

Development of Novel Zirconium/Cobalt/Chromium Electrochemical Nano Composites Sensor for Selected Pollutants in Groundwater

U.P. Ubu^{abc}, P.O. Ukoha^c, J.N. Asegbeloyin^c, M.T. Bankole^{ad}, M.A. Akpe^b, C.O. Ugorji^c, N.A. Usman^a

^aNanotechnology research group, Africa Centre of Excellence for Mycotoxin and food safety, Federal University of Technology, PMB 65, Bosso, Minna, Niger State, Nigeria

^bDepartment of Pure and Applied Chemistry, University of Calabar, P.M.B 1115, Calabar, Cross River State, Nigeria

^cDepartment of Pure and Industrial Chemistry, University of Nigeria, P.M.B 41000, Nsukka, Enugu State, Nigeria

Abstract:- This study focuses on the development of a novel Zirconium/Cobalt/Chromium electrochemical nanocomposite (Zr/Co/CrNC) sensor for selected pollutants in groundwater. The developed Zr/Co/CrNC was prepared through biosynthesis technique using aqueous extract of *Cassia fistula* leaves. The precursor salts were added together with the aqueous plant extract through wet impregnation method. High resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), X-ray Diffraction (XRD), BET, and Zetasizer were used to analyze the produced Zr/Co/CrNC. The HRSEM investigation of the Zr/Co/CrNCs revealed porous, distinct and clear morphology with irregular shapes (cube-like flake, rod-like, hexagonal, triangular, spherical, and icosahedral). The HRTEM micrograph showed different structural morphology with lattice fringes of icosahedral, hexagonal, and spherical shapes. The crystallinity of the nanocomposites was greatly influenced as indicated by SAED patterns and were further investigated by XRD pattern where the results reveals the crystalline nature of the produce Zr/Co/CrNCs Electrode Sensor with high intensity upon modifications. The BET results showed some enhanced surface properties with specific surface area as 276.3 m²/g, pore volume of 0.136 cc/g and pore size of 2.105 nm. Zr/Co/CrNCs Electrode Sensor was used as an Electrode to detect and remove selected heavy metal pollutants in the following order Cd²⁺, Pd²⁺, Ni²⁺ and As³⁺ and (0.8eV<0.6eV<0.5eV<0.3eV) from groundwater. The detection and removal potentials of Zr/Co/CrNCs Electrode Sensor were examining via a batch mode process. The optimum condition based on each parameters was 40 min of contact time, 0.3eV of conductivity, 97° C of temperature with detection of As showing higher removal efficiency compared to other analyzed metal ions. The dynamic light scattering analysis through Zetasizer revealed the Zr/Co/CrNCs size of 46nm. Hence, it can be deduced that aqueous extract of *cassia fistula* act as an efficient reducer and stabilizer for the biochemical synthesis of Zr/Co/CrNC sensor. This study demonstrated that Zr/Co/CrNCs shows exceptional properties which enhanced surface area and adsorptive capacity of the prepared material for the detection and removal of selected heavy metal ion.

Keywords:- Biosynthesis, electrochemical, composites, sensor and groundwater.

I. INTRODUCTION

An anthropogenic activity of man for his comfort is skyrocketing environmental pollution with particular reference to heavy metal pollutants [1]. These toxic pollutants pose serious threat all over the world and the effects ranges from sickness to death [2]. Considering these global issues, there is an urgent need to design and develop a strategic technique with higher efficiency and precision for the detection and removal of these pollutants that are threatening human race. Electrochemical approaches have lately demonstrated a number of benefits in chemical and biological investigation, including high sensitivity, cheap cost, rapid reaction, and ease of use [3]. There has been a growing interest in electrochemical detection of anion in the last decades [4]. The dominant electrochemical sensors are biosensors, mono and binary nanoparticles sensors. Biosensors which are enzyme based have many challenges like fluctuation in responses, ranging from instability in temperature, humidity and pH are factors commonly associated with enzyme-based biosensor [5,6]. It is hard for the transfer of electrons between the electrode and functional flanks of enzymes. More so, the fabrication procedure is complex and has poor stability [7].

The advent of nanotechnology has brought about the development of many nonenzymatic electrochemical sensors with good stability, cost effective, accurate, good selectivity and sensitivity to mitigate the challenges associated with the biosensing technique [8]. Hitherto, several nonenzymatic electrochemical sensors in most literature uses noble metal matrix for their detection (gold, silver, palladium, platinum) [9,10]. Due to these pollutants poisoning and high cost of noble metals and their alloys, they are not ideal for the commercial fabrication of electrochemical sensors [11]. However, transition metals such as Co, Zr, Ti, Cr and Zn have proven to be cost effective and efficient in the development of nano-based sensor materials [12].

Several techniques have been employed in the synthesis procedure of nano-based sensor materials [13]. One of the commonest techniques is solvothermal process which involve annealing at varying temperature [14]. However, these methods generate toxic chemicals in to the environment. The electrochemical activities of binary nickel

cobalt sulphide (NiCoS_4) nanocomposite are more than any single-metal nanoparticles. This is due to the synergistic effect of the multiple valence transition and high electronic conductivity of both Co and Ni [15]. However, there are still limitations in efficiency and precision of binary nanocomposites. Therefore, it is necessary to develop an all-inclusive method that is economical, sustainable and environmentally friendly.

The present study is focused on the development of a ternary electrochemical nanocomposite sensor; a method that offers higher sensitivity and selectivity, a wider detection range, more rapid response space with low cost instrumentations [16]. And Novel Zirconium/Cobalt/Chromium electrochemical nanocomposite sensor, a ternary nonenzymatic electroanalytical technique which detects and removes anionic pollutants as specified is birthed. In addition, (Zr/Co/CrNC) electrochemical sensors can be integrated for the detection of single and multiple pollutants simultaneously. Its thermal properties and large surface area to volume ratio is expected to enhance its long term stability, efficiency and precision.

II. EXPERIMENTAL METHODOLOGY

A. Synthesis of Zr/Co/C Nano Composites

The preparation of Zirconium, cobalt chromium (Zr/Co/Cr) nanocomposite, was done by reducing the salt of Zirconium (IV) Chloride 500g, Chromium Oxide 100g and Cobalt Chloride 500g using plant extract method with slight modification. The mixture of the precursor salts was measured and dispersed in a beaker containing 10ml solution of 0.5g of methylene blue. The resulting mixture was stirred for 40 minutes to obtain a homogeneous mixture. 25ml of the extract of plant was added to the mixture material. In a magnetic stirrer hot plate, the reaction was heated to 60°C and stirred for 5 hours. A dark-brown coloration indicating the formation of Zr/Co/Cr nanocomposites was determined due to the change in colour of the reacting mixture, as the colour of the solution intensifies, in order to avoid agglomeration of the nanocomposites, the solutions were kept in a dark room. The reaction was cooled to room temperature, finally. The resultant solution was kept at room temperature for an overnight period before the supernatant was discarded. Furthermore, the dispersion was washed with water many times in a centrifugation and decant cycle before being cleaned with ethanol. The product was oven dried for 8 hours at 120°C . The nanocomposites were subsequently calcined in a furnace at 450°C for 2 hours to improve material synergy and proof mechanization. Confirmation of zirconium, cobalt and chromium nanoparticle formation by the reduction of Zr^+ from $[\text{Zr}_4(\text{OH})_6]$ to Zr^0 , Co^+ from $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ to Co^0 and Cr^+ from $(\text{CrO}_4)_5(\text{H}_2\text{O})_2\text{Cr}^+$ was checked using UV-Visible spectrophotometer see Figure 3.1

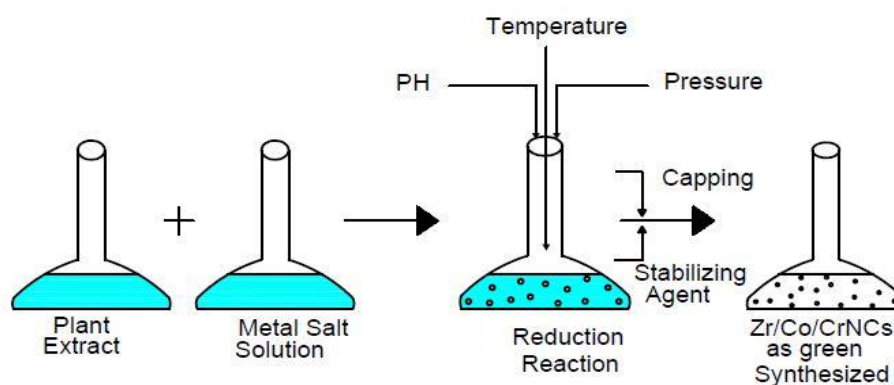


Fig. 1: Green synthesis procedure for Zr/Co/CrNCs

B. Preparation of the Zr/Co/Cr electrochemical nano composite Sensor

First of all, a certain amount of Zr/Co/CrNCs powder was dispersed in a suitable solvent for 15 minutes to form a suspension under the aid of ultrasound.

The next suspension was brushed onto the Zr/Cr/CoNCs tube, whose diameter and length is 1mm and

4mm respectively. The both ends of Zr/Cr/CoNCs electrodes was linked to platinum wire.

Finally, after being dried and aged for 3days, the ascendant sensing properties was tested.

C. Sensing examination of the developed Zr/Co/CrNCs electrode Sensor

All electrochemical analysis was performed in a conventional developed three electrode system containing a platinum wire as a counter electrode, saturated calomel electrode as a reference electrode and the prepared Zr/Co/CrNCs sensor as a working electrode.

The electrochemical response and analytical performance was measured by differential pulse voltammeter (DPV). And the effect such as time, conductivity, sensitivity, selectivity, electro potential difference was determine using differential pulse voltammeter (DPV). And the results were recorded. The procedure for each factor is explained as follows

D. Treatment of selected pollutants in Groundwater (GH₂O) using the Developed Zr/Co/CrNCs Electrode

The electrochemical system of Zr/CoCrNCs sensor developed comprises of the following components; Electrode base-unit, Electrolytic unit, control unit and display unit, Electrode base-unit, this unit is the region where the Zr/Co/Cr electrochemical nanocomposite Sensor (working electrode), the counter electrode and the reference electrode seat.

Electrolytic unit, this unit is designed to house the vessel in which the electrolyte or analyte. Control unit, with the help of this unit, the electrodes in the electrode base-unit moves towards the vessel containing the analyte (GH₂O) and once they are in contact, the electrocatalytic process begins. The process is necessitated by reduction and oxidation in the detection and removal of the target pollutants. Electrons flow from the working electrode to the counter electrode during oxidation, while electrons flow from the counter electrode to the working electrode during reduction. The movement of electrons in either direction generates an electric current flow that is proportional to the groundwater concentration. Which is measured using differential pulse voltammeter (DPV) and result shown in the display unit.

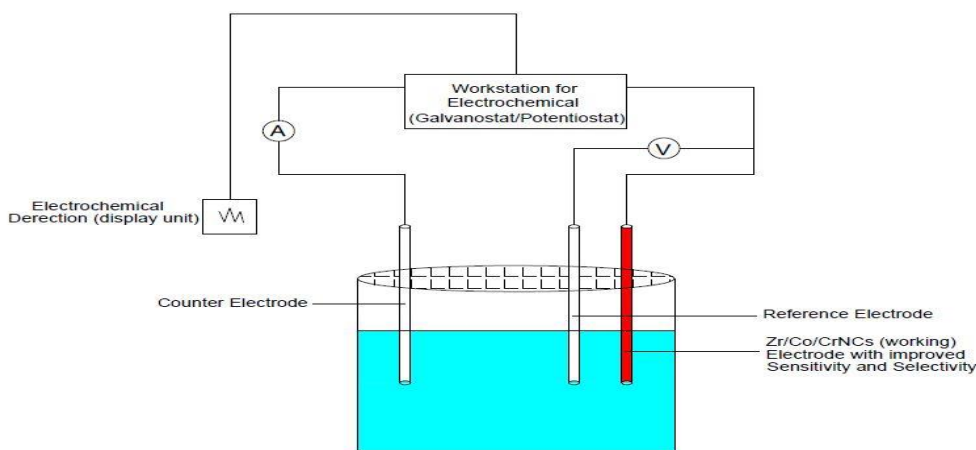
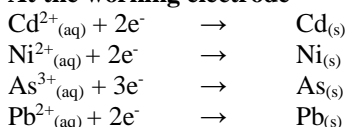


Figure 3.4: A diagram showing electrolytic activities of the developed Zr/Co/CrNCs electrode

Fig. 2: A diagram showing the Electrolytic Activities of the Developed Zr/Co/CrNCS electrode system

At the working electrode



III. RESULTS AND DISCUSSION

A. Morphological determination of Zr/Co/CrNCs nanocomposites

The HRSEM images of as-synthesized Zr/Co/CrNCs is as shown in revealed, as expected, that the Zr/Co/CrNCs are filaments with curve and interwoven web-like structures with shiny tips. The images also indicate a typical tube-like structure with diameters ranging from 15 to 32 nm. As shown in figure 4.1 below.

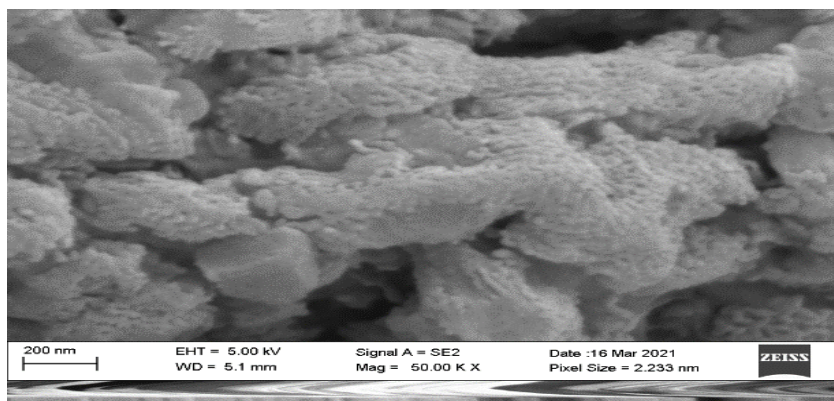


Fig. 3: High Resolution Scanning Electron Microscopy Images of as-Zr/Co/CrNCs

The result of the investigation of as-Zr/Co/CrNCs using HRSEM shown porous, distinct and clear structure with cube-like flake, rod-like, hexagonal, triangular, spherical, and icosahedral shapes. The HRSEM outcomes as shown in

figure 4.1, portrayed that the Zr/Co/CrNCs consist of multiple layers mainly. A linkage of tubular shapes appears in the micrograph of Zr/Co/CrNCs as analysed by HRSEM

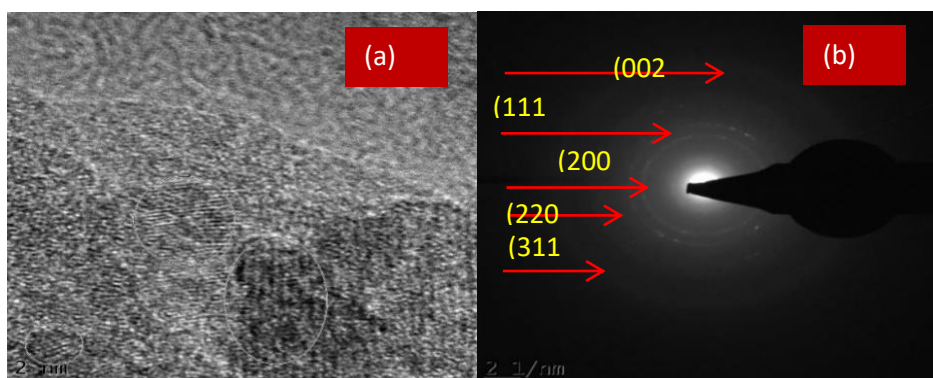


Fig. 4: High Resolution Transmission Electron Microscopy Images of Zr/Co/CrNCs (b) SAED pattern of Zr/Co/CrNCs, Nanocomposites

HRTEM analysis was carried out on the prepared Zr/Co/Cr nanocomposite to investigate the presence of Zr, Co, and Cr nanocomposites in the synthesized Zr/Co/CrNCs. "Different drawing of spherical forms was locked up within the interior chamber of the hollow tubes, and the pore diameter varied from 12 nm (internal diameter) to 32.5 nm (outer diameter)," according to the Zr/Co/CrNCs study. "A decrease in the layer on the outer wall of the Zr/Co/CrNCs electrode induced by tri-metallic Zr^o/Co^o/Cr^o embedment could be a valid explanation for the decreased inner-outer diameter after modification." Furthermore, the dark brilliant area visible when examining the HRTEM image at higher magnification indicates the location on the outer shell of the Zr/Co/CrNCs electrode surface where both metallic nanocomposites were concentrated (Hetero-junction). "The SAED pattern represented in figure 4.2b

indicates varying concentric rings which further established the graphitic nature of the Zr/Co/Cr-MMNC and the chief development in the order of crystallinity of the Zr/Co/Cr electrode nanocomposites". After immobilization with metallic nanocomposites thus, implying that the produced nanocomposite is polycrystalline in nature.

XRD Analysis of the as-synthesized Zr/Co/CrNCs nanocomposites, to validate the crystalline nature of the produced Zr/Co/CrNCs composites, powdered X-ray diffraction techniques were used to characterize them. The diffractogram of the Zr/Co/Cr nanocomposites as shown in figure 4.2 reveals the X-ray pattern of Zr/Co/CrNCs Composites. The appearance of peaks at 111, 113 and 011 corresponding with planes at 18.90°, 42° and 30° confirms the presence of Co, Cr and Zr Structure with 2D

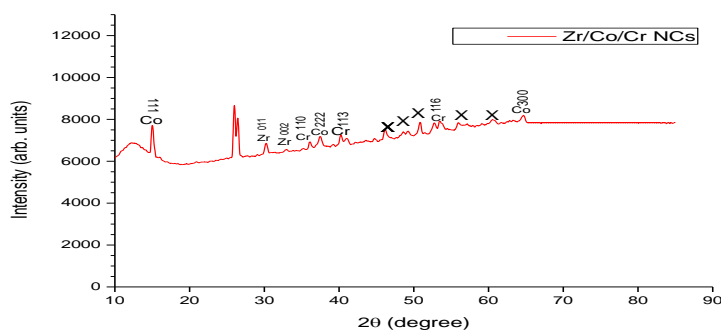


Fig. 5: X-ray Diffraction Pattern of Synthesized Zr/Co/Cr NCs

In addition, the diffraction pattern of Zr/Co/Cr NCs composites shows some further reflection angles at 2 values of 27.6°, 46°, 47.6°, 50.1°, and 57.2° that are indexed to (X). "These diffraction angles are most likely due to secondary metabolites contained in the plant extract used in biological Zr, Co, and Cr nanocomposite syntheses" [17]. On Zr/Co/Cr NCs composites, the Co (222), Cr (300), and Zr (002) peaks continue to rise. At 2 values of 61 °C and 38.54 °C, there is a minor shift in plane of Zr (121), Cr (110), and (116). The discrepancy in the ionic radii of the Zr, Co, and Cr ions is blamed for the crystal plane shift. Zr and Co ions have larger ionic radii than Cr ions (Zr: 0.80, Co: 0.65, and Cr: 0.62). The dopants (Zr, Co, and Cr nanocomposites) can thus be placed as interstitial atoms within the Zr/Co/Cr NCs

lattices. "This implies that the lattice parameters' placement varies, which effects the difference in ionic radii of the elements involved" [18]. The changes in the lattice planes could be due to this. It also suggests that in the impregnated on Zr/Co/Cr nanocomposite, both Zr, Co, and Cr have a synergistic impact.

The BET study provides a deeper understanding of the textural features of the synthesized Zr/Co/Cr NCs electrode materials, particularly their specific surface area, pore volume, and pore size distribution. Figure 4.3 shows the findings of the BET N₂ adsorption-desorption isotherm used to characterize the samples.

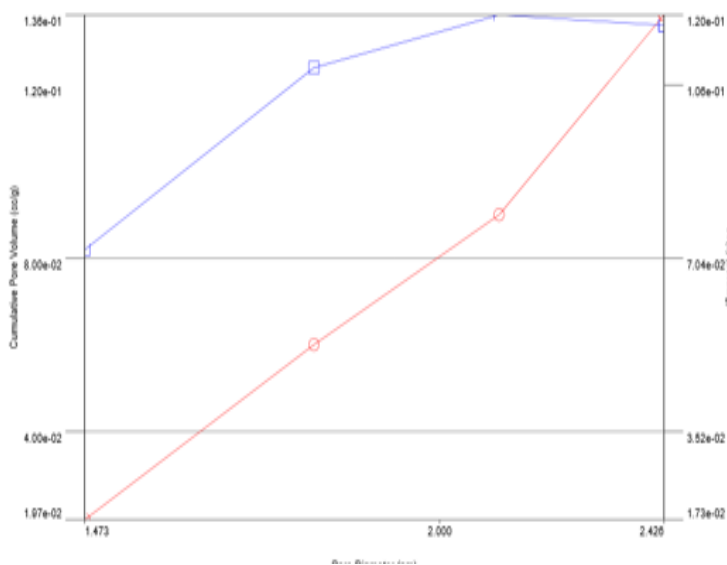


Fig. 6: Showing BET analysis of as-Zr/Co/Cr NCs

Figure 6 shows that the nanocomposites' pore size is 2.105 nm, which is within the 2-50 nm range defined by the International Union of Pure and Applied Chemistry (IUPAC). As a result, the produced nanocomposites in this work have a pore size that indicates they are mesoporous in nature. "Materials with pore sizes less than 2 nm are microporous, materials between 2 and 50 nm are mesoporous, and materials bigger than 50 nm are

macroporous in nature, according to IUPAC classification" [19,20]

"The increased pore size of the nanocomposites promotes the performance efficiency of the adsorbent materials, which allows charge transport during charge and discharge" [21].

IV. TREATMENT OF GROUNDWATER

Analysis of Selected Heavy Metals and Anionic Pollutants in Groundwater, based on the results of the

physicochemical analysis of the raw and treated groundwater, the Zr/Co/CrNCs sensor was chosen based on the removal of selected heavy metals.

S/N	Heavy metals	Raw sample	Treatment using Zr/Co/CrNCs sensor	Standard Limit WHO(2017)/EPA (2018) NIS (2007)
1	Cadmium(mg/L)	1.143±0.27	0.253±0.12	1.00
2	Nickel(mg/L)	0.979±0.36	0.010±0.06	0.5
3	Arsenic(mg/L)	0.747±0.28	0.114±0.09	0.3
4	Lead(mg/L)	0.423±0.21	0.102±0.103	1.0

Table 7: **4.1:** Mean Concentration of Selected Heavy Metals and Anionic pollutants (Cd^{2+} , Ni^{2+} , As^{2+} , Pb^{2+} in groundwater (before and after treatment Study) and Standard Limit

Table 4.5 shows the results of heavy metal ions tested from raw and treated GH_2O , along with WHO, EPA, and NIS guideline limits. This implies that the cadmium concentration was higher than the recommended levels. Cadmium concentrations in GH_2O was 1.143 mg/L before treatment with the Zr/Co/CrNCs electrode, and was reduced to 0.253 mg/L after treatment with the Zr/Co/CrNCs electrode. The Zr/Co/CrNCs electrode achieved a removal effectiveness of 77.86%, according to this study.

The Nickel concentration of the groundwater was 0.979 mg/L in the current investigation, respectively, and after treatment with the Zr/Co/CrNCs electrode, the value was 0.010 mg/L. "It was discovered that the electrochemical nanocomposites electrode eliminated approximately 99.84 percent of Ni from the groundwater samples, meeting the USEPA's maximum mandated level of 0.02 mg/L in 2018." Arsenic (As) is a necessary component for animal growth [22]. It's a dietary supplement that's utilized to boost physiological effects like blood pressure, organ weight, and nutritional status. When used for irrigation, however, its presence in excess in groundwater might lead to a build-up in plant species. This can have a negative impact on plant growth as well as the food chain. Arsenic in water is safe to consume at concentrations of 0.4-1 mg/kg of body weight per day, according to the USEPA [23]. Table 4.5 shows that before treatment, As concentrations was 0.747 mg/L, but after treatment with the designed Zr/Co/CrNCs electrode, As concentrations became 0.114 mg/L with an 88.36 percent removal efficiency. These findings show that the developed Zr/Co/CrNCs electrode was able to reduce As concentrations to levels below the WHO/0.5 EPA's mg/L standard limit.

"Although humans can manage relatively large amounts of lead (Pb), acute exposure can induce a variety of health problems, including diarrhoea, nausea, vascular injury, vomiting, and anemia, to name a few." As a result, these issues may lead to life-threatening diseases. It's worth noting that the Lead (Pb) post-treatment result demonstrates that it's acceptable for reuse because it's below the allowable limit of 1 mg/L. (see Table 5).

The choice of Zr/Co/CrNCs electrode for batch detection and removal experiments of specified heavy metal ions was based on the removal efficiency derived from the physicochemical data.

Analytical Performance of the Zr/Co/CrNCs Sensor

As demonstrated in fig. 4.4, the analytical performance of the Zr/Co/CrNCs Sensor was examined with various concentrations of groundwater under optimization conditions. The heavy metal pollutants were detected and removed in the following sequence, CdNiAsPb, according to the differential pulse voltammeter in the voltogram obtained in figure 4.5.1, at Zr/Co/CrNCs electrode in the presence of 1M concentration of NaCl in groundwater. This curve relates to the oxidation current of CdNiAsPb that may be measured. From 0.3eV to 0.8VeV, the Zr/Co/CrNCs Sensor signals dropped as the concentration of selected inorganic contaminants increased. As shown in figure 4.4, the Zr/Co/CrNCs Sensor has a better detection limit and linear range than prior efforts. This suggests that this method is extremely sensitive and has a lot of promise for detecting specific heavy metal pollutants in groundwater(GH_2O).

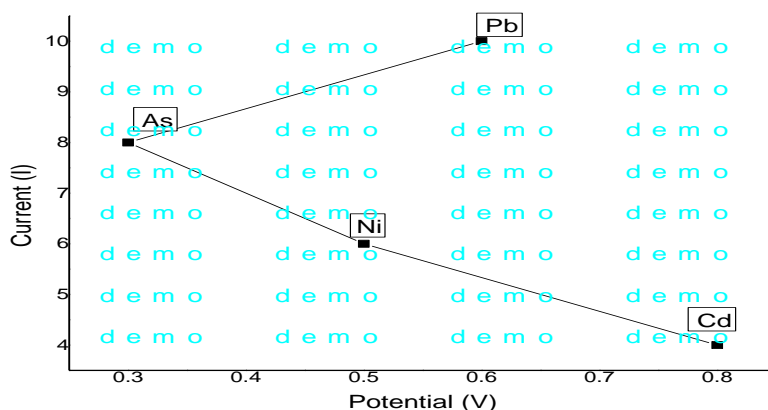


Fig. 8: 4.4: Removal of Metal pollutants detection by Zr/Co/CrNCs Nanocomposites on contact current

Additionally, in the detection and removal of (Cd^{2+} , Ni^{2+} , As^{2+} , Pb^{2+}) pollutants in groundwater in batches. The influence of various parameters on the detection (adsorption) effectiveness of the produced Zr/Co/CrNCs sensor for the removal of selected inorganic contaminants (Cd^{2+} , Ni^{2+} , As^{3+} , Pb^{2+}) from groundwater has been studied.

Figure 8 shows the results obtained with respect to each adsorption characteristic using the Zr/Co/CrNCs sensor, including conductivity, sensitivity, and selectivity. As a result, metals with smaller atomic radius would reach the surface binding site faster than those with bigger atomic radius.

S/N	Electrodes	Technique	Electrolyte pH	Sensitivity $\mu A/ppb-1$	LDR	LOD	REF
1	AuNPs/CeO ₂ -ZrO ₂ /GCE	SWASV	HAc-NaAc (pH 8.0, 0.1)	0.976	0.5-15	0.137	[24]
2	CoOxNPs/GCE	CV	PBS(pH7.0)	0.0015	0-3750	0.825	[25]
3	Electrode of Gold micowire	ASC	0.1M+0.01M NaCl(pH8.5)	0.0011	0.75-75	0.015	[26]
4	MEA-Au Electrode	DPASV	PBS(pH7.0)	0.0643	0.2-12	0.02	[27]
5	Au-IrM	SWASV	0.01MNaNO ₃	0.0026	0.75-3.75	0.075	[28]
6	ZrO ₂ /Nafion/Au electrode	Chronoamperometry	0.1MPS(pH7.4)	0.011	5-60	5	[29]
7	FePtNPs	SWV	0.01M PBS (pH7.0)	0.42	1-5	0.8	[30]
8	Zr/Co/CrNCs Electrode	DPV	GH ₂ O (pH7.0)	0.003	0.5-15	0.05	This study

Table 4.6: Comparison of the Analytical performance of the Zr/Co/CrNCs Electrode with Others Reported in Literature

For numerous electrochemical electrode nanomaterials systems, many researchers have reported the detection and removal capability of the examined metal ions. However, there is little or no research that discusses the Zr/Co/CrNCs electrode's ability to detect and remove the selected contaminants (Cd, Ni, As, and Pb) ions. "As a result, a direct comparison of the literature data with the current study may result in significant ambiguity because electrodes from the literature data have different structural properties (that is, different surface area, functional group, and experimental factors such as pH, temperature, and concentrations, among others)" Sargazi and colleagues [31]. "Cu and Ni detection capacities onto nanokaolinite are 0.76eV (Cd^{2+}) and 0.5eV (Ni^{2+}), respectively." [32]. The same metal ions found on the Zr/Co/CrNCs electrode have a similar value. 0.8 eV, 0.5 eV, 0.3 eV, and 0.6 eV are the detection capacities. It was discovered that Cd ion has a better detection capacity than other ions. Other metal ions' low detection capabilities may be linked to their larger concentration prior to treatment.

This could explain why they are removed from groundwater at a lower rate than the former (Cd ion).

B. Application of developed Zr/Co/CrNCs Sensor

The practical usefulness of the proposed Zr/Co/CrNCs Sensor was investigated by employing a conventional addition method to detect specified inorganic contaminants in groundwater (GH₂O) samples. Figure 4.5 shows that the recoveries ranged from 99 to 105 percent, confirming the applicability of the proposed Zr/Co/CrNCs Sensor for the detection of specified inorganic contaminants in groundwater (GH₂O) samples.

V. CONCLUSION

It was effectively designed and produced an electrochemical nanocomposite sensor measuring technology for the detection and removal of chosen contaminants. The discovered Zr/Co/CrNC was made using aqueous extract of Cassia fistula leaves and a green synthesis process. High resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), X-ray Diffraction (XRD), BET, and Zetasizer were used to analyze the produced Zr/Co/CrNC. The porous, distinct, and obvious morphology of the Zr/Co/CrNCs shown by HRSEM exhibited irregular forms (cube-like flake, rod-like, hexagonal, triangular, spherical, and icosahedral). The HRTEM image revealed a variety of structural morphologies, including icosahedral, hexagonal, and spherical lattice fringes. The crystallinity of the nanocomposites was considerably changed, as shown by SAED patterns, and was further explored by XRD patterns, which revealed the crystalline nature of the manufactured Zr/Co/CrNCs Electrode Sensor with high intensity after changes. With a specific surface area of 276.3 m²/g, pore volume of 0.136 cc/g, and pore size of 2.105 nm, the BET results revealed improved surface characteristics. The Zr/Co/CrNCs Electrode Sensor was used to detect and remove selected heavy metal contaminants from groundwater in the following order: Cd²⁺, Pd²⁺, Ni²⁺, and As³⁺ (0.8eV 0.6eV 0.5eV 0.3eV). A batch mode process was used to investigate the detection and removal potentials of the Zr/Co/CrNCs Electrode Sensor. The best setting based on each parameter was 40 minutes of contact time, 0.3eV of conductivity, and 97 °C of temperature, with detection of As demonstrating a better removal effectiveness than the other metal ions studied. Zetasizer's dynamic light scattering research found a Zr/Co/CrNC size of 46nm. As a result, it can be concluded that cassia fistula aqueous extract acts as an effective reducer and stabilizer in the biochemical synthesis of Zr/Co/CrNC sensor. This research found that Zr/Co/CrNCs have outstanding features that increase the surface area and adsorptive ability of the produced material for heavy metal ion detection and removal. The synthesized Zr/Co/CrNCs were used as a working electrode in a three-electrode system that included a platinum wire as a counter electrode, a saturated calomel electrode as a reference electrode, and a platinum wire as a counter electrode. A differential pulse voltammeter was used to measure the electrochemical response (DPV). The created Zr/Co/Cr nanocomposite has a high sensitivity, low potential, and long-term stability for detecting CdNiAsPb in groundwater, making it a suitable approach for non-enzymatic sensor development.

REFERENCES

- [1.] Sohni, S., Nidaullah, H., Gul, K., Ahmad, I., & Omar, A. M. (2018). Nanotechnology for Safe and Sustainable Environment: Realm of Wonders. *Khan, SB, Asiri, AM and Akhtar, K.(2018), Nanomaterials and their Fascinating Attributes–Development and Prospective Applications of Nanoscience and Nanotechnology*, 2, 37-117.
- [2.] Madhav, S., Ahamad, A., Singh, A. K., Kushawaha, J., Chauhan, J. S., Sharma, S., & Singh, P. (2020). Water pollutants: sources and impact on the environment and human health. In *Sensors in Water Pollutants Monitoring: Role of Material* (pp. 43-62). Springer, Singapore.
- [3.] Zhang, Y. N., Niu, Q., Gu, X., Yang, N., & Zhao, G. (2019). Recent progress on carbon nanomaterials for the electrochemical detection and removal of environmental pollutants. *Nanoscale*, 11(25), 11992-12014.
- [4.] Hein, R., Beer, P. D., & Davis, J. J. (2020). Electrochemical anion sensing: supramolecular approaches. *Chemical reviews*, 120(3), 1888-1935.
- [5.] Xu, X., Niu, X., Li, X., Li, Z., Du, D., & Lin, Y. (2020). Nanomaterial-based sensors and biosensors for enhanced inorganic arsenic detection: a functional perspective. *Sensors and Actuators B: Chemical*, 315, 128100.
- [6.] Mathew, M., Radhakrishnan, S., Vaidyanathan, A., Chakraborty, B., & Rout, C. S. (2020). Flexible and wearable electrochemical biosensors based on two-dimensional materials: Recent developments. *Analytical and Bioanalytical Chemistry*, 1-36.
- [7.] Matthews, C. J., Andrews, E. S., & Patrick, W. M. (2021). Enzyme-based amperometric biosensors for malic acid—a review. *Analytica Chimica Acta*, 338218.
- [8.] Rhouati, A., Majdinasab, M., & Hayat, A. (2018). A perspective on non-enzymatic electrochemical nanosensors for direct detection of pesticides. *Current Opinion in Electrochemistry*, 11, 12-18.
- [9.] Rhouati, A., Majdinasab, M., & Hayat, A. (2018). A perspective on non-enzymatic electrochemical nanosensors for direct detection of pesticides. *Current Opinion in Electrochemistry*, 11, 12-18.
- [10.] Dong, Q., Ryu, H., & Lei, Y. (2021). Metal oxide based non-enzymatic electrochemical sensors for glucose detection. *Electrochimica Acta*, 137744.
- [11.] Lu, L. (2019). Nanoporous noble metal-based alloys: A review on synthesis and applications to electrocatalysis and electrochemical sensing. *Microchimica Acta*, 186(9), 1-21.
- [12.] Elgarahy, A. M., Elwakeel, K. Z., Akhdhar, A., & Hamza, M. F. (2021). Recent advances in green synthesized nanoengineered materials for water/wastewater remediation: an overview. *Nanotechnology for Environmental Engineering*, 6(1), 1-24.
- [13.] Zappa, D., Galstyan, V., Kaur, N., Arachchige, H. M. M., Sisman, O., & Comini, E. (2018). "Metal oxide-based heterostructures for gas sensors"—A review. *Analytica Chimica Acta*, 1039, 1-23.

- [14.] Lian, X., & Yan, B. (2019). A dual-functional bimetallic-organic framework nanosensor for detection and decontamination of lachrymator in drinking water. *Sensors and Actuators B: Chemical*, 281, 168-174.
- [15.] He, X., Bi, T., Zheng, X., Zhu, W., & Jiang, J. (2020). Nickel cobalt sulfide nanoparticles grown on titanium carbide MXenes for high-performance supercapacitor. *Electrochimica Acta*, 332, 135514.
- [16.] Madhuvilakku, R., Alagar, S., Mariappan, R., & Piraman, S. (2020). Glassy carbon electrodes modified with reduced graphene oxide-MoS₂-poly (3, 4-ethylene dioxathiophene) nanocomposites for the non-enzymatic detection of nitrite in water and milk. *Analytica chimica acta*, 1093, 93-105.
- [17.] Shakeel, M., Ahsan, N., Ahmed, S., & Khan, N. A. (2021). Groundwater contamination and health risk posed by industrial effluent in NCR region. *Materials Today: Proceedings*.
- [18.] Ahmad, S. A., Khan, M. H., & Haque, M. (2018). Arsenic contamination in groundwater in Bangladesh: implications and challenges for healthcare policy. *Risk management and healthcare policy*, 11, 251.
- [19.] Sharma, M. (2021). Pesticide Residues in Drinking Water and Cattle Milk. High Time to find an alternative to Chlorinated Hydrocarbons. *Journal of Innovative Research in Clinical & Medical Sciences-ISSN, 2456, 7736*.
- [20.] Thangaswamy, S. J. K., Mir, M. A., & Muthu, A. (2021). Green synthesis of mono and bimetallic alloy nanoparticles of gold and silver using aqueous extract of Chlorella acidophile for potential applications in sensors. *Preparative Biochemistry & Biotechnology*, 1-10.] Thangaswamy, S. J. K., Mir, M. A., & Muthu, A. (2021). Green synthesis of mono and bimetallic alloy nanoparticles of gold and silver using aqueous extract of Chlorella acidophile for potential applications in sensors. *Preparative Biochemistry & Biotechnology*, 1-10.
- [21.] Chen, T., Foo, C., & Tsang, S. C. E. (2021). Interstitial and substitutional light elements in transition metals for heterogeneous catalysis. *Chemical Science*, 12(2), 517-532.
- [22.] Fletcher, A. J. (2008). Porosity and sorption behaviour. Adsorption.
- [23.] Moosavi, A., Amooey, A. A. & Marzbali, M. H. (2020). Extraordinary adsorption of acidic fuchsin and malachite green onto cheap nano-adsorbent derived from eggshell. *Chinese Journal of Chemical Engineering*, 28(6), 1591-1602.
- [24.] Li, L., Gao, P., Gai, S., He, F., Chen, Y., Zhang, M. & Yang, P. (2016). Ultra small and highly dispersed Fe₃O₄ nanoparticles anchored on reduced graphene for supercapacitor application. *Electrochimica Acta*, 190, 566-573.
- [25.] Llorens, J. V., Soriano, S., Calap-Quintana, P., Gonzalez-Cabo, P., & Moltó, M. D. (2019). The role of iron in Friedreich's ataxia: insights from studies in human tissues and cellular and animal models. *Frontiers in Neuroscience*, 13, 75.
- [26.] U.S. Environmental Protection Agency. (2018). 2018 edition of the drinking water standards and health advisories tables (EPA 822-F-18-001). Retrieved from <https://www.epa.gov/sites/production/files/2018-03/documents/dwtable2018.pdf>
- [27.] Li, D., Li, J., Jia, X., Han, Y., Wang, E. (2012). Electrochemical determination of Arsenic(III) on MercaptoEthylamine Modified Au electrode in neutral media, *Anal. Chem. Acta* 733:23-27.
- [28.] Bhanjana, G., Dilgbaghi, N., Chaudhary, S., Kim, K.H., Kumar, S., (2016). Robust and direct electrochemical sensing of Arsenic using zirconia nanotubes, *Analyst* 141:4211-4218.
- [29.] Moghini, N., Mohapatra, M., Leung, K.T., (2015). Biometallic nanoparticles for Arsenic detection. *Anal Chem* 87: 5546-5552.
- [30.] Touiloux, R., Tercier-Waeder, M.I., Bakker, E. (2015). Direct arsenic(III) sensing by a renewable gold plated I-based microelectrode, *Analyst* 140 (3526-3534).
- [31.] Salami, A. Mamkhezri, H., Hailaj, R., Soltanian, S., (2008). Electrochemical detection of trace amount of arsenic(III) at glassy carbon electrode modified with cobalt oxide nanoparticles sens. *Actuators B* 129 (241-254).
- [32.] Yang, M., Li, P., Xu, W., Wei, Y., Li, L., Huang, Y., Sun, Y., Chen, X., Liu, J., Huang, X., (2017). Reliable electrochemical sensing arsenic in nearby groundwater pH based on efficient adsorption and excellent electrocatalytic ability of AuNPs/CeO₂-ZrO₂ nanocomposites, *sensors and Actuators B: chgical* <http://dx.doi.org/10.1016/j.snb.2017>.
- [33.] Salaun, P., Planer-Friedrich, B. Van den Beerg, C.M., (2007). Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode, *Ana. Chim Acta*. 585:312-322.
- [34.] Sargazi, G., Afzali, D., & Mostafavi, A. (2019). A novel microwave assisted reverse micelle fabrication route for Th (IV)-MOFs as highly efficient adsorbent nanostructures with controllable structural properties to CO and CH₄ adsorption: Design, and a systematic study. *Applied Organometallic Chemistry*, 33(4), e4816.
- [35.] Alasadi, A., Khaili, F., & Awwad, A. (2019). Adsorption of Cu (II), Ni (II) and Zn (II) ions by nano kaolinite: Thermodynamics and kinetics studies. *Chemistry International*, 5(4), 258-26.