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RESEARCH ARTICLE

ADSORPTIVE CAPACITY OF COFFEE HUSK IN THE REMOVAL OF CHROMIUM (VI) AND ZINK (II) FROM TANNERY EFFLUENT: KINETICS AND EQUILIBRIUM STUDIES

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ABSTRACT

Tannery wastewater is the most challenging due to the complex toxic pollutants it releases into the environment. Similarly, coffee husk from coffee processing operations pollutes the environment. The use of coffee husk to remove hexavalent chromium (VI) and Zink (II)from tannery wastewater solves pollution problems due to untreated tannery wastewater and coffee husk. A batch adsorption process was conducted to determine chromium (VI) and Zink (II)adsorptive capacity of waste coffee husk to treat tannery wastewater. The effects of adsorbent dose (0.2-2.4 g/L), contact time (20- 60 min), agitation speed (50-250 rpm), and pH value (2-8) on the adsorptive capacity of coffee husk on the removal of hexavalent chromium (VI) & zinc (II) from tannery wastewater were studied. Using 2.4 g/L adsorbent dose, 250 rpm agitation speed, 60 min contact time, and pH value of 2, a maximum Cr(VI) removal capacity of coffee husk was 83%. The maximum Zn(II) removal capacity of coffee husk was found to be 79% at an adsorbent dose of 2.4 g/L, 60 min contact time, pH 7, and agitation speed of 250 rpm. Therefore, it can be concluded that coffee husk achieved significant removal of hexavalent chromium (VI) and zinc (II) from tannery wastewater.

KEYWORDS

Langmuir equation, bio-sorbent, coffee husk, hexavalent chromium, ionic solution, tannery wastewater.

1. INTRODUCTION

Water is the most important precious resource used for drinking, washing, recreation, irrigation and power generation. Without water the existence of life on Earth is impossible. Water with a high-quality standard is equally important to sustain life (Salnikow and Zhitkovich, 2008). Contamination of water with toxic metals is a serious problemasthese metals tend to persist and accumulate in the environment (Bedada et al., 2020). Water is got polluted when any substance present in excess of what is allowed for a particular water use. Water pollution by toxic metals (e.g., Cr, Zn, Pb, As, Cu, Cd) even at low concentration causes a high risk to human health (Qing et al., 2015). At lower levels, chromium and arsenic are highly carcinogenic causing cancer of the lungs, liver, bladder, and skin. And also human exposure to low-level of arsenic causes vomiting, abnormal heartbeat, reduction of erythrocytes and leukocytes, damages blood vessels and pricking sensation in hands and legs (Rao et al., 2017; Ayangbenro and Babalola, 2017).

Long-term exposure to Chromium and Arsenic leads to internal cancers, diabetes mellitus, formation of skin lesions, hypertension, pulmonary disease, neurological, and cardiovascular problems. Wastewater released from industrial sources contains different of toxic metals (Weldeslassie et al., 2018). These toxic metals may find their way to the water bodies through wastewater discharges (Kumar et al., 2019). Naturally heavy metals occur on earth crust rocks may enter groundwater by percolation through different means like climate change, precipitation, and agricultural practices (Baysal et al., 2013). Another way toxic heavy metals enters water bodies is through wastewater discharges from industries like leather, electroplating, mining, and paints (Zhou et al., 2018). Treatment technologies like reverse osmoses, electrodialysis, membrane filtrations can be used to removal toxic heavy metals from wastewater. However, these treatment units are costly and not affordable for developing county including Ethiopia.

Therefore, it is desirable to search for and investigate the removal of toxic heavy metals from industrial wastewater using locally available low-cost materials using a simple treatment method such as adsorption (De Gisi et al., 2016). Adsorption is a process in which a substance is captured material in void space of adsorbent (Yang and Xing, 2010). It can also be described as accumulation of adsorbates in the void space of the substance/adsorbent with or without a chemical reaction (Kong and Adidharma, 2019). Adsorbate molecules enter the structure of adsorbent during absorption, thus producing a solid solution (Inyinbor et al., 2016). Ions, biomolecules or atoms of pollutants, or dissolved solids can be sticken/adhered to the void space of the adsorbent. The created adsorbate is the film of the adsorbent surface formed by adsorption (Abbasi and Sardroodi, 2018).

1.1 Bio-Sorbents

A bio-material having the capacity or tendency to absorb other substances or materials (Crini et al., 2019). Bio-sorbents are materials from biological origin can uptake some targeted material such as metallic ions. This biological materialism one of the prime interest areas in environmentally friendly sustainable removal of toxic heavy metals. The strong adsorption behavior of certain bio-sorbent towards metallic pollutants is the ability

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of bifunctional groups (Hassan et al., 2020). Coffee husk is the most abundant waste material produced during coffee processing operations. Ethiopia is home to coffee Arabica & the leading coffee producer in Africa and has several coffee processing plants. Jimma, a town in southwest Ethiopia has four main coffee processing units, each processing approximately 3000kg per day. Based on the information obtained from these raw coffee processing plants, 600kg of the coffee husk will be extracted from every 900kg of raw coffee. Coffee husk (Figure 1) has a very good potential as bio-sorption application (Ayalew and Aragaw, 2020). The use of Coffee husk as a bio-sorbent to remove toxic heavy metals from industrial wastewater is a golden opportunity to regulate and prevent environmental pollution due to toxic heavy metals and Coffee husk itself.

Figure 1: Coffee husk

Nowadays, there has been an increasing global environmental concern due to emissions of pollutants into water, soils, and air constantly. In coffee-producing countries, the coffee husk is one of the major wastes which cause severe environmental pollution. The use of coffee husk as adsorbent is becoming popular in wastewater treatment (removing waste by waste) (Anastopoulos et al., 2017). The objective of this study was to investigate the adsorptive capacity of coffee husk in removing chromium (VI) and zinc (II) from aqueous solution.

1.2 Infrared spectroscopic studies

The FTIR Spectroscopic analysis of coffee husk (husk of *Coffee arabica*) indicates broad bands at 3,441 cm^{-1}, which may be representing bonded –OH groups rather than -NH groups. This is because the peak of -OH stretching is wide with an adjusted tip, but the peak for the bonded-NH group is a broad peak with both two spikes sharp (primary amines), a broad peak with one sharp spike (secondary amines), or no signal (tertiary amines). The bands observed at 2,955–2,852 cm^{-1} may show the nearness of C-H extending, but not aldehydic C-H because the aldehydic C-H stretching vibration occurs within the border of 2,830-2,700 cm^{-1} within the appearance of two intense bands. The peaks about 1,722 cm^{-1} compared to the C=O group and at 1,652–1,616 cm^{-1} C=C. The C–O band absorption peak was also observed at 1,035 cm^{-1}. These functional groups are important sorption sites of coffee husk to participate in metal binding from aqueous solution of industrial effluents (Nguyen et al., 2019).

1.3 Mechanism of Bio-sorption process

The removal method is commonly used in different articles to take up heavy metals from polluted water. The mechanism of sorption for the modified and raw forms of adsorbent is linked to the role played by the essential stretching functional groups like hydroxyl (–OH), the carboxylic acid (-COOH), carbonyl (C=O), Si-O-Si, Si-OH, aromatic and phenolic groups existing in the sorbent (Rodiguez et al., 2018). For instance, Na (OH) and H_2SO_4 decrease or remove low molecular weight lignin compounds, increasing the concentration of -COOH and -OH groups (Liu et al., 2017). Ion exchanges also play a significance role in sorption of toxic heavy metals.

1.4 Adsorption isotherms

The equilibrium of adsorption for any particular adsorbent-adsorbate system is generally quantified using an adsorption isotherm (Piccin et al., 2017). Equilibrium adsorption isotherms show how metal ions are divided between the adsorbent and liquid stage at equilibrium (Piccin et al., 2017). The basic requirements for the design of adsorption systems and to provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system of conditions are pH of metal ion solution, metal ion initial concentrations, contact time, etc. Among the different adsorption isothermal models, Freundlich and Langmuir's models have been used in most adsorption studies (Gunasundari, 2017).

1.4.1 Langmuir isothermal model

In many pollutant adsorption process treatments, the Langmuir isothermal model has been successfully efficient, and it is the most commonly used adsorption isotherm for the take-up of solute from anaqueous solution. The Langmuirmodel demonstrates the monolayer scope of adsorbent surface and no interaction of adsorbate in the plane of the surface of the adsorbent (Hokkanen et al., 2016). In addition, the model incorporates maximum adsorption capacity (q_m) corresponding to complete monolayer, and low values of K_a are reflected in the steep initial slope of an adsorption isotherm.

1.4.2 Freundlich isotherm

The basic assumption of this model is that there is an exponential variation in site energies of adsorbent; i.e., heterogeneity of surface sites. The Freundlich isothermal model is the earliest model indicates whether the adsorption proceeds with ease or difficulty (Lau et al., 2016).

1.5 Factors Affecting Bio-sorption

Major factors that affect the bio-sorption process are temperature, pH of solutions, contact time and agitation speed, adsorbent dose and, so on. It influences the activity of biomass functional groups and the concentration of the metallic ions. Adsorbent dose seems to influence the specific uptake.

2. MATERIALS AND METHODS

2.1 Equipment and chemicals required

Materials used during this study include pH meter, atomic adsorption spectroscope (AAS), Electronic balance, Mechanical shaker, Mortar and pestle, Sieve, Erlenmeyer flask, Whatman (45 µm). filter paper, and Hot air oven drier. Laboratory grade standard chemicals including HNO_3, NaOH, and HCl were used during experimental processes.

2.2 Collection and Preparation of coffee husk as bio-sorbent

The raw coffee husk collected from a local coffee processing firm was pre-treated to separate and remove impurities like dust, sand, woods, and fine coffee husk. The pretreated coffee husk was washed with distilled water to remove some water-soluble impurities. Then the washed coffee husk was dried at 105°C for 24 h in a hot air oven. Then washed with 2% formaldehyde solution and ground with a mortar and pestle. It was then allowed to pass through a 200 µm sieve. Finally, coffee husk with an appropriate size for effective adsorption process was prepared as shown in (Figure 2).

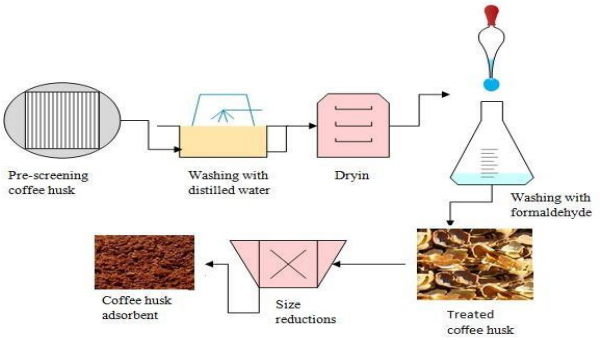

Figure 2: Process flow diagram (PFD) of bio-sorbent preparation

2.3 Batch mode adsorption studies

Batch mode adsorption studies for removing zinc (II) and chromium (VI) metal ions were carried out at room temperature using adsorbent dose ranging from 0.4 - 2.4 g/L. The effects of different parameters, including concentration of adsorbate, agitation speed, contact time, and pH of solution were studied. The batch process adsorptions were carried out in a 250 mL flask for the prescribed time length, and the flask was shaken on a shaken. Finally, filtration was done using filter paper, and the remaining amount of Zn (II) and Cr (VI) ions in the solution were determined by atomic absorption spectrophotometer (FAAS).

2.3.1 Effects of agitation speed and contact time

The effect of agitation speed was investigated at different agitation speeds such as at 50, 100, 150, 200, 250 rpm by keeping other parameters constant. Contact time is a significant variable that affects coffee husk adsorption removal capacity of metal ions. To determine the rate of adsorption of metal ion by coffee husk from 100 mL aqueous solution, the quantity of metal ion adsorbed was determined at the contact time of 20,

25, 30, 35, 40, 45, 50, 55, and 60 min while keeping other parameters constant.

2.3.2 *Effects of pH and initial concentration of metal ions*

To determine the effect of pH, solution pH was adjusted to 2, 3, 4, 5, 6, 7, and 8 using 0.1 M HCl and 0.1 M NaOH solutions while keeping other parameters constant before carrying out the batch adsorption experiments. To determine the effect of metal ions concentration on adsorbent for removal capacity, the concentration of metal ions8, 14, and 18 mg/L was used, while keeping other parameters constant.

2.3.3 *Effect of adsorbent dose*

Another factor that determines the removal efficiency of chromium and zinc metal ions is adsorbent dose. Adsorption experiment was carried out at room temperature using adsorbent doses (coffee husk) ranging from 0.4 - 2.4 g/L while keeping other factors constant.

2.4 Adsorption isotherms

The adsorption isotherms describe the mathematical models of the distribution of adsorbate species among liquid and solid phases atequilibrium (Piccin et al., 2017). The amount of adsorbate taken up by adsorbet depends on the characteristics and concentrations of adsorbate and temperature. Several isotherms' models were developed but Langmuir and Freundlich models are commonly used to describe experimental data. In order to construct adsorption isotherm for coffee husk, experiments were carried using 8, 14, and 18 mg/Lof initial concentration of metal ions in 100 mL solution by keeping other parameters constant.

The Langmuir isotherm is described by the following equation (Ghosal and Gupta, 2017):

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

where qe is amount adsorbate adsorbed per unit mass of adsorbent (mg/g), Ce is equilibrium concentration of adsorbate in solution after adsorption (mg/L), qm is the maximum adsorption for monolayer complete capacity (mg/g), Ka is adsorption equilibrium constant (L/mg).

The linearized Langmuir isotherm equation allows the calculation of adsorption capacities and Langmuir constants is given by the following equation (Ghosal and Gupta, 2017):

$$\frac{Ce}{qe} = \frac{1}{qm\ Ka} + \frac{Ce}{qm} \quad (2)$$

Langmuir isotherm constants can be determined by plotting Ce/qe vs. Cewith slope of 1/qm and intercept of 1/Ka. The necessary Langmuir isotherm equation can be explained in terms of a dimensionless constant called separation equilibrium parameter (K_L) or factor:

$$K_L = \frac{1}{1 + K_a C_o} \quad (3)$$

where Co is the initial adsorbate concentration and Ka is the Langmuir constant (L/mg). The parameter K_L indicates the nature of adsorption process (KL> 1; Unfavorable; K_L= 1; Linear; 0 < K_L< 1: Favorable; KL = 0: Irreversible).

The Freundlich isotherm is represented by the following equation (Gusain et al., 2016):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

wheren and KF constants that affect the adsorption intensity and capacity respectively.

The linearized Freundlich isotherm is represented by the following equation:

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \quad (5)$$

where log K_F is the y-intercept, 1/n is the slope

2.5 Determination of metal ions by FAAS

Concentrations of metal ions were determined using atomic flame absorption spectrometer (FAAS). For calibration purposes, standards and blank (de-ionized water) were run in a flame atomic absorption spectrometer before analyzing the samples. Then, a metal ion concentration was determined from the curve of calibration Figure 4 (a and b). All determinations were performed in three replicates per experiment, and the average values were reported. Chromium-specific cathode hollow lamp (wavelength 357.9 nm) and Zinc specific cathode hollow lamp (wavelength 213 nm) were used for the absorption readings. Finally, the capacity of removal was calculated by using the following relationship.

$$(\%)\ \text{Adsorption} = \frac{C_O - C_e}{C_O} \times 100 \quad (6)$$

The coffee husk adsorption efficiency was calculated based on the following equation:

$$q_e = \frac{V(C_O - C_e)}{m} \times 100 \quad (7)$$

Where m represents the adsorbent weight (g) and V represents a volume of solution metal ion.

2.6 Data Analysis and interpretation

The data generated were analyzed using origin pro software to compute standard deviation, and linear regression values. The Edraw max software was also used to draw the process flow diagrams and response surface methodology (RSM) was used to determine the interaction effects of variables on the metallic ion removal by coffee husk adsorption.

3. Results and Discussion

3.1 Adsorption isotherms

The Langmuir and Freundlich equations were used to explain the nature of adsorption for the two metal ions [Cr (VI) and Zn (II)] on adsorbent. Graph was drawn using Ce (X-axis) vs. Ce/qe (Y-axis) in the Langmuir equation while it was drawn using log Ce (X-axis) vs. log qe (Y-axis) in Freundlich equation.

Table 1: Adsorption isotherm of Cr (VI) ions

Initial conc. Co (mg/L)	Equilibrium conc. Ce (mg/L)	Adsorption capacity (qe) (mg/g)	Ce/qe	Log Ce	Log qe
8.10	3.24	0.49	6.67	0.51	-0.31
14.20	6.53	0.738	8.52	0.82	-0.12
18.04	8.66	0.94	9.23	0.94	-0.03

For the adsorption of chromium by coffee husk, the empirical constants qm and Ka were found to be 2.083 mg/g and 0.0925respectively (Figure 3 and equation2). Accordingly, value of qmindicate that one gram of the coffee husk can adsorb 2.083 mg chromium. The value of KL indicates a favorable adsorption, i.e. (0 < 1/ (1+0.0925Co) < 1). This show that coffee husk is a good adsorbent in removing Cr (VI) ions from aqueous solution. The Freundlich adsorption isotherm is the most widely mathematical equation use dequation to describe adsorption for an aqueous system. The K_F and n show the capacity of adsorption and intensity of adsorption respectively (equation 5).

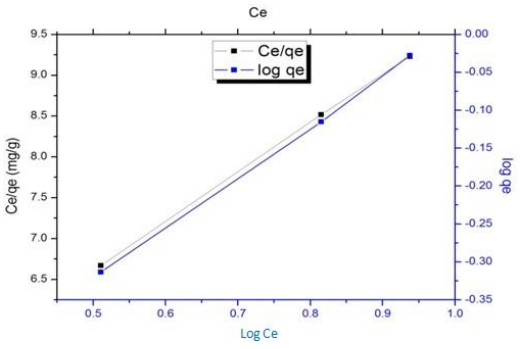

Figure 3: Langmuir and Freundlich adsorption isotherms for Cr (VI) ions

The log qe vs. log Ce was graphed to determine the fit of experimental data to isotherm equation. This graph was employed to generate the intercept value of log K_F and the slope of 1/n. The Freundlich constants K_F and n were found to be 0.2218 and 1.503 respectively (Figure 3 and equation 5). The value of 1/n shows the concentration of solute adsorption. If the value of 1/n is an approach to 1, it shows that just a little concentration change can relatively affect the adsorption. If n > 1, the adsorbent can effectively adsorb the solute (Freundlich, 1906). Since the values of 1/n (0.6653) lie between 0 and 1 and n > 1, it indicates that the coffee husk can adsorb Cr (VI) ions effectively. The chromium adsorption on coffee husk fitted to both Langmuir and Freundlich adsorption isotherms since the correlation coefficients (R^2) are 0.9839 and 0.9995 respectively. Therefore, each site of a coffee husk can accommodate one chromium ion, or it is characterized by heterogeneity of surfaces of coffee husk.

Table 2: Adsorption isotherm of Zn (II) ions.

Initial conc. C_o (mg/L)	Final conc. Ce (mg/L)	Adsorption capacity (qe) (mg/g)	Ce/qe	Log Ce	Log qe
8.10	3.807	0.429	8.868	0.581	-0.3672
14.20	6.816	0.738	9.231	0.834	-0.132
18.04	9.020	0.902	10	0.955	-0.045

The empirical constants qm and Kafor Zn (II) were found to be 4.728 mg/g and 0.0265respectively (Figure 4 and equation 2). The value of $K_L$liesbetween 0 and 1 (0 <K_L< 1) indicating favorable adsorption conditions. This shows coffee husk is a good adsorbent for the removal of Zn (II) ions from aqueous solution. Thus, Zn (II) ions removal by coffee husk is feasible.

The Freundlich constants K_F and n for Zn (II) ions adsorption were found to be 0.135 and 1.15respectively (Figure 4 and equation 5). Since the values of 1/n (i.e. 0.8713) lie between 0 and 1 and n > 1, coffee husk adsorbs Zn (II) ions effectively from aqueous solution. The adsorption of Zn (II) ions on coffee husk are better fitted to the Freundlich model than to the Langmuir model as the correlation coefficients (R^2) are found to be 0.9164 and 0.9963, respectively.

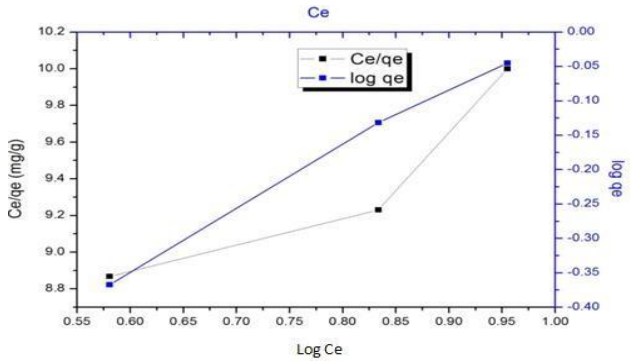

Figure 4: Langmuir and Freundlich adsorption isotherms for Zn (II) ions

3.2 Process optimizationfor Cr (VI) and Zn (II) Ions Removal by Coffee Husk

3.2.1 Effect of agitation speed

The effect of agitation speed on Cr (VI) and Zn (II) ionsadsorptionby coffee huskis shown in figure 5).

Table 3. Effect of agitation speed on Cr (VI) and Zn (II) adsorption.

Speed (rpm)	Co (mg/l)	Ce (mg/l) Cr(VI)	Ce (mg/l) Zn(II)	% ads Cr(VI)	% ads Zn(II)
50	14.2	9.088	11.360	36	20
100	14.2	7.100	10.650	50	25
150	14.2	4.544	7.810	68	45
200	14.2	3.550	3.408	75	76
250	14.2	7.398	8.463	80	85

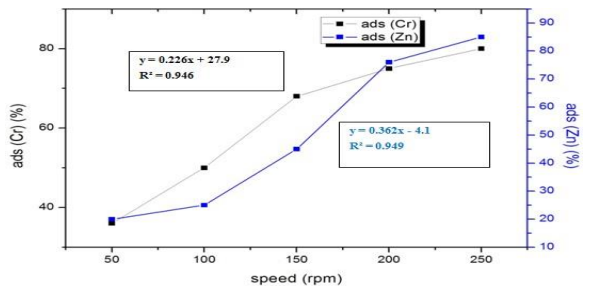

Figure 5: The effect of agitation speed on Cr (VI) and Zn (II) ions removal capacity (%), fixing maximum points for time pH, and dose

The effect of agitation speed on Cr (VI) and Zn (II) ions removal capacity (%) at contact time = 30 min, initial conc. = 14.2 mg/L, solution pH for (Cr (VI) = 2 and for Zn (II) = 7), dosage = 2g, volume of solution= 200ml) from table 3.

From Figure 5, the removal efficiency of the adsorbent increased from 35 ± 0.5 to 80± 0.5% for Cr (VI) ions as agitation speed increase from 50 to 250 rpm and 20 to 85% for Zn (II) ions with increasing agitation rate from 50 to 250 rpm as well shows table 3. The blue color line and black line show the zink and chromium adsorption, respectively. Increase the agitation speed solves the diffusion of metal ions for the adsorbent surface, and the same thing was observed in this Study (Saleh, 2016). Therefore, the optimum agitation speed of 250 rpm was obtained for Zn (II) and Cr (VI) ions. Agitation rate has been reported to be an essential parameter that is relevant for increased volumetric mass transfer of substances. The adsorption rate is managed by film and pore diffusion, depending on stirring speed (Hans et al., 2016). Low agitation speed output in film thicker layer of the solvent bounders the adsorbent and fits the film layer, and becomes the rate-controlling step (Yuvaraja et al., 2019). When the stirring speed is high, the thickness of the solvent film layer gets thinner. Therefore, the movement of the metal ions through the film layer takes place very fast, and the diffusion through the pores becomes the rate-controlling step.

3.2.2 Effect of contact time

Time is one of the most important factors to be considered for economical wastewater treatment.

Table 4: Effect of contact time on hexavalent Chromium and trivalent Zink Adsorption.

Time (min)	Co	Ce (Cr)	Ce (Zn)	% Ads. (Cr)	% Ads. (Zn)
20	14.2	9.060	8.335	36.2	41.3
25	14.2	7.200	7.341	49.3	48.3
30	14.2	5.595	5.382	60.6	62.1
35	14.2	5.041	5.197	64.5	63.4
40	14.2	3.280	4.998	76.9	64.8
45	14.2	2.826	4.743	80.1	66.6
50	14.2	2.442	4.501	82.8	68.3
55	14.2	2.173	3.706	84.7	73.9
60	14.2	2.144	3.692	84.9	74.0

The effect of contact time on the adsorption efficiency of Cr (VI) and Zn (II) ions is a significant factor shown in figure 4.

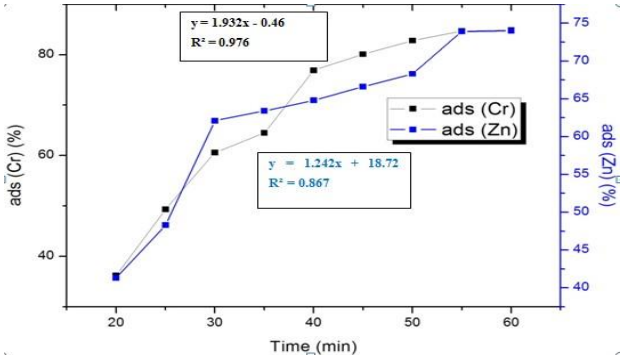

Figure 6: Effect of contact time on Cr (VI) and Zn (II) ions adsorption efficiency (%), fixing on maximum for agitation speed, pH, and dose.

The Effect of contact time on Cr (VI) and Zn (II) ions adsorption efficiency (%) (Solution
pH (Cr (VI) = 2, Zn (II) = 7), Co = 14.2 mg/L, agitation speed = 250 rpm, dosage = 2g) from (Table 1). The plots in (Figure 6) reveal that the percentage rates of both chromium and zinc adsorption have rapidly increased at the starting. This is due to the larger pore area of the husk being available at the beginning for the adsorption of Cr (VI) and Zn (II) ions. in the progressive of these sites, the adsorption process becomes slower on zinc ions. 85% Cr (VI) ions were removed in the first 60 minutes. In the case of Zn (II), 74% of the ions were adsorbed at the first 60 minutes. However, although there is a slight decrease in some data points of zinc ions, the adsorption with contact time is increasing. In the case of chromium ions, the graph shows stability between 55 and 60 minutes. Hence 60 minutes in metal ions can be taken as sufficient agitation times for attaining equilibrium.

3.2.3 *Effects of pH*

The pH effects on the adsorption capacity of coffee husk on Cr (VI) and Zn (II) ions are shown in (Fig).

Table 5: Effect of pH on hexavalent Chromium and trivalent Zink Adsorption.

pH	Co(mg/L)	Ce (mg/L) Cr (VI)	Ce (mg/L) Zn (II)	% ads (Cr)	% ads (Zn)
2	14.2	2.840	8.946	80	37
3	14.2	3.124	8.094	78	43
4	14.2	6.248	7.810	56	45
5	14.2	7.100	5.396	50	62
6	14.2	8.236	4.828	42	66
7	14.2	9.088	3.692	36	74
8	14.2	9.656	4.544	32	68

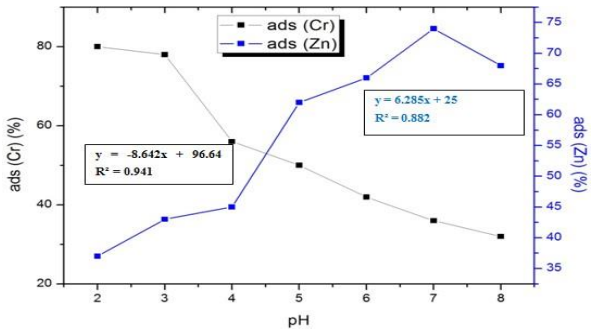

Figure 7: Effect of solution pH on Cr (VI) and Zn (II) ions adsorption (%), fixing on maximum for agitation speed, contact time, and dose.

The plots in (Fig) depict that the adsorption efficiency of Zn (II) ions onto the surface of bio-sorbent (coffee husk) increases from 35 to 74% as the pH of the metal ion solution increases from 2 to 7 and at pH 7, adsorption becomes saturated. However, the reverse is observed on chromium ions. About Table 2, adsorption decreases from 80 to 32%, as pH solution increases from 2 to 7. These values were taken to be the optimum amounts of the metal ions that could be removed from the respective solution via adsorption on the coffee husk surface. There is excessive protonation of the active sites of the coffee husk surface in pH above two that might have prohibited the formation of links between the Cr (VI) ions and the active sites. The peak percentage adsorptions of Cr (VI) and Zn (II) were attained at pH 2 and 7, respectively. After optimum pH or at higher pH values (pH >7), the OH- ions may compete forZn(II) ions with the active sites on the surface of the adsorbents, causing a decrease in the adsorption speed of Zn(II) ions. Besides this, Zn (II) ions start precipitating as $Zn(OH)_2$.

The pH of a solution affects the concentration and solubility of metal ions of the counterions on the functional groups of the coffee husk (Cechinel et al., 2018). This is partly because hydrogen ions (H^+) themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the functional groups onto the adsorbent surfaces (Wang et al., 2020). At low pH, due to high positive charge density and protons on the surface sites during uptake of metal ions, electrostatic repulsion will be high between protons at the surface of adsorbing metal ions resulting in lower removal efficiency (Zhang et al., 2016). At the same time, electrostatic repulsion decreases with increasing pH. Thus, enhancement of metal ion adsorption is noted.

3.2.4 *Effects of adsorbent dosage*

The adsorbent dosage effect on the adsorption efficiency of Cr (VI) and Zn (II) ions is shown in Figure 8. The effect of the adsorbent dose was studied at room temperature by varying the adsorbent amounts from 0.2 to 2.4 g. For all these runs, the initial concentration of Cr (VI) and Zn (II), pH, agitation speed, and contact time were constant. Since adsorption capacity is expressed as the mass of metal ion adsorbed per unit mass of the adsorbent, its value decreases when the mass of the metal ion adsorbed gets smaller for the same increase in the mass adsorbent.

Table 6: Effect of adsorbent dose on hexavalent Chromium and trivalent Zinc Adsorption

Dosage	Co(mg/L)	Ce (Cr) mg/L	Ce (Zn) mg/L	%ads (Cr)	% ads (Zn)
0.2	14.2	11.218	10.650	21	25
0.4	14.2	10.650	9.940	25	30
0.6	14.2	9.230	9.230	35	35
0.8	14.2	6.390	9.088	55	36
1	14.2	4.260	8.946	70	37
1.2	14.2	3.550	7.668	75	46
1.4	14.2	2.84	5.680	80	60
1.6	14.2	2.130	4.260	85	70
1.8	14.2	2.130	3.550	85	75
2	14.2	1.846	2.840	87	80
2.2	14.2	1.704	2.840	88	80
2.4	14.2	1.704	2.840	88	80

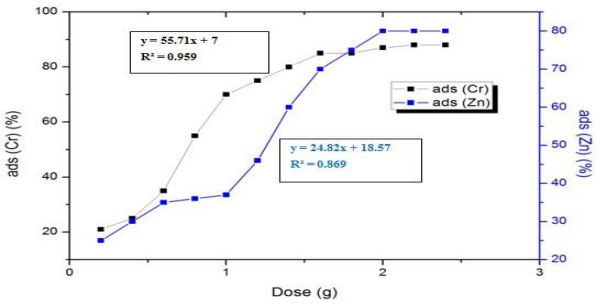

Figure 8: Effect of adsorbent dosage on Cr (VI) and Zn (II) ions adsorption efficiency (%), fixing on maximum for agitation speed, pH, and contact time.

The availability and accessibility of the adsorption site are controlled by adsorbent dosage. The effect of the mass of adsorbent loading on heavy metal removal using coffee husk was investigated by varying the adsorbent weight from 0.2 to 2.4 g per 200 ml of metal ions solutions shown in table S4. It can be easily inferred from the above graph that the percentage removal of chromium and zinc ions increased with the increasing weight of coffee husk. This is due to the greater availability of the exchangeable sites or surface area at a higher dose of the adsorbent and becomes saturated 2 to 2.4 g.

3.3 Variable interaction on the coffee husk adsorption capacity

Agitation speed, contact time, pH, and adsorbent dosage are the basic factor variables that affect the coffee husk adsorption capacity on the Cr (VI) and Zn (II). The two interactions of variable on adsorption capacity leads positive or negative effects. The two-factor interaction effects on coffee husk adsorption capacity of Cr (VII) were analyzed by ANOVA shown in figure 9.

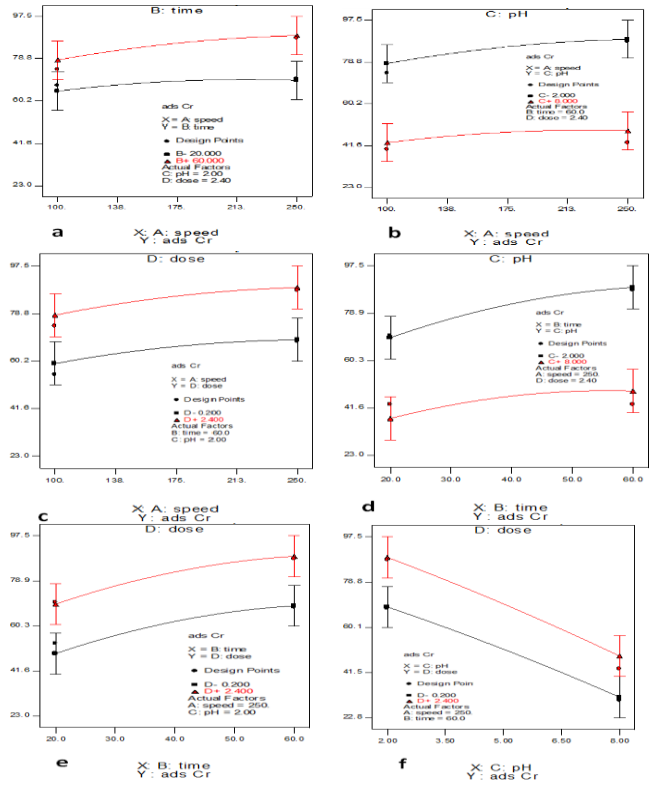

Figure 9: Two variable interaction effects on coffee husk adsorption capacity for Cr (VI)

This graph shows that the interaction of time and speed (a), pH and speed (b), adsorption dose and speed (c), pH and time (d), adsorption dose and time (e), adsorption dose, and pH (f) leads the different on adsorption effects respectively. Figure 7 (a, c and f) interaction shows positive effects on coffee husk adsorption efficiency in different magnitudes. And Figure 7 (b, d, and e) interaction shows negative effects on adsorption efficiency in different magnitudes.

Similarly, there were interactions of variables on the coffee husk adsorption efficiency on Zn (II) shown figure 8.

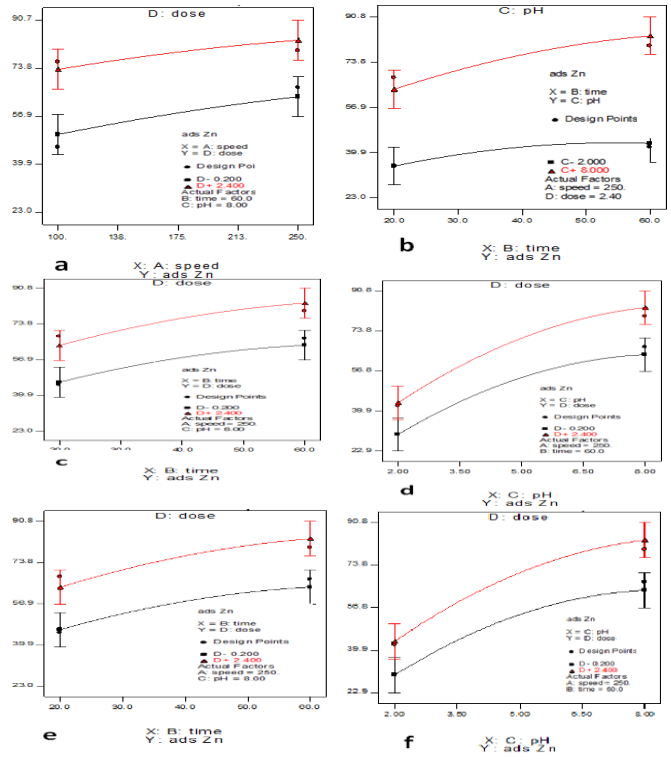

Figure 10: Two variable interaction effects on coffee husk adsorption capacity for Zn (II)

All the two variables interactions effects on coffee husk adsorption capacity for Zn(II) leads positive responses shown (figure 8 b, c, d, and e), except adsorption dose and agitation speed integration responses negative effects on the coffee husk adsorption on Zn (II) shown figure 8a From the three positive effects responses pH and time interaction responses was in great positive magnitudes than the others.

4. Conclusion

Some industries are releasing their effluents directly to the water bodies without treatment. Bio-sorption is a strong choice for the removal of heavy metals from wastewater. The coffee husk is an agricultural byproduct. The adsorption process of toxic pollutant metal ions from water and wastewater using coffee husk is a sustainable treating waste by waste. In this study, batch adsorption experiments for the biosorption of Cr (VI) and Zn (II) ions from aqueous solutions and tannery wastewater have been carried out using the coffee husk, a readily available bio-sorbent. The bio-sorption characteristics have been examined at different pH values; initial metal ion concentrations prepared stock solution, contact time, and agitation speed. Removal of chromium and zinc ions by coffee husk has been shown to depend significantly on the pH, initial metal ion concentration, agitation speed, and contact time. Coffee husk has shown a good adsorption capacity on chromium than zinc ions. The obtained results can be summarized as follows: Increase in agitation speed leads to an increase in Cr (VI) and Zn (II) ions adsorption due to increasing the external film diffusion rate. Maximum uptake of Cr(VI) and Zn(II) ions was obtained at an agitation speed of 250 rpm. The equilibrium time for adsorption of Cr(VI) and Zn(II) ions from wastewater and aqueous solutions was achieved within 60min. The pH experiments showed tha t the governing factors affecting the adsorption characteristics of all adsorbents are competition of the (H+) ions with metal ions at low pH values, maximum adsorption at pH are 2 and 7 for Cr(VI) and Zn(II) ions, respectively. At higher pH, precipitation onto the adsorbents occurred. The removal efficiency of coffee husk for Cr(VI) and Zn(II) ions was increased when the dosage increases due to many available bio-sorption sites to bind the metal ions. The maximum adsorption capacity by coffee husk was 2.083 and 4.728 mg/g for Cr(VI) and Zn(II) ions. In both case (Cr(VI) and Zn(II)) metal ions, the value of KL and n indicates a favorable adsorption ($0 < KL < 1$ and $n > 1$).

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