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Removal of Chromium (VI) Ion Fromaqueous Solution Using Exotic and Indigenous Breed Hen Eggshell: A Comparative Study

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ABSTRACT: This study focused on the removal ofChromium (VI) ion from aqueous solution using exoticbreed hen eggshell (EHES) and indigenous breed hen eggshell (IHES)as adsorbents. The effects of adsorbent dosage, contact time, solution pH and solution temperature were investigated in a batch process and evaluated. The results showed that the optimum conditions were adsorbent dose of 6g, contact time of 3 h, pH of 3 and temperature of 60 ^{o}C for both adsorbents. Meanwhile, under these conditions, the percentage removal of Chromium (VI) ion for EHES and IHES powder was found to be 80.30% and 73.50% respectively. These indicate that both types of adsorbents could be used as effective, low cost adsorbents to remove Chromium (VI) ion from a wastewater. However, the EHES powder is more efficient.

Key words: Exotic Hen Eggshell, Indigenous Hen Eggshell, Chromium (VI) ion, Aqueous Solution

I. INTRODUCTION

Environmental pollution may refer to an unfavourable alteration of our surroundings by human activities which directly or indirectly cause negative changes in energy patterns, radiation levels, chemical and physical constitution of organisms (Kushwaha et al., 2013). Environmental pollution is a major concern around the globe especially in the developing countries for many decades. The major source of water pollution is the indiscriminate discharge of untreated or poorly treated industrial effluents into the environment (Susu and Folami, 2014).The textile industry is well-known as one of the largest generators of wastewater with high colour and, dissolved organic and inorganic compounds (Yonten et al., 2015). Also, there is observed ignorance of the harmful effects of releasing poorly treated wastewater from these processes directly into the environment (Hubbe et al., 2012). Generally, food wastes contain some sort of valuable minerals which have to be extracted so as to reducethe high cost of disposal and environmental nuisance caused by such wastes (Ahmed et al., 2017). Eggshell (ES) and eggshell membranes (ESM) are wastes produced in large quantities from sources such as poultries, homes, restaurants, bakeries and food manufacturing units. Bakeries and food industry producethe largest quantity of ES and ESM and their disposal has always been a challenge to the industry (Baláž, et al., 2016; Baláž, 2014). ES consists of three layers:cuticle, testaand mammillary layers. Both cuticle and mammillary layers formed a matrix composed of protein fibers and constructed in such a way that there are numerous pores which allow transpiration of water and gaseous exchanges. Each ES has been reported to contain between 7000 and 17,000 pores (Mittal et al., 2016; Kaewmanee et al., 2009). Eggshell has many bioactive compounds with high economic values. It is a network of protein fibers with minerals such as $CaCO_3$, $MgCO_3$ and $[Ca_3(PO_4)_2]$ including trace amount of Na^+, K^+, Zn^{2+}, Mn^{2+}, Fe^{2+}/Fe^{3+} and Cu^{2+} ions (Zaman et al., 2018; Park et al., 2016). A quality eggshell may contain 2.2 – 5.5 g $CaCO_3$ which is about 94 – 96%. $CaCO_3$ is a major constituent of many processing industries (Guru and Dash, 2014). In order to reclaim the energy, water and minerals present in food wastes, adequate and functional disposal system is inevitable. Moreso, strict compliance to regulations concerning landfills will promote useful applications of these wastes (Folami and Adegbola, 2018; Yu et al., 2012).

Surface analysis of ES and ESM also revealed that they are porous materials and

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therefore can be employed as cost effective adsorbents for the removal of hazardous chemicals thus, lessening the wastes going to landfill (Mopoung and Jitchaijaronekul, 2017; Tsail et al., 2006). Eggshell has been used for purification of hydrogen generated for fuel cells (Mittal et al., 2016), adsorption of dye (Tsai et al., 2008) or heavy metals (Guo et al., 2011; Tang et al., 2010; Meena et al., 2008) from wastewater and CO_2 from combustion gases in a fluidized bed (Botome et al., 2017; Mohammadi et al al., 2014). Literature survey also revealed that different sources of adsorbents had used for adsorption of impurities from wastewater.These include low cost activated carbons from agricultural wastes such as coir pith (Chowdhury and Fatema, 2016), pinang frond (Ahamd et al., 2014), ash of aloe vera (Malakootian et al., 2014), mango nut (Kwaghger et al., 2012) corn cob (Ahmad et. al, 2011), mangosteen peel (Ahmad and Alrozi, 2010), rice husk (Yahaya et al., 2010), cotton plant wastes (Tunc et al., 2009), oil palm empty fruit bunch (Hameed et al., 2009), coconut husk (Tan et al., 2008), etc.

Other significant applications of eggshell include production of Tri-calcium phosphate and Hydroxyapatite, ceramic raw material for tiles and sanitary sectors, as mineral fillers in thermoplastic materials such as high density polyethylene to enhance rigidity, thermal stability and density of plastics. It is also being used to improve both physical and mechanical properties of soil, in biodiesel production as well as renewable raw materials for catalyst synthesis (Zaman etal., 2018; Tan et al., 2015). Moreover, extraction of the bioactive compounds in eggshells would be highly valuable and sustainable raw material source to cosmetic, pharmaceutical, glass, glass-ceramic or ceramic industries (Camaratta etal., 2009).

Chromium is usually found in industrial effluents such as electroplating, leather tanning and textile industries. Chromium, in wastewater can exist both as Cr (III) and Cr (VI) ions. But, in potable waters, Cr (VI) appears as the most stable species due to the aerobic conditions in the environment (Mishra and Gottipati, 2012). The trivalent form is not toxic. On the other hand, the detrimental effects of hexavalent chromium to biological systems and the environment had been well documented. Exposure to Cr (VI) beyond the tolerance levels (0.05 mg/l) can have devastating ffects on the human physiological, neurological and biological systems (Mishra and Gottipati, 2012; Guo et al., 2011).

In order to minimize this menace, several physico-chemical methods, such as reverse osmosis and ultrafiltration, oxidation/reduction, precipitation, adsorption electrodialysis, ion exchange, evaporation and concentration, electrolysis and electroplating, ion flotation, activated sludge process and carbon adsorption etc. had been adopted for the removal of heavy metals including Cr (VI) from aqueous phase (Park et al., 2016; Kushwaha et al., 2013;Mishra and Gottipati, 2012). In all, adsorption had been reported the most preferred due to its high efficacy, cost-effectiveness, versatility and easy handling (Mittal et al., 2016; Tang et al., 2010). Currently, not much comparative study has been done on the EHES and IHES as adsorbents for the removal of Chromium (VI) ion from aqueous solution. This paper therefore sought to evaluate the potentials of hen eggshell, a low cost bio-sorbent, to remove Chromium (VI) from aqueous solution. The effects of the adsorbent dose, contact (agitation) time, temperature and pH of the solution were also evaluated.

II. MATERIALS AND METHODS

2.1 Materials: The materials employed in this work include: EHES, IHES, de-ionized water, Chromium (VI)solution ($K_2Cr_2O_7$), 0.1 M HCl, 0.1 M NaOH, digital weighing balance, Isothermal water bath shaker, measuring cylinder, oven, screen, stop clock, 250 ml Erlenmeyer flasks, conical flaks,Atomic AdsorptionSpectrophotometer (UNICAM 929, London).

2.2 Preparation of Adsorbents: The hen eggshell samples were washed thoroughly with de-ionized water to remove the dust and other stains, and then dried in an oven at 85 ^oC for 30 minutes. The clean and dried sampleswere ground and screened to 150 µm particle sizes. That was done for both the EHES and IHES.

2.3 Preparation of $K_2Cr_2O_{7(aq)}$Solution from Stock Solution: A solution of concentration 0.06 g/l $K_2Cr_2O_{7(aq)}$was prepared by the dilution of initial stock solution1.0 g/l$K_2Cr_2O_{7(aq)}$ using de-ionized water.

2.4. Batch Equilibrium Studies: Batch equilibrium studies were used to determine the adsorption of Cr^{6+} on the EHES and IHES. The effects of the adsorbent dose, contact time, solutiontemperature and solution pH on the adsorption uptakes werealsoinvestigated. 1.0 g of the eggshell was added into 100 mladsorbate (0.06 g/l $K_2Cr_2O_{7(aq)}$) solution in an Erlenmeyer flasks. The flask was placed in an isothermal water bath shaker with rotation speedof 120 r.p.m.

The measure of the adsorption (Cr^{6+} removal) at equilibrium, q_e(g/g), and Cr^{6+} percentage removal

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was evaluated using equation 2.1 and 2.2 respectively:

$$q_e = \frac{(C_o - C_e)V}{W} \quad 2.1$$

$$\text{Cr (VI)ion \% removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad 2.2$$

Where, $C_o$and C_e (g/l) are the liquid-phase concentrationsof Cr^{6+} at initial and at equilibrium concentration respectively. Vis the volume of the solution and Wis the mass of HESused.

2.4.1 Effect of Adsorbent Dose: Different masses of the adsorbent (1, 2, 3, 4, 5, 6, 7 or 8 gEHES) wasadded to 100 ml of the 0.06 g/l $K_2Cr_2O_{7(aq)}$solution and placed in an isothermalwater bath shaker for 2 h. The solution temperature, the solution pH and rotation speed ofthe water bath shaker were set at 30 ^oC, 2 and 120 rpm respectively. The concentration of the Cr^{6+} in the filtrate in each case was determined using AA-Spectrophotometer. This experiment was repeated using the indigenous IHES.

2.4.2. Effect of Contact Time: The effect of contact time on the adsorption process was studied by taking agitation time as 0.5, 1,1.5, 2, 2.5, 3, 3.5or4 h. In each batch adsorption study, the adsorbent dose was 6 g while the solution temperature, the solution pH and the isothermal water bath shaker speed were kept constant for both exotic and indigenous breed HES. The concentration of the Cr^{6+} in the filtrate in each case was determined using AA-Spectrophotometer.

2.4.3 Effect of Solution Temperature: The effect of the solution temperature on the adsorption process wasevaluated by settingthe temperature at 30, 45, 60, and 75^oCthrough adjusting the temperature controller on the water bath shaker. Meanwhile, the adsorbent dose, the contact time, the solution pH and agitation speed used were 6 g, 2 h, 2 and 120 r.p.m. respectively for both exotic and indigenous breed HES. The concentration of the Cr^{6+} in the filtrate in each case was determined using AA-Spectrophotometer.

2.4.4 Effect of Solution pH: The initial pH of solution of adsorbate wasset at 1, 3, 5, 7, 9, 11 and 13 by adding 0.1M HCl and/or 0.1M NaOH to it. But, adsorbent dose, contact time, the solution temperature and agitation speed used were 6 g, 2 h, 30 ^oC and 120 r.p.m. respectively for both exotic and indigenous breed HES. The concentration of the Cr^{6+} in the filtrate in each case was determined using AA-Spectrophotometer.

III. RESULTS AND DISCUSSION

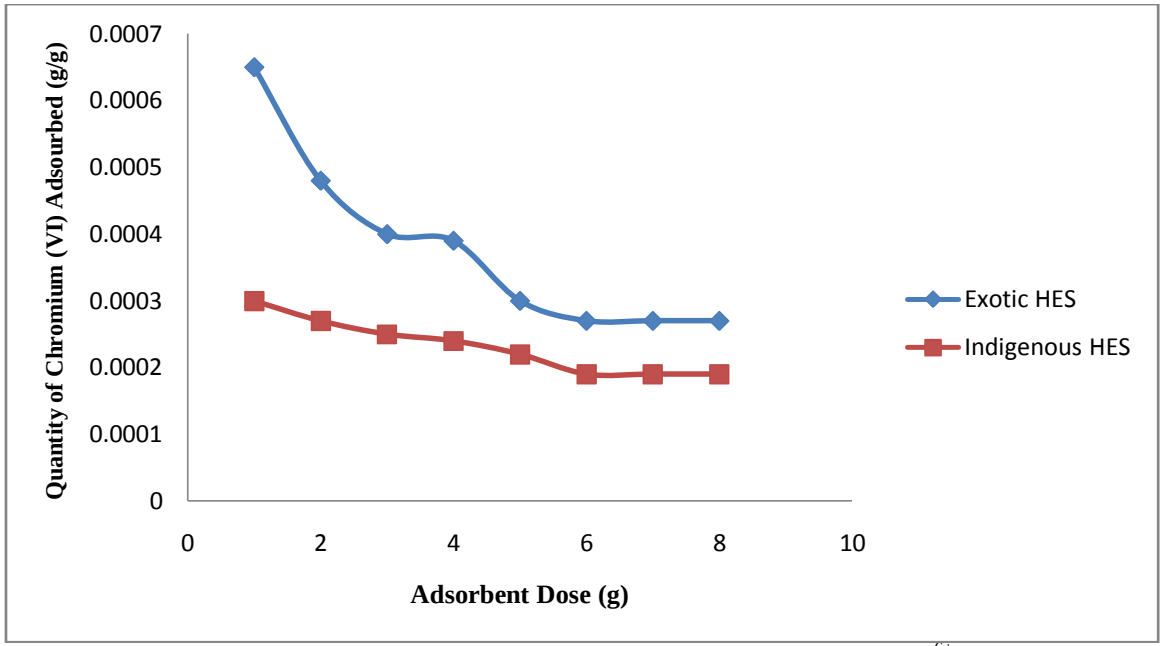

Figure 3.1: Effect of Adsorbent Dose (EHES and IHES) on Percentage Removal of Cr^{6+} ion from Aqueous Solution:0.06 g/l $K_2Cr_2O_{7(aq)}$, at 30 ^oC, pH 2 and 2 h

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3.1 Effect of Adsorbent Dose

Figures 3.1showed the effect of the adsorbent dose on the removal of Cr^{6+} ion from Aqueous Solution. In Figure 3.1, different doses of adsorbents (EHES and IHES powder) ranging from 1.0 – 8.0 g were considered and other process parameters were maintained constant (30 ^{o}C, 2 h, pH 3 and 120 r.p.m). The maximum percentage removal of Cr (VI) was 60.33% and 52.95% for EHES and IHES respectively. For EHES, the adsorption capacities decreased from 0.00065 to 0.00027 g/g with increase of adsorbent dose from 1.0 to 6.0 g but remain unchanged with further increase. For IHES, the adsorption capacities decreased from 0.00030 to 0.00019 g/g with increase of adsorbent dose from 1.0 to 6.0 g but had no effect with further increase. The Cr (VI) uptake were found to decrease with the increase of adsorbent dose, reach the optimum value, and remain unchanged with further increase. These observations agreed with earlier ones made by previous researchers (Slimani et al., 2014; Dubey and Gopai, 2007; Mohanty et al., 2005). The optimum adsorbent dose for both EHES and IHES was found to be 6 g. The decrease in adsorption capacity can be attributed to the formation of aggregates between the eggshell powder at high adsorbent dose, thus, reducing the effective active sites (Barkat et al., 2007).

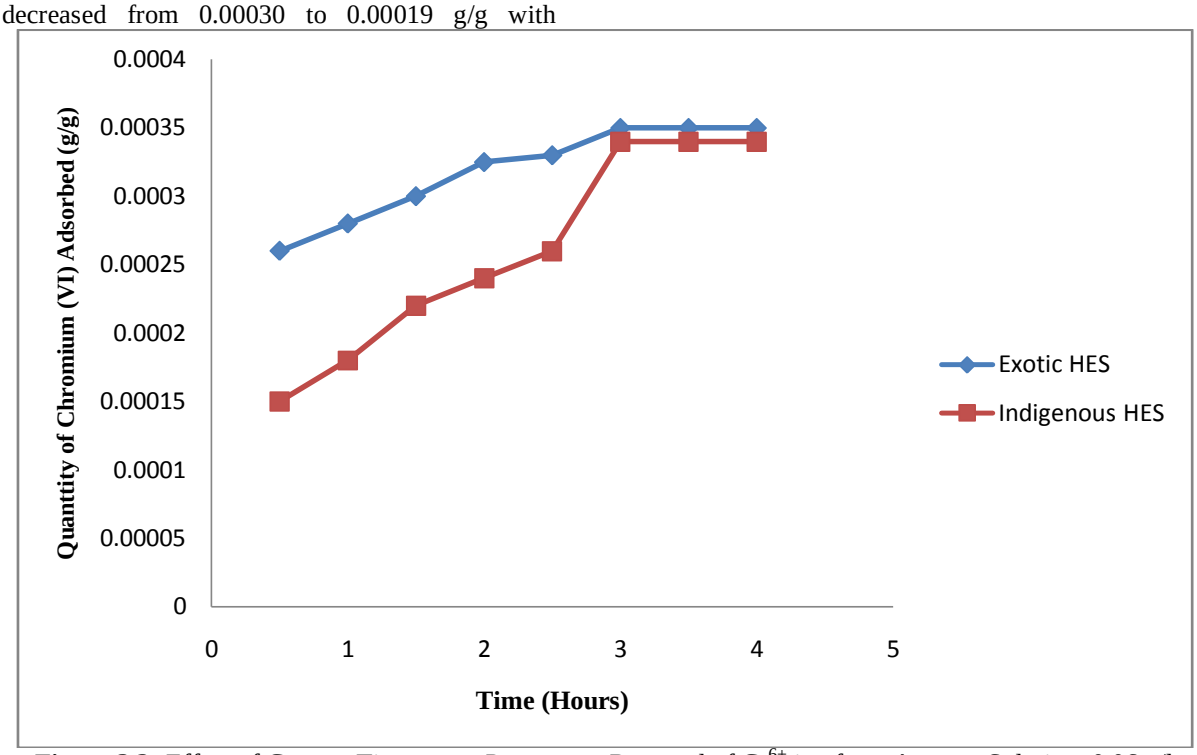

Figure 3.2: Effect of Contact Time on on Percentage Removal of Cr^{6+} ion from AqueousSolution: 0.06 g/l $K_2Cr_2O_{7(aq)}$, at 30 ^{O}C, pH2and 6 g Adsorbent Dose.

3.2 Effect of Contact Time

Figure 3.2 showed the effect of the contact time on the removal of Cr^{6+} ion from Aqueous Solution. Agitation time ranging from 0.5 – 4.0 h were investigated with other parameters maintained at 30 ^{o}C, 6 g adsorbent dose, pH 3 and 120 r.p.m. For EHES, the adsorption capacities increased from 0.00026 to 0.00035 g/g with increase in contact time from 0.5 to 3.0 h but remain unchanged with further increase.Similarly, for IHES, the adsorption capacities increased from 0.00015 to 0.00034 g/g with increase in contact time from 0.5 to 3.0 h.No changed was observed beyond this agitation time. Similar trends were also observed in the works of Mishra and Gottipati (2012) and Guo et al. (2011). The adsorptive removal progressively increased with contact time due to the limited mass transfer of the adsorbate molecules from liquid to the external surface of eggshell, and reached equilibrium due to slower internal mass transfer within the adsorbent particles (Folami and Adegbola, 2018; Acharya et al., 2009; Babu and Gupta, 2008). For both EHES and IHES, the optimum contact time was found to be 3 h with the percentage removal of Cr (VI) ion obtained as 70% and 68% respectively.

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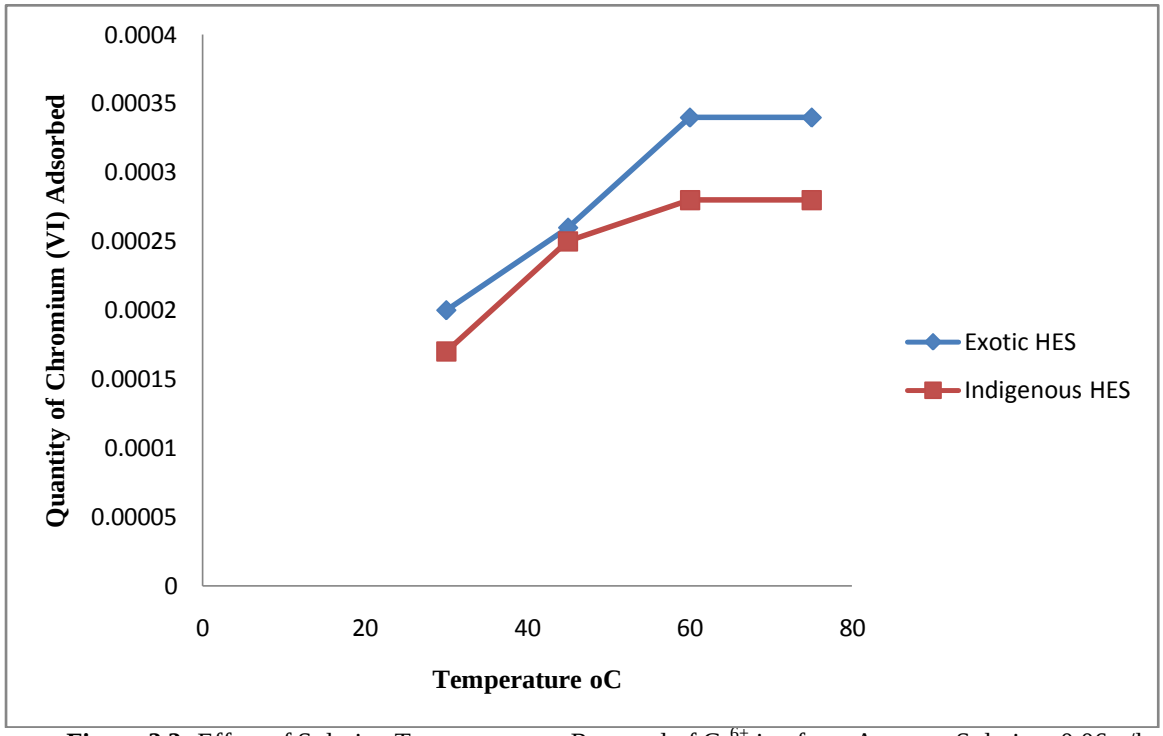

Figure 3.3: Effect of Solution Temperature on Removal of Cr^{6+} ion from Aqueous Solution: 0.06 g/l $K_2Cr_2O_{7(aq)}$, 6 g Adsorbent Dose, pH 2 and 2 h

3.3 Effect of Solution Temperature

Figure 3.3 shows the effect of the solution temperature on the removal of Cr^{6+} ion from aqueous solution. The solution temperature range investigated was 30 ^oC – 75 $^oC$with other process parameters kept constant (6 g adsorbent doe, pH 3, 2 h and 120 r.p.m.). For EHES, the adsorption of Cr^{6+} increased from 0.00020 to 0.00034 g/g with increase in solution temperature from 30 ^oC to 60^oC h but significant changed registered with further increase in temperature while for IHES, the adsorption uptake of Cr^{6+} also increased from 0.00017 to 0.00028 g/g in the same solution temperature range but remain unchanged with a further increase. With the increase of temperature, the uptake of Cr (VI) increases continuously (Slimani etal., 2014; Acharya et al., 2009; Barkat et al., 2007). The adsorption of Cr (VI) on eggshell powder increases as the temperature increases and thus the adsorption reaction is endothermic which is in conformity with earlier observations (Folami and Adegbola, 2018; Ahamad et al., 2014; Mishra and Gottipati, 2012).

The positive change in adsorption capacity may be due to the chemical interaction between adsorbate ions and adsorbent, creation of some new adsorption sites or increase in the intra-particle diffusion of Cr (VI) ion into the pores of adsorbent at higher temperatures (Nasrollahxadeh et al., 2016). Increased adsorption with temperature may also be attributed to the increase in number of adsorption sites generated as a result of breaking of some internal bonds near edge of active surface sites of the adsorbent (Meena et al., 2008). The more increase in temperature, the higher the removal rate. This is explained by a combination of 'activated diffusion' and an increase in surface area caused by oxidation associated with the observed reduction of ions on the surface of carbonaceous material (Mishra and Gottipati, 2012).

3.4 Effect of Solution pH Value

Figure 3.4 showed the effect of the solution pH on the removal of Cr^{6+} ion from aqueous solution. The pH of the solution is an important factor for the removal of Cr (VI) by adsorption. Different solution pH ranging from 1 – 13 was investigated and other process parameters were constant (6 g adsorbent doe, 30 ^oC, 2 h and 120 r.p.m.). For EHES, the adsorption of Cr^{6+} increased from 0.00038 to 0.00040 g/g within pH 1 – 3, then, decreased to 0.00019 g/g with increase in solution pH from 3 to 11 with no changes occurred with further increase in pH. In the case of IHES, the adsorption also increased from 0.00033 to 0.00037 g/g within pH 1 – 3, then, decreased to 0.00020 g/g with increase in solution pH from 3 to

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11 and no effect with further increase in pH. This trends is similar to the observation of earlier researchers (Folami and Adegbola, 2018; Mishra and Gottipati, 2012; Tang et al., 2009).The effect of pH on the adsorption of Cr (VI) may be attributed to the interactions between ions in solution and complexes formed at the adsorbent surface. The removal of Cr (VI) at low pH is governed by active reduction reaction (Mohan et al., 2005).

The rapid decrease in the removal of Cr (VI) with the increase of pH may also be due to the fact that low pH leads to an increase in H^+ ions on the adsorbent surface which results in significantly strong electrostatic attraction between Cr (VI) ion and adsorbent surface (Babu and Gupta, 2008). Folami and Adegbola (2018) and Bhatti et al., (2007) also found that the sorption capacity of AC prepared from almond shells was higher in acidic pH (<5) due to the negatively charged chromium species bind through electrostatic attraction to positively charged functional groups of the adsorbent surface. At pH less than 5, the decrease in sorption capacity is due to the increase of the negative charge on the adsorbent surface, thus the electrostatic force of attraction between the adsorbent surface and adsorbate ion decreased (Mishra and Gottipati, 2012).

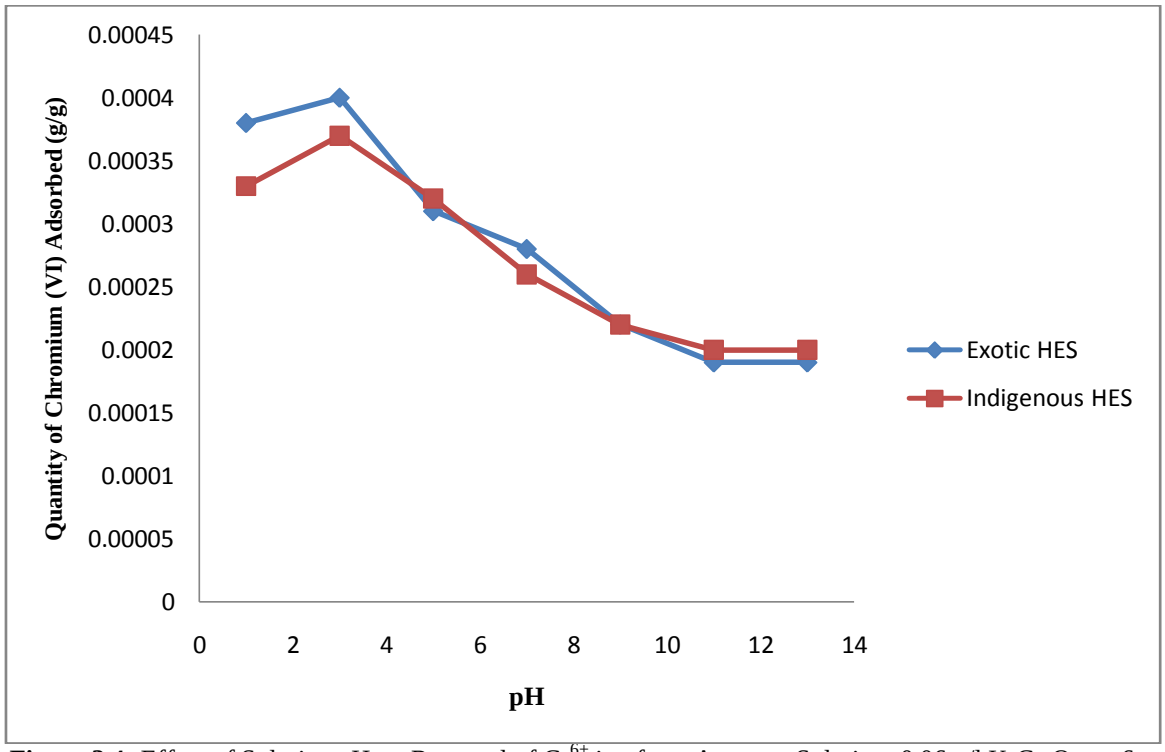

Figure 3.4: Effect of Solution pH on Removal of Cr^{6+} ion from Aqueous Solution: 0.06 g/l $K_2Cr_2O_{7(aq)}$, 6 g adsorbent dose, 30 ^oC and 2 h

IV. CONCLUSION

Chromium (VI) is usually found in industrial effluents such as electroplating, leather tanning and textile industries. Chromium, in wastewater can exist both as Cr (III) and Cr (VI). It has been widely reported that the exposure to Cr (VI) beyond the tolerance levels (0.05 mg/l) can have damaging effects on the human physiological, neurological and biological systems. In this light, this workhad investigatedthe suitability of EHES and IHES powder as adsorbents for the removal of Chromium (VI) ion from aqueous solution. The effects of adsorbent dosage, contact time, solution pH and solution temperature were evaluated in a batch process. The optimum conditions were adsorbent dose of 6 g, contact time of 3 h, pH of 3 and temperature of 60 ^oC for both adsorbents. Under these conditions, the percentage removal of Chromium (VI) ion for EHES and IHES powder was found to be 80.30% and 73.50% respectively. Both adsorbents could be used as low cost and effective adsorbent to improve the purity of wastewater containing Chromium (VI) ion with EHES preferable.

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