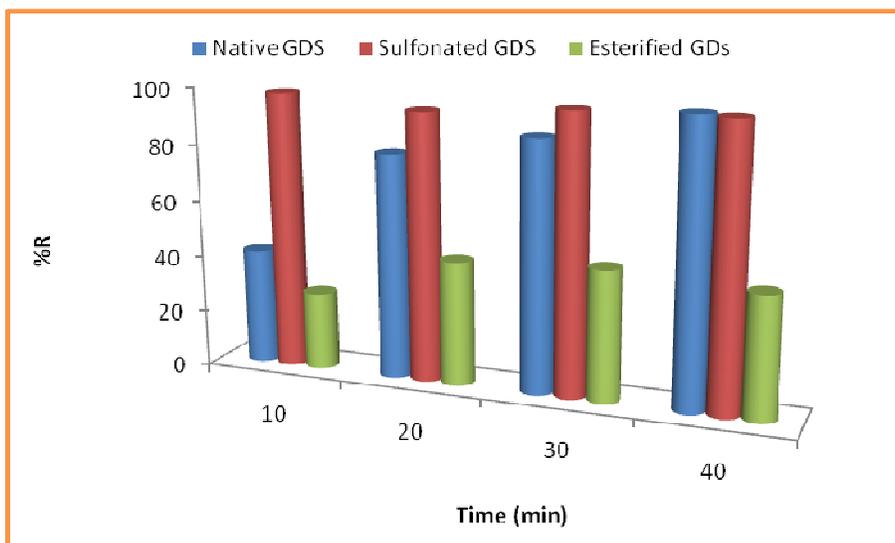


Figure 7 Influence of surface modification of GDS on percentage removal of Pb

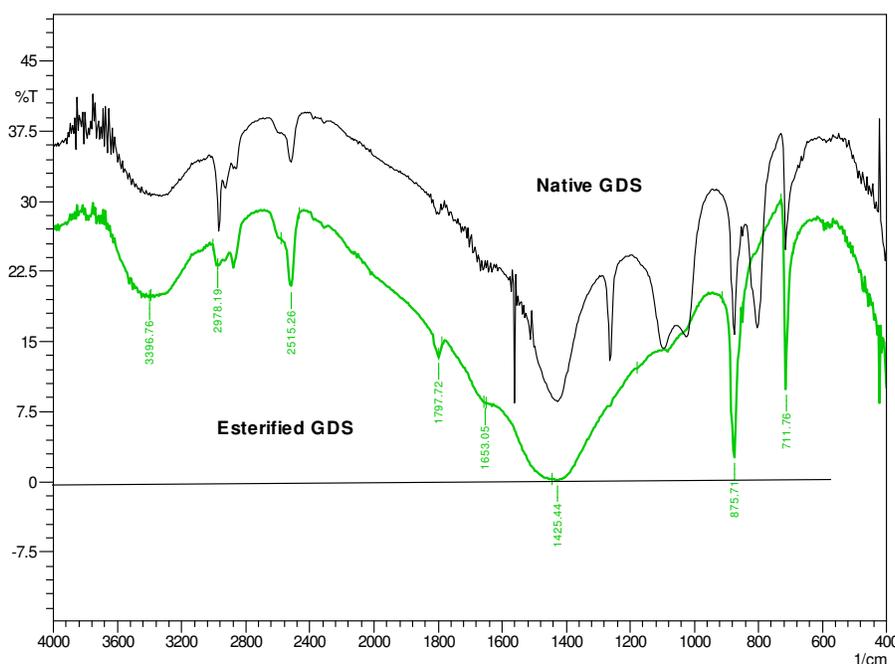


Figure 8 Methanol Esterified GDS

CONCLUSIONS

The results reveal that the sorption of Pb^{2+} ions on to the GDS biomass was inexpensive and effective for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means. Removal was noted to fall within the range of 83-94%, depending on the adsorbent dose and solution composition. Maximum uptake capacity was found at pH 7.0. This may provide an affordable technology for small and medium scale industries.

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