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Impact of Ph on Cr (VI) Ions Remediation from Contaminated Water Using Endod Saponin-Chitosan-Zeolite-Metal Oxide Nanocomposite

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Abstract – Contamination of water bodies by heavy metals due to discharge of metal containing effluents into the water bodies is one of the environmental issues. Long term exposure of Cr (VI) levels of over 0.1ppm causes respiratory problems, kidney and liver damage. Sorption has proved to be the most efficient method of removal of toxic heavy metals from wastewater because of easy operation and availability of cheap adsorbents.

This study aimed at removing Cr (VI) ion from contaminated water. Impact of pH was studied in the removal of Cr (VI) ions. The study involved assembling chitosan impregnated with saponin and zeolite. In addition, the oxides and hydroxides of Iron and Aluminum were cross linked in the matrix. Chitosan was the only biopolymer in the matrix. Batch experiments were carried out to investigate the impact of pH. The adsorption of Cr (VI) ions as a function of pH was in the initial pH range of 1 to 8. The results indicated that acidic pH strongly favored the adsorption. The Langmuir model was used as experimental data. The data obeyed the Langmuir model (R^2=0.99) which shows a multilayer adsorption of Cr (VI) onto the heterogeneous surface. FTIR spectroscopy, XRD analysis were done on the adsorbent before Cr (VI) attachment. This study concluded that adsorption of Cr (VI) was pH depended, removal efficiency of the nanocomposite increased with decreasing pH. Maximum removal was at pH 2 where about 1.1ppm was the residual chromium concentration from an initial of 10ppm.

Keywords – Adsorption, Matrix, Nanocomposite, Depended, Efficiency, Contamination.

I. INTRODUCTION

Chromium is extensively used by a number of industries and discharged into the environment through various industrial processes including tanneries, metal finishing, industries plastic processing, mining activities, dyes and pigments, chromate preparation, ceramic paints and fertilizer industries. [1], [2] High concentration of chromium in water may be harmful to the environment [3]. Hexavalent chromium and its compounds are highly toxic and are considered carcinogenic as well as mutagenic [4]. The introduction of these harmful pollutants into water points such as hand dug wells and bore holes in countries like Kenya, where ground water serves as a primary drinking water source [5] and which are commonly used to supplement partial or intermittent piped water coverage in many urban informal settlements in Africa is due to surface runoff during rainy season, leaking sewage lines and septic tanks and careless disposal of industrial waste [5]. Situations are particularly alarming if the water table is high. Kisumu city in Kenya has high water tables, consequently shallow wells are easily contaminated by overflowing pit latrines and

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industrial wastes that is poorly managed and inadequate drainage systems [6], [7]. In the list of complicated environmental pollution problems, pollution of water resources with industrial and sewage effluents ranks high. According to WHO, long term exposure of Cr (VI) levels over 0.1ppm causes respiratory problems, liver and kidney damage and carcinogenicity. The need to treat effluents to reduce Cr (VI) concentration in water and waste water before its transport and cycling cannot be overemphasized [1]. Other effects of chromium (VI) on human health include lung cancer, liver, kidney and gastric damage, the epidermal irritation and sensitization [8]. Most surface water contains 1 to 10 µg/litre of hexavalent chromium. The current guidelines as per WHO value is 0.05mg/L (WHO/SDE/WSH/ 03.04/04).

Various methods used in the removal of chromium from water include reduction, precipitation, ion exchange, solvent extraction among others. these methods are ineffective and require high energy for operation. Adsorption is considered as the most effective and widely used technique due to high removal efficiency simplicity and low cost [9].

A variety of adsorbents have been reported for the removal of hexavalent chromium from water such as activated carbon (AC) [10], [11] chitosan polymer [8], zeolite [9], activated alumina [9], olive, wool, leaves [12], saw dust [13] rice husk, wheat bran [14], bentonite , metal oxides such as ferric hydroxide, Fe [15] ion exchange resin [16], nanostructured adsorbents [14] among others. most of the adsorbents have low adsorption.

II. Materials and Methods

2.1 Materials

Materials included: Chitosan, Zeolite, Saponin, Hydrated Aluminium sulphate ($(Al_2SO_4)_3.18H_2O$). Hydrated Iron (III) Chloride ($FeCl_3.6H_2O$) analytical reagent grade. Potassium dichromate ($k_2Cr_20_7$) analytical grade was used as a source of Cr (VI).

Data Analysis

Data analysis was carried out using origin 8 which was used to draw the curves showing the relationship between pH and hexavalent chromium concentration.

2.2 Method

2.2.1 Preparation of Nanocomposite

The nanocomposite material which consist of aluminiumsulphate, iron oxyhydroxide, chitosan, sodium sulphateunhydrous, saponin and zeolite nanostructures, was synthesised by the hydrolysis of 1.3 g of chitosan which was dissolved in 100 mL of 1%HCl and mixing done using a magnetic stirrer at 400 revolutions per minute (RPM). The mixture was left to incubate for 24 hours and its pH was recorded and it was filtered. 25 mL of chitosan was incubated for 5 mins. 10 mL of 0.5M $Al_2(SO_4)_3 \cdot 18H_2O$ was added to the incubating chitosan and mixing continued for 30 mins. After 30 mins of mixing 7 mL of 1M $FeCl_3.6H_2O$ was added and mixing continued for 30 mins. About 3.6 g Na_2SO_4 was added in one step. The mixture was precipitated and the pH brought to of 6.5 by slow addition of 2M NaOH. The mixture was then left to incubate for 12 hours at ambient temperature. After 12 hours the pH of the mixture was checked and once again adjusted to 6.5 in the event of any fluctuations. Vacuum filtration was carried out in the next step to obtain the gel. The subsequent gel was washed with large amount of water in order to remove soluble salts. This step is essential for the removal of excess soluble salts. The electrical conductivity (EC) of the filtrate was determined and should be conventionally less than 100 μS. The gel was dried at room temperature for 12 hours. Finally, after drying the material was crushed into smaller particles.

2.2.2 Preparation of Cr (VI) Solution

A standard stock solution of 500ppm was prepared by dissolving 0.05g dried K_2CrO_4 in 18.2MΩ- cm de ionized water and diluted to 100ML.

2.2.3 Variation of pH

The pH of the solution is one of the key parameters that determine adsorption capability of an adsorbent material. In this study adsorption of chromium (VI) ion was studied in the pH range of 1, 2, 3,4,5,6, 7 and 8. The pH adjustment was carried out using 0.01M HCl and 0.01 M NaOH. The pH was measured using pH meter.

2.2.4 Adsorption

Adsorption was carried out in a 500mL volumetric flask using a 100ml Cr (VI) ions solution. The flasks were placed on a Gallenkampp Orbital Incubator Shaker running at 100rpm, 30^OC for 10hr. the amount of Cr (VI) adsorbed by the nanocomposite (Q_e).

$$Qe = \frac{co - ce}{w} \quad (1)$$

Where Q_e (mg/g) is the adsorption capacity, C_o (mg/L) is the initial concentration of Cr (VI), C_e (mg/L) is the equilibrium concentration of Cr (VI), W (L) is the volume of the solution of Cr(VI), W (g) is the weight of adsorbent added, and C_o and C_e are initial and final respectively (11-12 A)

2.2.5 Material characterization

The identification of the phase(s) of the prepared sample was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu-Kα radiation at λ = 1.5418 Å. Polychromatic Mg Kα was used as the X-ray source (hv = 1253.6 eV). Binding energy was calibrated with respect to C 1s at 284.5 eV. Total chromium and lead concentrations in water were estimated using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies, 7700x ICP-MS and PerkinElmer NexION 300 ICP-MS). Atomic Force Microscopy (AFM) measurements were done using a Witec GmbH confocal Raman microscope (CRM-Alpha300 S).

III. Results and Discussions

3.1 Effect of pH

The effect of pH on adsorption of Cr ions were studied by varying the pH of the samples from pH 1 pH 8 table 1. While having a constant concentration and mass of the nanocomposite. Adsorption was carried out for a period of 2 hours to ensure that maximum adsorption had taken place. The results are represented in figure 1. Residual concentration of chromium ions were observed to be lowest at pH 2. The residual concentration at pH 1 was 1.3ppm. At pH 4 the residual concentration was 2.0ppm.

Table 1. Initial Cr (VI) concentration, Residual Cr (VI) concentration and concentration of the WHO limits.

pH	Initial Cr(VI) concentration(ppm)	Residual Cr(VI) concentration(ppm)	WHO limit
1	10	1.3	1.5
2	10	1.1	1.5
3	10	1.7	1.5
4	10	2.0	1.5
5	10	2.7	1.5
6	10	3.0	1.5
7	10	3.5	1.5
8	10	3.2	1.5

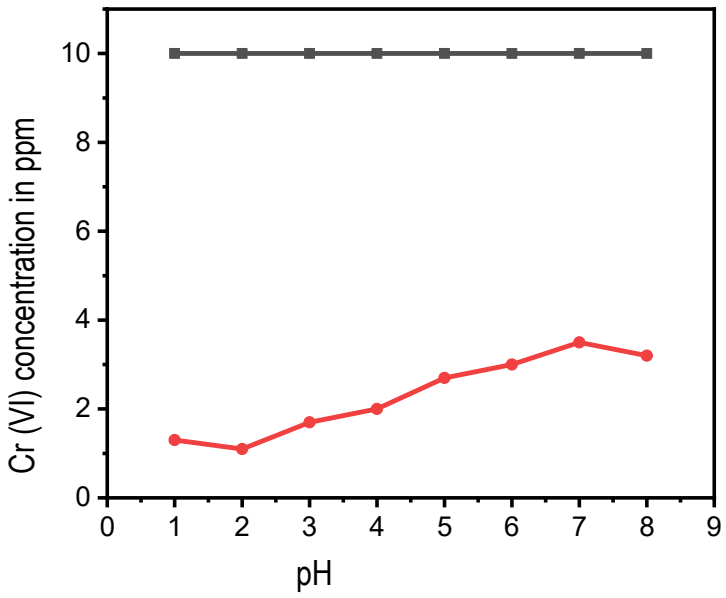

Figure 1. Residual Cr (VI) ions concentration of as a function of pH

3.2 XRD Spectrum

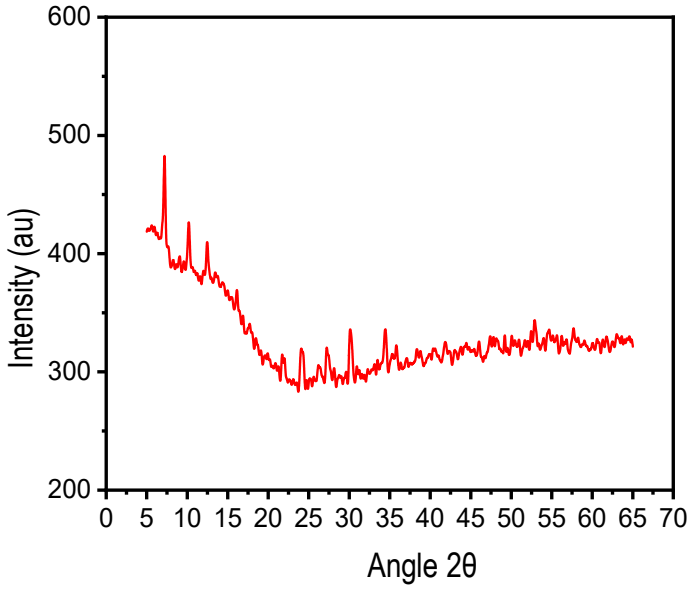

Figure 2. XRD spectra of the nanocomposite

3.3 FTIR Spectrum

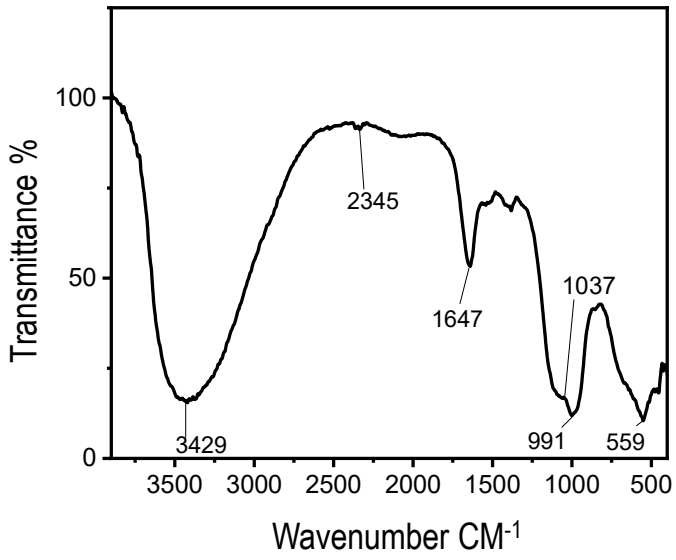

Figure 3. FTIR spectra of the nanocomposite

IV. Discussions

4.1 Effect of pH

The effect of pH on adsorption of Cr (VI) ions were studied by varying the pH of the samples from pH 1 pH 8 as shown in table 1. While having a constant concentration and mass of the nanocomposite. Adsorption was carried out for a period of 2 hours to ensure that maximum adsorption had taken place. The results are represented in figure 1. Residual concentration of chromium ions were observed to be lowest

at pH 2. The residual concentration at pH 1 was 1.3ppm. At pH 4 the residual concentration was 2.0ppm.

The adsorption capacity of the nanocomposite was clearly pH depended. Similar trend is observed by [17]–[19] who proposed the reduction of Cr(VI) to Cr(III) under acidic conditions.

At low pH

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

At moderate pH

$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$

Cr(VI) exists mainly in the soluble form of both $HCrO_4^-$ and $Cr_2O_7^{2-}$ at low pH of 2 to 6.5 [20], [21] and $HCrO_4^-$and $Cr_2O_7^{2-}$ anions account for about 80% and 20% respectively in the pH range of 2-5[22]. Based on these facts, when pH value is low, the positive surface charge would electrostatically attract the Cr (VI) species ($HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}) to enhance adsorption on the nanocomposite.

Further, $Cr_2O_7^{2-}$/ $HCrO_4^-$ anions in water will exchange with numerous hydroxyl groups to promote chemisorption process [23]–[25]and hence greatly improve adsorptive capacity of these adsorbents.

At high pH, the hydrolysis of Cr (VII) is impeded and this could be the reason for low adsorption [1], [26]. At low pH, the high number of H^+ ions, neutralizes the negatively charged exterior of the adsorbent hence increasing diffusion of dichromate ions. It is believed that the impact of pH on adsorption is also controlled by the build out of an electric double layer on the adsorbent. The contrariety of the double layer on the adsorbent exterior may be changed from positive to negative as the H^+ ion concentration changes from acidic to basic with the increase of pH. [1]

At low pH, the system reach equilibrium faster and percentage adsorption enhanced [27]. pH solution plays a critical role during adsorption and impact the surface charge of the nanocomposite, the extent of ionization and speciation of the adsorbate. The pH of the solution affects the solubility of the metal ions, concentration of counter ions, the functional group of the sorbent during the reaction [1].the active site on the sorbent can either be protonated or deprotonated depending on the pH.

4.2 XRD Spectrum

Figure 2 shows the x-ray diffraction patterns for the nanomaterial, it shows 2θ diffraction peaks at 7^0, 10^0, 12^0, 21^0, 24^0, 27^0, 30^0, 34^0, 35^0 and 52^0. It was found that the intensity descends sharply hence crystallinity of the nanocomposite had decreased. This shows that the nanocomposite has good compatibility which leads to the formation of a porous network. The XRD pattern also indicated that the nanocomposite displays an amorphous form which may participate in biocidal applications.

4.3 FTIR Spectra

In the spectrum, a band observed at 3429cm^{-1} is attributed to O-H stretching vibration while the band at 2345 is due to C-H stretching of the – CH_2 group. The bands at 1647cm^{-1} and 1037 cm^{-1} can be ascribed to C-H bending and O-H bending respectively. The weak bonds at 999cm^{-1} are due to the ring stretching and ring deformation of α-D (1-4) and α- α (1-6) linkages. The formation of the amorphous nanocomposite is confirmed from the characteristic peak at 559cm^{-1} with a band at 3440 due to the O-H bonding on the surface. The decrease in the band related to the hydroxyl group in the FTIR spectrum indicate immobilization.

V. Conclusion

This study concluded that adsorption of Cr (VI) was pH depended, removal efficiency of adsorbent increased with decreasing pH. Maximum removal was at pH 2 where about 1.1ppm was the residual chromium concentration from an initial of 10ppm. The study showed that the nanocomposite was effective adsorbent for Cr (VI) metal ions removal from contaminated water.

The nanocomposite was found to be an advantageous adsorbent. Characterization with FTIR and XRD confirmed ability of binding Cr (VI) onto the nanocomposite.

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