ADSORBENTS CHARACTERIZATION AND EFFECT OF REACTION INDICES ON THE UPTAKE OF CADMIUM (II) AND CHROMIUM (VI) IONS FROM WASTEWATER

[1]**D. O. Ochi,** [2]**A. K. Babayemi and** [3*]**L. O. Ekebafe**

[1]Department of Chemical Engineering Technology, Auchi Polytechnic, Auchi, Nigeria
[2]Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University,
Uli, Anambra State, Nigeria
[3*]Industrial Chemistry Research Group, Department of Chemistry, University of Lagos, Akoka, Nigeria
Correspondence E-mail: lawekebafe@gmail.com, ochidanielokey@gmail.com

ABSTRACT

The effect of reaction variables on the uptake of heavy metals from wastewater using modified chitosan and plantain peels carbon based adsorbents was explored in this study. Plantain peels were carbonized, activated with phosphoric acid and the activated carbon was separated into various proportions and impregnated with various percentages of chitosan to make the composite biosorbents. Deproteinization, deminerization, and deacetylation techniques were used to extract chitosan from a snail shell. Fourier transform infrared (FTIR), energy dispersive X-ray (EDAX), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) techniques were used to analyze the adsorbents. Effects of process parameters: pH of wastewater, adsorbent dosage, temperature, initial concentration and contact time were determined. In the blending ratios of the biosorbents, 75% oxalic acid modified chitosan-25% activated plantain peel (CH_T-APP_5) was best blend and the optimum process variables for the removal efficiency were time (60-65mins), adsorbent dosage (2-2.125g/dm^3), pH(6-6.5), initial concentration of wastewater(20-85mg/dm^3) and temperature (308-325K). The results obtained showed that the maximum adsorption capacities of 90.9090, 55.5556 and 142.8571mg/g for Cr(VI) while 62.500, 83.3333 and 43.4783mg/g Cd(II) were obtained for CH_T, APP_1 and CH_T-APP_5 respectively. The results showed that blends have the potential to be used as alternative efficient low-cost biosorbent in the removal of heavy metals from wastewater.

Key word: Adsorption, wastewater, plantain peels, chitosan, sorption parameters

INTRODUCTION

Domestic activities and industrialization are currently having a huge negative impact on the ecological system. Because of their non-biodegradable, bio-accumulative, and toxic properties, heavy metal contamination in effluents has been a source of environmental and public health concern since the beginning of urbanization and industrialization. Waste water is a common by-product of many industrial processes, whether they are petroleum processing industries, pharmaceutical manufacturing, food processing, steel processing, or electroplating plants. The majority of these effluents contain toxic substances, most prominently heavy metals[1]. Wastewater is described as any water that has been negatively affected by human or animal use. Industrial wastewater is traditionally polluted with a variety of organic and inorganic substances such as dye, phenol, suspended solids, dissolved organic compounds, heavy metals, and so on, and it is recommended that the wastewater be treated to an environmentally acceptable limit before use or disposal [2, 3]. The current challenges in industrial wastewater treatment are primarily caused by the increasing pollution of natural bodies such as streams, rivers, underground water, and ponds by organic and heavy metal compounds that are non-biodegradable because these substances resist the self-purification capabilities of rivers and streams as well as physical decomposition in traditional wastewater treatment plants and industries[4]. These heavy metals are becoming increasingly dangerous as environmental pollutants because it takes a long time for the metals to accumulate in the body based on the route from the source of discharge or disposal[5]. If their concentrations exceed acceptable limits, they pose a health risk to humans and aquatic life. According to reports, the metals of environmental concern due to industrial applications and potential pollution impact on the environment are Cr, Zn, Pb Cu, Ar, while Cd, Hg, and Pb top the list of environmental threats because even at low concentrations they can cause brain damage in humans[6]. The recent increase in demand for alkaline Zn manganese batteries rather than mercury-based batteries poses challenges when those batteries are improperly disposed.

Despite the fact that different methods for treating wastewater have been used in the past, such as chlorination, reverse osmosis, alum, oxide of iron, and ion exchange, the expense and health risks associated with chemical use have restricted their acceptability[7]. Activated carbon is a type of amorphous carbon that has been prepared to have a larger surface area for adsorption and chemical reactions. It can be used for water purification, gas purification, decaffeination, food and beverage processing, odor removal, medicine, metal extraction, and air filters in gas masks, among other things. Because of its high degree of micro-porosity and significant large surface area, it is an excellent adsorbent for heavy metals in both liquid and gas. When production factors are taken into account, the use of locally prepared activated carbon from renewable agricultural wastes proves to be more effective than commercially available alternatives. Amuda and Ibrahim[8], on the other hand, compared the adsorption potentials of coconut shell-based activated carbon and the adsorption qualities of commercial carbon on organic pollutants from beverage industrial wastewater. Due to its high well-developed porous structure and large surface area, activated carbon has been reported to have high and fast adsorption potentials.

Snails are gastropod molluscs, belonging to the phylum mollusc and class gastropoda. Snail meat is popular among men because of its high protein content and low cholesterol levels. Demand for snail meat has increased globally as a result of its nutritional value and availability. Snail shells have been used in poultry feed due to their high calcium content[9], but they are also a good source of chitosan. Researchers such as Kaewboonruang *et al*.,[10] and Akpan *et al.*,[11] have reported on the extraction of chitin and chitosan from snail shells.

The aim of this research is to evaluate the reaction indices for the heavy metals uptake from contaminated water using locally sourced agricultural wastes (chitosan and plantain peel-based activated carbon) and their blends.

MATERIALS AND METHODS

Materials

Achatina fulica (Snail shells) used in processing of chitosan and plantain peels used in production of activated carbon were sourced from Auchi, Nigeria. Unless otherwise mentioned, the chemicals used were analytical grade and products of Sigma-Aldrich, Germany.

The precursor samples were washed with tap water before distilled water to remove any dirt, salts, or other impurities. The samples were sundried for four days before being dried for 12 hours at 105°C in an oven. The samples were crushed into smaller pieces with a mortar and pestle before being ground to expand their surface areas. They were sieved to 0.150 mm particle size[12].

Treatment and synthesis of chitosan

Two kilograms of pretreated achatina snail shells were converted into chitosan through deproteinization, demineralization, and deacetylation processes as described by Hosain and Igbal[13]. The yield(Y) of the synthesized chitosan is calculated by:

$$\% \, Chitosan\ yield(Y) = \frac{weight of chitosan(g)}{weight of snail shell(g)} \times \frac{100}{1} \qquad 1$$

Carbonization and activation of Plantain peels were carried as described by Pandhram and Nimbalkar[14].

To enhance the physicochemical and adsorptive properties, the activated plantain peel (APP) was blended with chitosan adsorbent derived from achatina snail in accordance with mixing ratios obtained through an optimization process using an experimental design expert (User defined design expert). For blending, a 200ml of 10% (w/v) oxalic acid solution was combined with 30g of chitosan (CH) at 50°C and 150 rpm for 1 hour to make chitosan-activated plantain peel composites (blends as described by Sharififard *et al.*,[15], and Asokogene *et al.*,[16]. The design of experiment (DOE) format of Chitosan and activated plantain peels was then combined according to Table 1

Table 1: The Design of Experiment (DOE) for blending ratios of Chitosan (CH_T) and activated plantain peels (APP) using User-Defined Design Expert 10.0

Std	Run	Sample Code	Component 1 A:Chitosan (g)	Component 2 B:Activated plantain peel (g)
3	1	APP_1	0.00	100.00
11	2	CH_T-APP_2	25.00	75.00
5	3	CH_T-APP_3	50.00	0.00
8	4	CH_T-APP_4	50.00	100.00
10	5	CH_T-APP_5	75.00	25.00
6	6	CH_T-APP_6	0.00	50.00
15	7	CH_T-APP_7	75.00	50.00
13	8	CH_T-APP_8	50.00	25.00
16	9	CH_T-APP_9	50.00	75.00
9	10	CH_T-APP_{10}	25.00	25.00
14	11	CH_T-APP_{11}	25.00	50.00
12	12	CH_T-APP_{12}	75.00	75.00
7	13	CH_T-APP_{13}	100.00	50.00
17	14	CH_T-APP_{14}	50.00	50.00
2	15	CH_T-APP_{15}	100.00	0.00
4	16	CH_T-APP_{16}	100.00	100.00
1	17	CH_T-APP_{17}	0.00	0.00

The pH, bulk density, surface area, conductivity, water binding power, loss of ignition, moisture content, FT-IR, SEM, XRD, and BET were all used to characterize the adsorbents using standard methods.

X-ray Diffraction Techniques

The mineralogical structures or phases were determined using an X-ray Diffraction (XRD) test. (SHMADZU Model 6000 XRD diffractometer). To obtain the necessary diffractograms, the samples were set and screened between the angles of 2.0 and 65 degrees at a speed of 3.0Deg/min for 21 minutes (Idris, 2015).

FTIR Analysis of chitosan, plantain peels activated carbon and their blends

To characterize the samples, a Fourier transform infrared spectrophotometer (SHIMADZU, Model: IR affinity) was used. The FTIR ranged from 4000 to 400 cm-1, with a resolution of 4 cm-1. 0.20g of the granulated adsorbent sample was encapsulated in 200mg of KBr (sigma)[17].

Scanning Electron Microscopy (SEM)

The surface morphology and texture of chitosan samples were examined using a Karl Zeiss scanning electron microscope (SEM). Before inspection, the sample was spread onto adhesive carbon tape, placed on a metallic disk, and gold-coated. At various magnifications, SEM images were obtained.

Energy dispersive X-ray (EDX) analysis

EDX analysis was performed on the prepared adsorbents to ascertain the elemental compositions of the activated carbon using BRUKER EDX two-dimensional VANTEC-500 detector.

The determination of Surface area by Brunauer-Emmett-Teller (BET) technique

The textural qualities of the samples were measured using a Micromeritics ASAP2010 analyzer (Thermo Scientific, USA). Brunauer-Emmett-Teller (BET) technique for adsorbent materials out gassing was performed on the sample. Moisture and volatiles that might impair the isotherms were removed overnight at 250 ±1 °C in a vacuum.

Preparation of synthetic wastewaters (standard solutions of Cd^{2+} and Cr^{6+})

Aqueous standard solutions of Cd (II) and Cr (VI) were made by dissolving 2.1032g of Cadmium nitrate $Cd(N0_3)_2$ and 2.8298g of potassium dichromate ($K_2Cr_2O_7$) salt in 1liter double-distilled water to obtain a metal ion concentration of 1000mg/l. Appropriate aliquots of these criteria were taken for further dilution to the desired concentration level. pH was adjusted with 0.10mol/1 NaOH and HC1 solutions. By using an Atomic Absorption Spectrometer (AAS) with a copper hallow cathode lamp (1 = 324.8 nm) and acetylene-air as the fuel-oxidant, the total cadmium and chromium concentrations in solution samples were calculated (Idowu, 2015)[33].

The simulated wastewater sample was analyzed using standard methods developed by APHA[18] and Sawyer *et al.,*[19].

The amount of Cd (II) and Cr (VI) adsorbed on the adsorbent was calculated from the difference between the initial concentration and the equilibrium concentration of the ions. The percent metal ion removal efficiency (η) was calculated using the following equation:

$$\eta = 100\frac{(C_i - C_f)}{C_i} \qquad 2$$

Also, the adsorption capacity or the equilibrium adsorption capacity per unit mass of activated carbon q_e (mgg^{-1}) and the removal was calculated by using equation 3 below.

$$q_e = \frac{(C_i - C_e)V}{W} \qquad 3$$

Where, V = volume of the solution in liters (l), W = weight of the adsorbent in grams (g),

C_i and C_f are the initial and equilibrium concentrations of the adsorbate respectively.

The reported value of $Cd^{2+}$and Cr^{6+} ions adsorbed by adsorbents in each test was the average of at least three measurements considering the following factors below.

The Effect of Initial Concentrations of Cd^{2+} and Cr^{6+}solution on the Adsorption

Batch mode adsorption experiments in 100ml flasks were carried out. The following adsorption conditions were used: 0.1g sorbent in 50cm^3 metal ion mixture solution, pH 6.50, and 180 minutes of stirring at 150 rpm. The experiment was conducted at room temperature (27°C) with a simple reciprocating shaker and a 100 cm^3 polythene bottle as the reactor. All metals had working concentrations of 20, 40, 60, 80, 100, and 120 mg/dm^3, respectively. The samples were diluted 10-fold to bring the Cd^{2+} concentrations in the samples within the calibration range of 2 to 10 ppm.

The Effect of temperature on the Adsorption of Cd^{2+} and Cr^{6+}

The sorption capacities and efficiencies of the adsorbents were evaluated at different temperatures in 50cm^3 water sample. The conditions employed to generate sorption thermodynamic values are: pH of 6.5 for all the experiments; sorbent dosage of 0.1g in 50cm^3 solution; metal ion concentration of 20 mg/dm^3, contact time of 180minutes. The temperatures used in these experiments are 15, 25, 35, 45, 60, 75 and 90^{o}C.

The Effect of pH of wastewater on the sorption of heavy metals (Cd^{2+} and Cr^{6+})

Using different pH values of 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 in a solution containing 0.1g of adsorbent at 27^{o}C, the effect of initial pH on the removal efficiency of heavy metal ions (20mg/dm^3) was investigated. To prevent the formation of metal hydroxide complexes, a higher pH value of acidic media was chosen. The contaminant was adsorbed for 180 minutes at 150rpm in a 100 cm^3 flask of 50 cm^3 of wastewater.

The Effect of contact time on the Adsorption of Heavy Metals (Cd^{2+} and Cr^{6+})

Place 0.1g of sorbent in a 50cm^3 metal ion working solution of 20mg/dm^3 to conduct experiments on the dependence of contact time on adsorption. The contact time on adsorption of selected metals was determined using an incubator shaker at a constant speed of 150rpm, pH 6.50, and temperature of 27^{o}C. The contact time on adsorption of selected metals were determined, the employed time were 10, 25, 40, 60, 80, 100 and 120 minutes.

The Effect of Adsorbent Dosage on the Removal of Heavy Metals (Cd^{2+} and Cr^{6+})

The adsorption efficiency of synthesized adsorbents on these selected metals was determined using adsorbent dosages of 0.25, 0.50, 1.0, 1.50, 2.0, 2.5, and 4.0g. Each of these pre-weighed adsorbents was mixed with 50ml of a solution containing 20mg/dm3 of selected heavy metals and agitated for 180 minutes on a stirrer at 150 rpm and room temperature (27^{o}C). By adding 0.1 M HCl and 0.1 M NaOH solutions, the pH of the solutions was adjusted to 6.50. The concentrations of the residual heavy metals were determined by using AAS technique[20].

RESULTS AND DISCUSSION

Results of the Characterization of the snail shell particulate (SSP), chitin (CT), Chitosan (CHT) and Activated Plantain Peels (APP) with their Blends.

From Table 2, the pH values of chitosan (CH) and chemically modified chitosan (CH_T) in slurry were determined to be 11.28 and 10.24 respectively. The results obtained suggest that CH and CH_T have basic surface functional groups. The pH values of chitosan/ activated plantain peels composites are between 6.50 and 9.95. This slight decrease in pH shows the development of acidic groups on the chitosan surface[21]

Table 2: Characterization of the adsorbents and their blends

Adsorbent samples	pH of slurry at 28°C	Bulk density (g/ml)	Surface area (m^2/g)	Loss on ignition (%)	Moisture content (%)	Water binding capacity (%)	Ash content (%)	Conductivity (S/m)	Dry matter (%)
APP_1	7.42	0.32	305.38	68.9	5.24	365.4	2.20	164.5	94.76
CH_T-APP_2	6.50	0.35	ND	68.0	4.73	339.2	2.00	160.0	95.27
CH_T	10.24	0.58	325.38	58.7	1.52	335.6	0.57	144.1	98.48
CH_T-APP_4	6.88	0.37	ND	67.4	4.47	337.4	1.86	158.3	95.53
CH_T-APP_5	8.40	0.56	667.43	59.0	1.51	355.1	0.59	146.2	98.49
APP_1	7.42	0.32	305.38	68.9	5.24	365.4	2.20	164.5	94.76
CH_T-APP_7	7.73	0.51	ND	63.0	1.89	347.2	0.87	151.7	98.11
CH_T-APP_8	9.95	0.50	ND	62.5	3.42	343.5	0.98	148.5	96.58
CH_T-APP_9	9.90	0.48	ND	65.1	3.77	341.8	1.75	155.0	96.23
CH_T-APP_{10}	9.30	0.49	ND	66.2	3.58	338.3	1.35	150.2	96.42
CH_T-APP_{11}	6.85	0.37	ND	67.4	4.47	337.4	1.86	158.3	95.53
CH_T-APP_{12}	7.44	0.49	ND	66.4	3.58	338.5	1.35	150.4	96.42
CH_T-APP_{13}	7.90	0.50	ND	62.5	3.42	343.7	0.98	148.5	96.58
CH_T-APP_{14}	10.05	0.49	ND	66.3	3.58	338.4	1.36	150.4	96.42
CH_T	10.24	0.58	325.38	58.7	1.52	335.6	0.57	144.1	98.48
CH_T-APP_{16}	6.75	0.49	ND	66.4	3.58	338.9	1.38	150.7	96.42
CH_T-APP_{17}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH	11.28	0.58	362.32	62.8	2.11	328.5	0.49	135.9	97.89
CT	8.47	0.54	282.99	59.7	4.18	319.7	0.47	117.8	95.82
PPC	6.85	0.23	251.00	73.6	10.3	279.3	4.80	108.2	91.97
SSP	6.76	1.13	356.34	71.3	8.74	308.9	3.93	117.5	93.26
CC	6.58	0.49	314.18	53.7	1.08	462.5	0.87	310	98.92

ND = Not determined

The bulk densities of plantain peel carbon (PPC) and activated plantain peels (APP_1) were 0.23 g/cm^3 and 0.32 g/cm^3 respectively as shown in Table 2. Also, the bulk densities of chitosan (CH) and chemically modified chitosan (CH_T) were the same, 0.58 g/cm^3. This proved that the modification process has negligible effect on their bulk densities. From Table 2, the PPC has the lowest surface area, 251.00 m^2/g and CH_T-

APP$_5$ has the highest value of 667.43m^2/g. Therefore, CH$_T$-APP$_5$ could be considered the best and highly porous adsorbent. The values of surface area of APP are comparable with those reported for groundnut (arachislypugea) husk by Okieimen and Okieimen, [22].

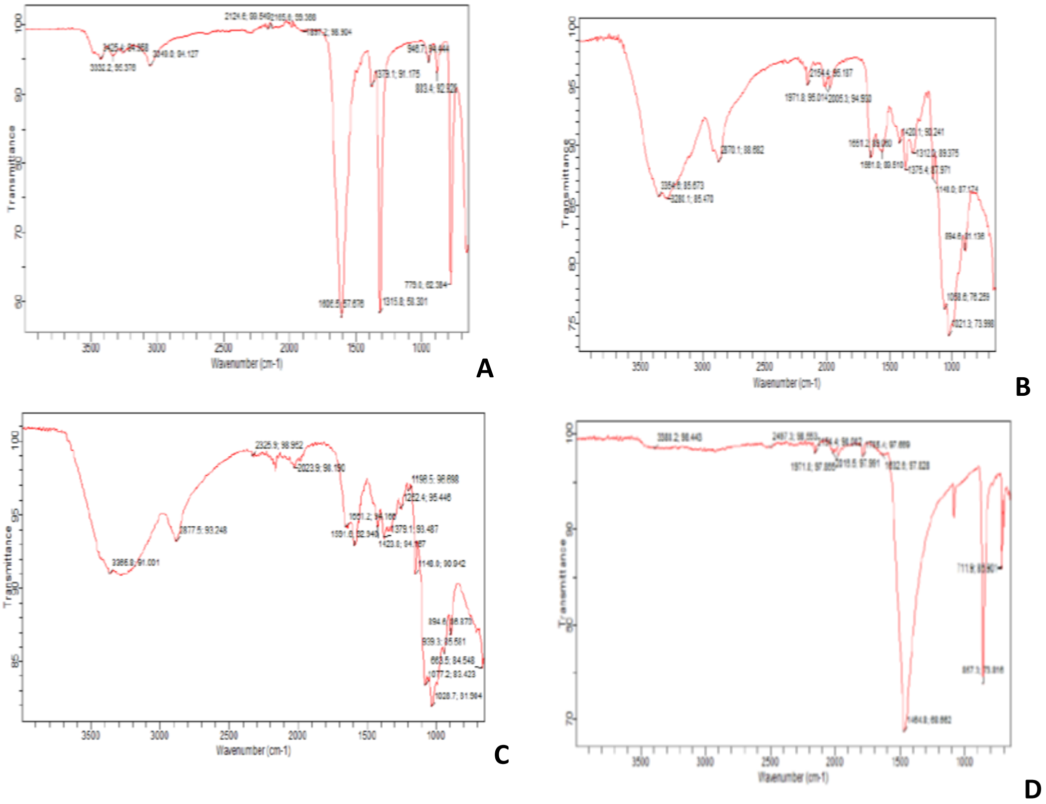
Table 2 shows that PPC is rich in organic matter, accounting for the highest value of loss on ignition 73.60%. This shows that activation process reduced loss on ignition in APP$_1$. Similarly, the modification of chitosan reduced the loss on ignition from 62.80% to 58.70%. The percent moisture of (CH$_T$ 1.52%) is in agreement with 2.81% for chitosan reported by Sambo[23].

From Table 2, the WBC values of the prepared adsorbents were between 279.3% and 365.4% which are agreement with similar studies on modified chitosan which were reported to be in the range of 138 to 492% for chitosan synthesized from fish, crab and shrimp[20, 24]. From Table 2, the percentages of ash content for adsorbents were found to be from 0.47% to 4.80%.

Results of the Fourier Transform Infrared Analysis

The FTIR transmittance spectra of the extracted activated plantain peel (APP$_1$), modified chitosan (CH$_T$), chitosan-activated plantain carbon blend (CH$_T$-APP$_5$), chitosan (CH) and plantain peels carbons (PPC) are shown in Figures 1A-D.

The FTIR spectrum of activated plantain peel, APP$_1$ (Figure 2A-B) shows the major bands assigned to different bonds The FTIR spectra showed the presence of ionisable functional groups that are able to interact with proton or metal ions in the adsorption process, for instance O-H in the range of 3000-3700cm, from 600-1400cm in the fingerprint range C=C, C-O and C=N bonds were suspected. All the hetero-atoms (functional groups) are able to involve in adsorption process via ion exchange mechanism[25]. The FTIR spectrum of modified snail shell chitosan CH$_T$ (Figure 2A-B) shows the major bands assigned to different bonds.



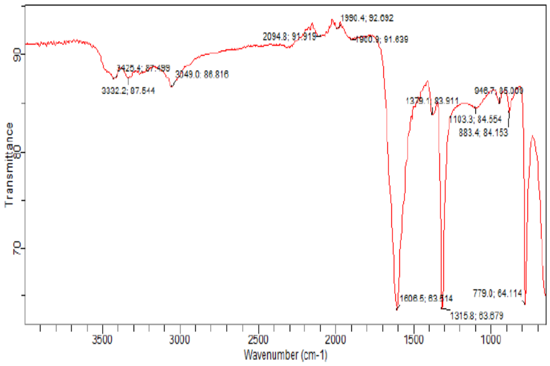


Figure 2C: FTIR transmittance spectrum of modified chitosan-activated plantain peel carbon CH_T-APP_5

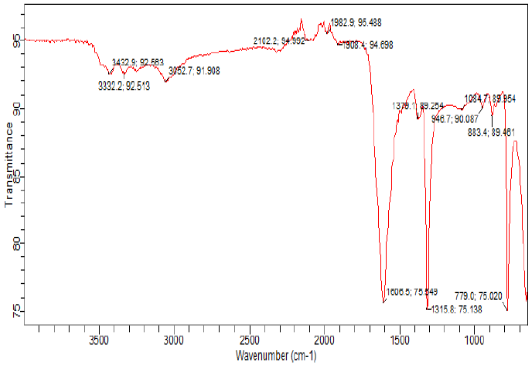


Figure 2D: FTIR transmittance spectrum of CH_T-APP_5 after adsorption

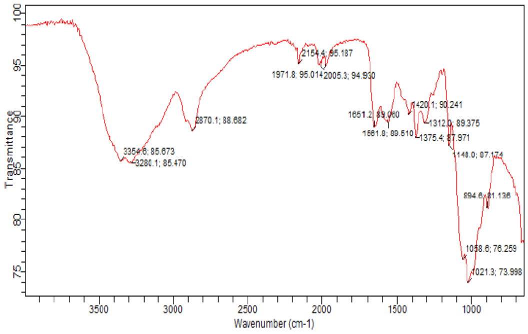


Figure 2A: FTIR transmittance spectrum of modified chitosan CH_T

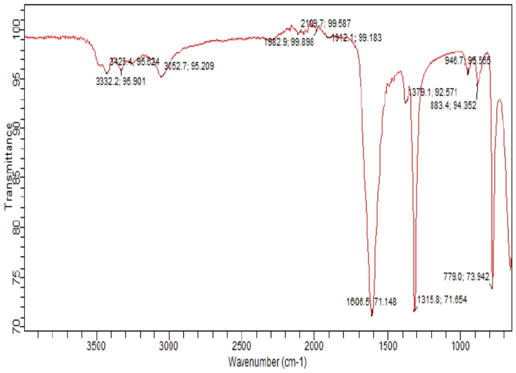


Figure 2B: FTIR transmittance spectrum of modified chitosan CH_T after adsorption

The FTIR spectra of chitosan materials of before and after adsorption are presented in Figure 2A and Figure 2B respectively. The samples show absorption bands in the region of 3425.4 - 3280.1cm^{-1} which corresponds to hydrogen bonded O-H and N-H stretching vibrations primary and secondary amines/amides[20].

The FTIR spectrum of modified chitosan-plantain peel activated carbon CH_T-APP_1 (Figure 2C and 2D) shows the major bands assigned to different bonds

The FTIR spectra of the prepared adsorbent blends materials of before and after adsorption were studied in the range of 4000 to 400cm^{-1}and presented in Figure 2C and Figure 2D respectively. The materials indicate absorption bands in the region of 3425.4 -3332.2cm^{-1} which corresponds to stretching hydrogen bonded O-H and N-H stretching vibrations primary and secondary amines/amides[20, 26]. The FTIR spectrum of plantain peel, PPC (Figure 2E) shows the major bands assigned to different bonds.

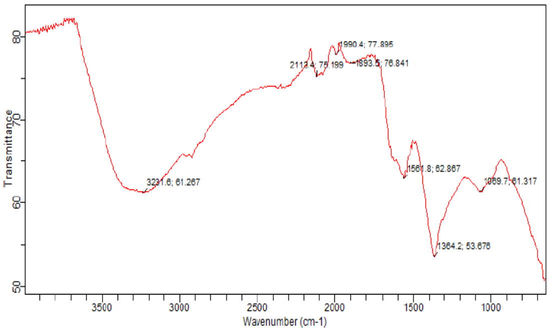


Figure 2E: FTIR transmittance spectrum of plantain peel carbon

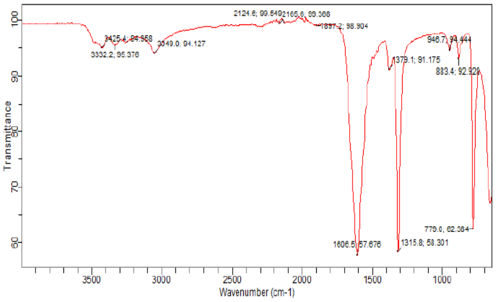


Figure 2F: FTIR transmittance spectrum of chitosan (CH)

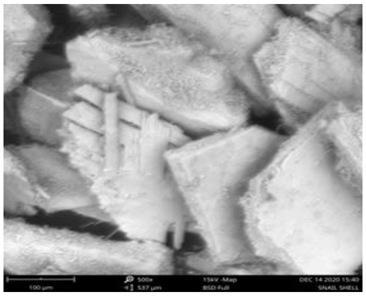
Many chemical functional groups such as alkane, alkyne, amide, carboxylic, alkanol and nitrile are responsible for binding metallic ions to an adsorbent.

Scanning electron microscopy was used to determine the morphologies of the adsorbent surface. Figure 3 shows the SEM images of chitosan material.

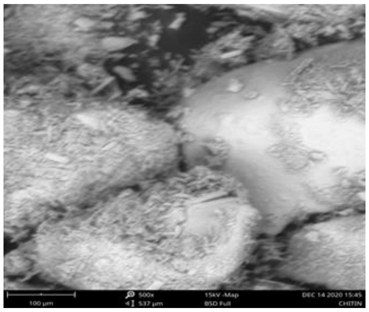
Chitosan (CH) has uneven patterns which could be owing to flakes forming during the synthesis. The internal surfaces of the adsorbents have pores of various sizes, shapes, and fibril structures, while the external surfaces of the adsorbents have pores of various sizes, shapes, and fibril structures. Large numbers of intra-aggregated pores may result from the aggregation of these tiny primary nanoparticles, resulting in a large microporous volume. Tight porous, broken, and fibril structures are also present. The snail shell, chitin and chitosan have well aggregated particles and a less porous look on the surface. Modification of the adsorbents caused the most significant changes. The structure of CH_T is hard and organized, with minor fissures.

The XRD spectrum of APP_1 is shown in Figures 4A-C, the spectrum showed weak and broad peaks which indicated the amorphous nature of the adsorbent. This indicates that metal ions can readily penetrate or adsorb the surface of APP_1 for sorption process

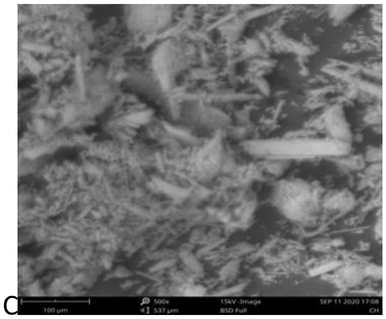
A



B



C



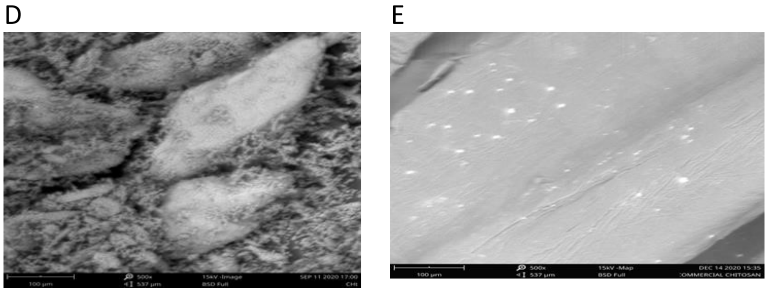


Figure 3: SEM images of snail shell particulate, chitin and chitosan, (A) SSP (B) CT (C) CH (D) CHT (E) CC at 500X magnifications

XRD Analysis of Oxalic Acid Modified Chitosan (CH_T) and Activated Plantain Peels (APP_1)

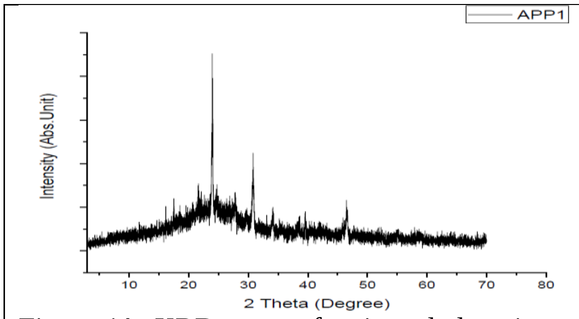


Figure 4A: XRD patter of activated plantain peel carbon (APP_1)

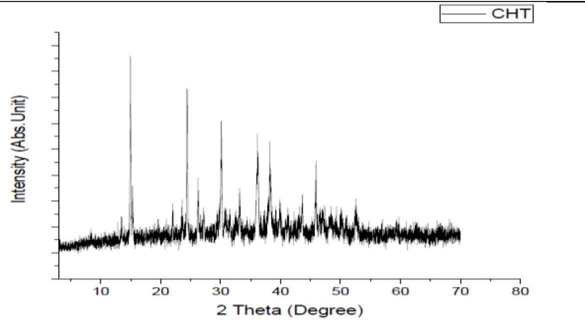


Figure 4B: XRD pattern of oxalic acid modified snail shell chitosan (CH_T)

Results of the Characterization of the Synthesized Wastewater

Table 3: Characterization of the synthesized wastewater

Parameters	**Units**	**Wastewater**	**WHO limits (WHO1973)**	**FEPA limits (FEPA 1991)**
pH	-	6.24±0.02	6.5-8.5	6.0-9.0
Colour	Hazen	Yellowish	Not objectionable	Not objectionable
Temperature	ºC	26.00±0.10	10-30	<40
Odour	-	Slightly offensive	Unobjectionable	Odorless
Turbidity	NTU	24.12±2.00	5.00	5.00
Conductivity	µS/cm	1800.00±5.00	300.00(WHO 2003)	-
TSS	mg/l	34.10±1.00	10.00	30.00
TDS	mg/l	546.50±1.00	500.00	2000.00
TS	mg/l	574.10±0.02	500.00	-
Taste	-	Bad taste	Unobjectionable	Tasteless
BOD	mg/l	9.00±0.00	50.00	10
COD	mg/l	87.00±1.00	10.00	80
DO	mg/l	0.55±0.01	6.00	5.00
Total coliform Cnt	Cfus/ml	NIL	5000	400MNP/100ml
Cd	mg/l	118.60±0.01	0.01	0.05
Cr	mg/l	120.00±0.01	0.05	< 1.00

From Table 3, the pH value of the wastewater was 6.24±0.02. The wastewater produced is slightly acidic, as evidenced by this. The pH levels between 6.0 and 9.0 are considered acceptable for wastewater discharge into the atmosphere (FEPA, 1991. From the results in Table 3, wastewater has a yellowish color similar to the color reported for wastewater obtained from sewage [27]. The temperature of the wastewater was 26.00±0.10°C. This is within the range recommended by WHO[28] (10-30°C). From Table 3, the turbidity value of the wastewater was 24.12±2.00 NTU, which shows that the colloidal materials are slightly high, compared to FEPA value of between 0 to 5.0 NTU; this is an indication of slightly high suspended and colloidal matter.

The electrical conductivity is measure of ability of solution to conduct electrical current. The conductivity value of the wastewater was 1800 ±5.00 µS/cm which shows that it contains ions, an indication that both physical and chemical methods can be employed in the treatment process of the wastewater. The value of the total suspended solids of wastewater was 34.10±1.00 mg/l. The TSS value of the wastewater is higher than FEPA [28] limits of 30.00mg/l which calls for treatment before discharge into the environment. The total dissolved solids (TDS) value of the wastewater is 546.50±1.00mg/l. Waters with high dissolved solids may induce an unfavourable physiological reaction when consumed. The TDS value of the wastewater is within the FEPA[28] limit of 2000mg/l.

The total solids (TS) are the sum of total suspended solids and total dissolved solids (TDS). From Table 3, the total solid (TS) of the wastewater is 574.10±0.02 mg/1. The TS of the wastewater exceeds the FEPA[28] maximum of 30 mg/l, necessitating treatment before discharge into the environment or final treatment for human use. Chemical oxygen demand (COD) is 87.001.00 mg/l, according to Table 4.19. This is significantly higher than the FEPA cap of 80 mg/l[28], indicating that the water has contamination potential and must be properly treated before reuse or discharge[29]. This wastewater has a dissolved oxygen level of 0.55 mg/l. This is lower than the FEPA limit of 5mg/l for drinking water and the WHO limit of 6mg/l for drinking water. The dissolved oxygen concentration in healthy water should be at least 6.5-8 mg/l[30].

There is no biological oxygen demand (BOD) in the wastewater, indicating that no biological materials are present that would reduce the dissolved oxygen in the water.

Heavy metal concentrations in wastewater range from 118.60 to 120.05 mg/l. These values are above FEPA standard limit of less than one (1.0) and therefore require treatment before it can be discharged into the environment or reuse.

From Table 4, the pH values of the treated water improved closer to neutrality. This shows that the interaction of some metal ions in the water has reduced. The results are within the WHO [28] pH limits (6.5 - 8.5) for drinking water; the water turned colorless after treatment similar to the color reported for clean water obtained from borehole[27]. This indicates that the adsorbents are effective in color removal. The temperatures of the water were 26.00 ± 0.20°C as shown in Table 4. These are within the range recommended by WHO [28] (10-30°C). The results of turbidity values show that there were drastic reductions after treatment of the wastewater. This implies that the colloidal substances that were responsible for the turbidity in the wastewater had been reduced. The values of conductivity reduced considerably after treatment implying that there was a reduction in the values of ionic compounds in the water sample.

Table 4: Characterization of the wastewater after treatment with adsorbents

Parameters	Units	Wastewater	Treatment withAPP_1	Treatment withCH_T	Treatment withCH_T-APP_5
pH	-	6.24±0.02	7.20±0.02	7.50±0.01	7.34±0.01
Colour	Hazen	Yellowish	colourless	colourless	Colourless
Temperature	°C	26.00±0.10	26.00±0.10	26.00±0.10	26.00±0.20
Odour	-	Offensive	Odorless	Odorless	Odorless
Turbidity	NTU	24.12±2.00	7.50±0.02	8.90±0.03	8.12±0.01
Conductivity	µS/cm	1800.00	316.00±0.05	275.00±0.01	287.50±0.02
TSS	mg/l	34.10±1.00	6.70±0.01	9.50±0.01	7.85±0.02
TDS	mg/l	546.50±1.00	215.00±0.05	172.00±0.05	185.50±0.02
TS	mg/l	574.10±0.02	224.00±0.03	183.00±0.02	198.30±0.01
Taste	-	Bad taste	Tasteless	Tasteless	Tasteless
BOD	mg/l	9.00±0.00	2.50±0.01	2.00±0.01	2.00±0.02
COD	mg/l	87.00±1.00	9.20±0.01	8.00±0.02	8.50±0.01
DO	mg/l	0.55±0.01	6.50±0.05	6.00±0.01	6.35±0.05
Total coliform Cnt	Cfus/ml	NIL	NIL	NIL	NIL
Cd	mg/l	18.60±0.01	0.096±0.01	0.033±0.01	0.034±0.01
Cr	mg/l	20.00±0.01	0.015±0.02	0.028±0.01	0.021±0.01

From Table 4, the values of total suspended solids (TSS), total dissolved solids (TDS) and total solids (TS) were greatly reduced from their initial values after treatment. These show that there were substantial reductions of the total suspended solids (TSS), total dissolved solids (TDS) and total solids (TS) after treatment with the prepared adsorbents. There was reduction in the value of the chemical oxygen demand (COD). This is an indication that the sorption was efficient in the treatment process as recorded in Table 4. The efficiency of activated carbons is basically as a result of the high surface area and the high surface charge which enhance adsorption and the ability to pick up charged particles from solution[31].

Results of the Effect of Process Variables on Adsorption

Effect of Contact Time on Adsorption Process of Selected Metals

The equilibrium time is an important process variable for heavy metal removal. The Figures 5A-B showed the effect of contact time on the adsorption efficiency of Chromium and cadmium from 10-180 minutes. From the Figure 5A, increase in time increased the removal efficiency of chromium ions very rapidly during first 60minutes with percent adsorption increasing from 57.96-91.82 % for CH_T, 64.12-93.15% for APP_1 and 60.74-94.75% for CH_T-APP_5. Thereafter the rate of chromium removal as the time increased has little or no change. The effect of time on cadmium (Figure 5B) followed the same trend as for chromium. The rates of cadmium removal were very rapid within the first 60minutes, with percent adsorption from 66.15 - 92.82%, 60.25-90.07% for APP_1 and 62.44 to 91.58% for CH_T-APP_5. The optimum adsorptions were established at 60min for CH_T, APP_1, CH_T-APP_5 with Cr^{6+} and Cd^{2+}. The patterns of the curves suggest that the adsorption is time dependent on which adsorption capacity was proportionally related to the time[32].

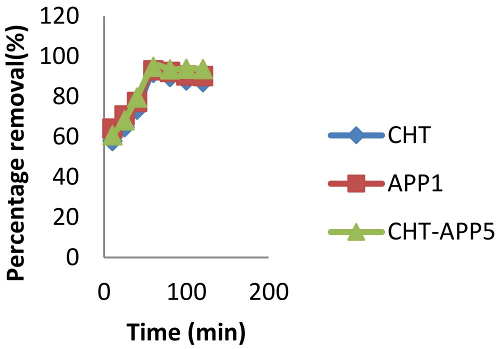


Figure 5A: Effect of contact time on adsorption of Cr^{6+} onto CH_T, APP_1 and CH_T-APP_5

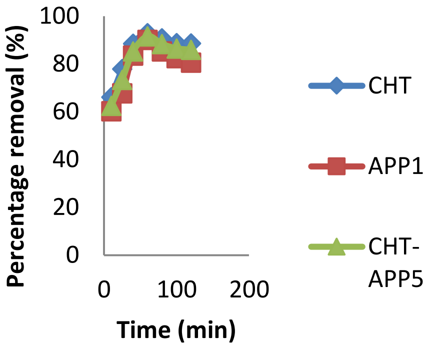


Figure 5B: Effect of contact time on adsorption of Cd^{2+} onto CH_T, APP_1 and CH_T-APP_5

Effect of Adsorbent Dosage on Adsorption Process of Selected Metals

The effect of adsorbent dose was determined between 0.25-4.0g in $1dm^3$ of wastewater at constant temperature of 298K, pH of 6.5, concentration of $20mg/dm^3$ and time of 60mins. From Figures 6A-B, the percent removal of metal ions was found to increase with an increase in the mass of CH_T, APP_1, CH_T-APP_5 owing to the availability of more binding active sites. Highest chromium and cadmium removal on CH_T was at 93.50% and 93.1 %, APP_1 at 94.05% and 91.85% and CH_T-APP_5at 94.85% and 93.88% respectively. Thereafter, the removal of the selected metal ions slightly declined with increasing in mass of adsorbents. Furthermore, significant changes in value of adsorbent dosage (2.50 to 4.00g) yield little or no change in percentage adsorption of the metal ions as shown in Figures 5C-D. This could be due to the conglomeration of active adsorption sites which usually leads to reduced access of adsorbate molecules at high dosage, thereby decreasing adsorption capacity. Also, due to insufficient of active binding site at low adsorbent doses, lower removal was obtained[33].

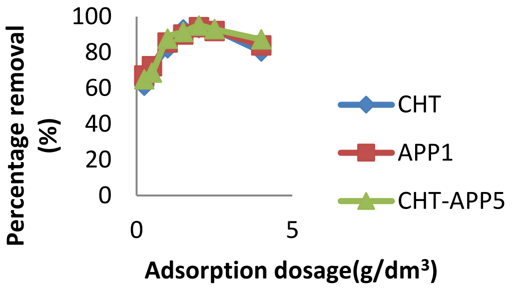


Figure 5C: Effect of adsorbent dosage on adsorption of Cr^{6+} onto CH_T, APP_1 and CH_T-APP_5

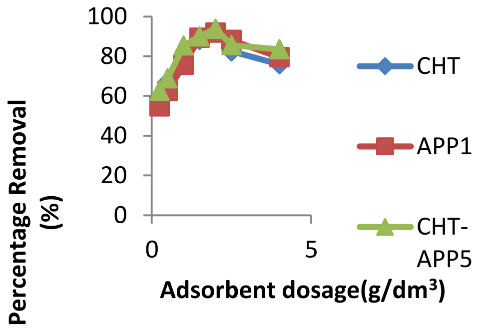


Figure 5D: Effect of adsorbent dosage on adsorption of Cd^{2+} onto CH_T, APP_1 and CH_T-APP_5

Thus, 2.0 g ($0.1\ g/50cm^3$) of composite adsorbents and $20\ mg/dm^3$ of metals (cadmium and chromium) ion concentrations were chosen as optimum conditions for this experiment.

Effect of Initial pH on Adsorption Process of Selected Metals

The results of the pH-dependent experiments are shown in Figures 5E and 5F. The effect of initial pH on chromium and cadmium ion adsorption was investigated at pH ranges 3-11 while maintaining operational parameters (initial metal ion concentration, agitation level, and particle size 150μm). It was observed that the adsorption efficiency of Cr^{6+} and Cd^{2+}onto CH_T, APP_1 and CH_T-APP_5 increased as pH increased until optimum pH value of 6, and then decreased when the pH was increased. This may be as a result of the formation of soluble hydroxyl complexes in the solution. Metal hydrolysis and precipitation usually start at pH > 6 and the competitive sorption between H+ and heavy metals (Cr^{6+} and Cd^{2+}) for active sites on the adsorbent surface[34].

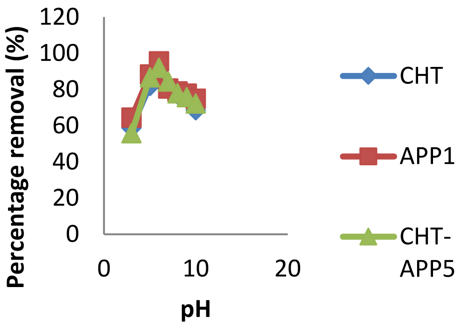


Figure 5E: Effect of pH on adsorption of Cr^{6+} onto CH_T, APP_1 and CH_T-APP_5

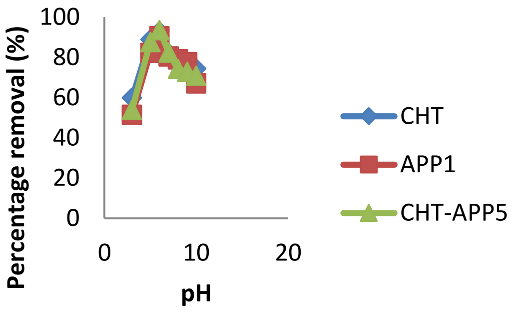


Figure 5F: Effect of pH on adsorption of Cd^{2+} onto CH_T, APP_1 and CH_T-APP_5

Effect of Initial Concentration of Cr^{6+} and Cd^{2+} solution on Adsorption Process

The efficiency of metals absorption by adsorbents strongly depends on the initial metal ion concentration of the wastewater solution. Figure 5G-H represents the effect of initial metal ion concentration of selected metals adsorption. As the initial metal ion concentration increased, the percentage of metal ions removed from the CH_T, APP_1, and CH_T-APP_5 decreased. The relatively reduced number of active sites available on adsorbents may be the cause of the decrease in adsorption performance. The decrease in percentage removal can also be explained by the fact that as the concentration of the adsorbate increases so does the metal loading on the adsorbent[35], while the number of adsorbing sites available for the adsorption is constant for all concentration.

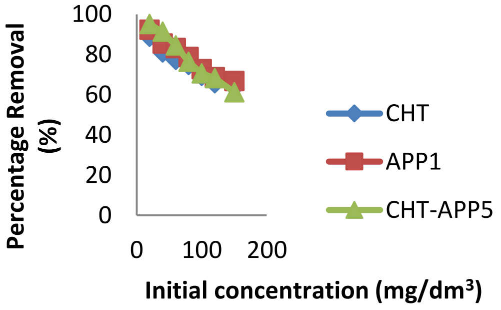


Figure 5G: Effect of initial concentration on adsorption of Cr^{6+} onto CH_T, APP_1 and CH_T-APP_5

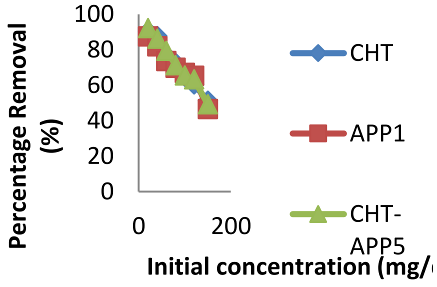


Figure 5H: Effect of initial concentration on adsorption of Cd^{2+} onto CH_T, APP_1 and CH_T-APP_5

Effect of Temperature on Adsorption Process of Selected Metals

At different solution temperatures, the removal efficiency of chromium and cadmium by CH_T, APP_1, and CH_T-APP_5 is shown in Figures 5I and 5J. (20-90ºC). Other process variables such as concentration (20 mg/dm^3), dose (2 g), pH (6), and time (60 minutes) remained constant. The adsorption of heavy metal ions increased slightly with increasing temperature (20-30ºC), but decreased as the temperature rose higher. This indicates that the process of physisorption is endothermic. Because of the reduced viscosity at 298-308K, the metal ions were more mobile and interacted more with the external boundary layer and internal pores, increasing the adsorption performance. However, a further increase in the solution temperature to 363K reduced the adsorptive forces between the adsorbate and the adsorbents which in turn led decreased removal efficiency or even result to desorption[36]. For Cr^{6+} from figure 4.54, with maximum % removal being 92.87, 95.12, and 93.97 for CH_T, APP_1 and CH_T-APP_5 respectively. Similarly for Cd^{2+} from figure 4.55, with maximum percentage removal being 92.52, 91.10, and 89.88 for CH_T, APP_1 and CH_T-APP_5 respectively.

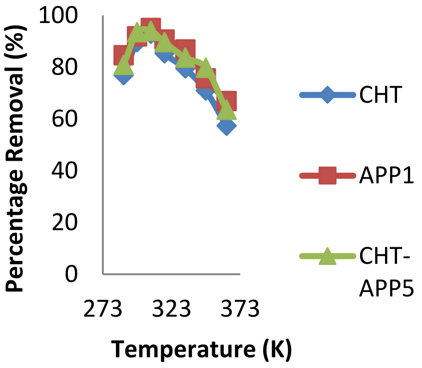


Figure 5I: Effect of temperature on adsorption of Cr^{6+} onto CH_T, APP_1 and CH_T-APP_5

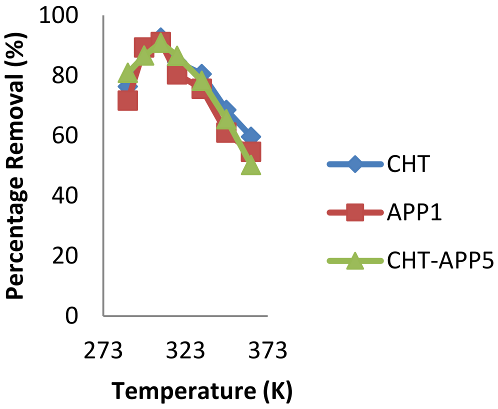


Figure 5J: Effect of temperature on adsorption of Cd^{2+} onto CH_T, APP_1 and CH_T-APP_5

CONCLUSION

The blends of biosorbents were prepared from a *chatina fulica* shell (snail shells) and plantain peels for adsorption of Cr^{6+} and Cd^{2+} ions from a synthetic industrial wastewater. Chemical modification using oxalic acid on chitosan from snail shells and chemical activation using phosphoric acid improved the adsorptive qualities while blending of APP and CH_T further enhanced the characteristics of the adsorbents. In the blending ratios of the biosorbents, 75% oxalic acid modified chitosan-25% activated plantain peel(CH_T-APP_5) was best blend and the optimum process variables for the removal efficiency were time (60-65mins), adsorbent dosage (2-2.125g/dm^3), pH (6-6.5), initial concentration of wastewater(20-85mg/dm^3) and temperature (308-325K). The removal efficiencies of Cr (VI) and Cd(II) ions using the derived adsorbents were effective in the acidic medium. While the composite adsorbent of CH_T-APP_5 exhibited the most effective removal efficiency of both Cr^{6+} and Cd^{2+}, APP_1 showed better removal efficiency of Cr(VI) ions than CH_T and CH_T displayed better removal efficiency of Cd(II) ions than APP_1.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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