

Cu²⁺ and Cr⁶⁺ recovery from Simulated Waste Water using Zinc oxide Loaded Potato Peel Nanocomposites

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Abstract

In the present study, potato peel loaded nanoparticles were employed as adsorbent materials for the removal of Cu²⁺ and Cr⁶⁺ from aqueous solutions. Experimental observations indicated that different nanoparticles exhibited significant adsorption potential toward ampicillin. The maximum adsorption capacities were calculated as 128.6 mg/g for copper and 98.99 mg/g for chromium using ZnO@PP nanoparticles. Equilibrium analysis revealed that the adsorption behavior was best represented by the Freundlich isotherm model, suggesting multilayer adsorption on a heterogeneous surface. Kinetic investigations further indicated that the adsorption process is mainly controlled by a chemisorption mechanism. The removal of both metals is likely governed by several interactions, including surface complexation, electrostatic attraction, and hydrogen bonding between the adsorbent surface and antibiotic molecules. Thermodynamic evaluation demonstrated that the adsorption process is spontaneous and thermodynamically favorable. In addition, all combinations of nanoparticles showed satisfactory regeneration ability, maintaining considerable adsorption efficiency for up to three successive reuse cycles.

Keywords: Antibiotics, copper oxide NPs, iron oxide NPs, synthesis and characterization, adsorption studies.

Introduction

Heavy metals including chromium, lead, arsenic, copper, and cadmium are toxic and persistent pollutants commonly found in industrial wastewater. They can contaminate the

environment, including water sources, and accumulate in the ecosystem, potentially entering the food chain (Lou et al., 2021; Mondal and De, 2022). Therefore, removing these metals from wastewater and other environmental media is crucial.

Copper in its divalent form Cu(II) is broadly released in to water resources from various activities like mining, electroplating, metal finishing and electrical industries and during various agrochemical productions. However, it is trace required for biological systems but excessive use can lead to several health problems and ecological hazards. Copper, especially in its Cu(II) form present in industrial wastewater, is considered potentially hazardous. Excessive exposure to Cu(II) can lead to its buildup in the liver, causing gastrointestinal disturbances. The permissible concentration of Cu(II) in treated surface water is 3 mg·L⁻¹ (Taylor et al., 2020).

Chromium (Cr) is a trace element whose levels in the environment have been steadily rising, raising significant ecological concerns (Prasad et al., 2021). As the world's leading producer and consumer of sodium dichromate, China faces considerable environmental challenges associated with chromium pollution (Wang et al., 2020). Hexavalent chromium (Cr(VI)) is highly soluble in water and resistant to biodegradation, making it a persistent contaminant that poses serious health risks when exposure occurs (Lou et al., 2021). Water containing Cr(VI) concentrations exceeding 50–100 µg·L⁻¹ is regarded as hazardous (Yu, 2010). Chronic ingestion of Cr(VI) in amounts between 0.01 and 0.09 mg per day has been linked to damage to vital organs such as the liver, kidneys, and lungs, and can also lead to gastrointestinal issues including vomiting and ulcer formation (Hu et al., 2007).

Commonly discharged metals include silver, iron, zinc, copper, manganese, lead, arsenic, antimony, aluminum, and selenium, among others (Akcil and Koldas, 2006). Heavy metals and metalloids pose a significant threat to surface and groundwater quality due to their non-biodegradable nature, high toxicity even at low concentrations, and tendency to bioaccumulate in living organisms (Carolyn et al., 2017; Vardhan et al., 2019). Exposure to these contaminants can lead to severe health effects, ranging from cancer to neurological disorders (Malik, 2004; Visa, 2016). Consequently, research and development of sustainable methods for the removal of such pollutants have become a critical focus in recent years.

At present, various technologies are employed for the treatment of wastewater contaminated with heavy metals. These treatment approaches include physical, chemical, biological, physicochemical, and biochemical processes. Among them, physicochemical methods such as coagulation–flocculation, membrane filtration, ion exchange, and adsorption have been widely implemented because of their operational effectiveness and reliability. Nevertheless, these techniques are often associated with significant limitations, including high operational costs, complex maintenance requirements, and the generation of large quantities of sludge (Leiva et al., 2021; Prasad et al., 2021). In wastewater streams containing high concentrations of heavy metals, some conventional treatment methods become economically unfeasible. Moreover, excessive sludge production may contribute to secondary environmental contamination, affecting soil and natural water systems. Consequently, both developed and developing nations continue to seek sustainable and cost-effective alternatives.

Among the available technologies, adsorption has emerged as an efficient and dependable method for the removal of heavy metals, particularly when low-cost adsorbents are utilized (Hlihor et al., 2014; Fertu et al., 2022). In recent years, nanostructured adsorbents have attracted considerable attention as innovative alternatives to conventional adsorbent materials. Their superior performance is mainly attributed to their nanoscale size, high specific surface area, enhanced regeneration capacity, reusability, thermal stability, and, in some cases, magnetic properties that enable easier separation from treated water (Leiva et al., 2021; Prasad et al., 2021).

Traditional adsorbents derived from agricultural and plant-based wastes—such as tea waste, orange peel, walnut shells, rice husk, and sawdust—have also demonstrated significant potential for heavy metal removal. Furthermore, the incorporation of nanomaterials onto these bio-based substrates leads to the formation of nanocomposites, which significantly improve adsorption efficiency and physicochemical properties (Kataria & Garg, 2019; Leiva et al., 2021; Prasad et al., 2021). Agricultural derived waste products as adsorbents have considerably courtesy as sustainable alternatives. Potato peel is available as by products from several agricultural industrial by-products, this having variety of functional sites like carboxyl, hydroxyl and carbonyl groups so it is used for adsorption of both metal ions. But due to low surface area and weak binding affinity, potato peel exhibits a limited absorption capacity. To combat these limitations, metal oxide loading and surface

modification strategies have been used to increase the potato peel adsorption efficiency.

Zinc oxide nanoparticles and loading zinc oxide nanoparticles are widely studied for its non-toxicity, high surface activity, chemical stability, high reactivity and strong affinity towards pollutants. Loading ZnO nanoparticles over the potato peel give rise to the hybrid ZnO loaded potato peel nanocomposites (ZnO@PP), which synergistically joins high reactivity of ZnO and adsorption capability of the biomass. This nanocomposites provides multiple adsorption mechanisms such as surface adhesions, electrostatic interactions, ion exchanges as well as π - π bonding enabling the removal of heavy metals from aqueous systems. In this section we focuses on the adsorption performance of ZnO nanoparticles (ZnO NPs) and ZnO@PP NPs for the removal of Cu(II) and Cr(VI) form simulated wastewater. This section highlights the potential of these nanomaterials as an ecofriendly, efficient and cost effective adsorbents for applications in wastewater treatments.

Materials and Methods

Synthesis of Zinc Oxide nanoparticles:

The Zinc oxide nanoparticles was synthesised by adding 3 g of zinc acetate dihydrate into deionized water under strong stirring at 65 °C on magnetic stirrer so that it is equally dispersed in solution. Subsequently, 5 g of Polyvinylpyrrolidone (PVP), capping agent, particularly for nanoparticle synthesis, helping to control size, shape, and prevent aggregation was added and well dissolved to the above solution maintaining same temperature. Further the solution was subjected to vacuum drying at 65 °C until we get solid substance, after that it was dried at 100 °C in oven and calcination at 600 °C for 60 minutes. Finally, we obtained nanocrystalline ZnO powder and grounded using pestle and motor.

Synthesis of ZnO@PP nanocomposites

Potato peel waste was collected from home, cleaned many times, dried, crushed, sieved and finally powder and were kept 12 hours at 250 °C in a muffle furnace. A beaker with water : ethanol ratio (1:2) were used; 3.0 g of synthesized ZnO nanoparticles were added to 12 g of PP in another beaker. The suspensions was first stirred for two hours and then kept in ultrasonic bath tub for 3 h under sonication. We obtained ZnO@PP nanocomposites after centrifugation, washing (twice with deionised water and ethanol) and calcination at 200°C. All adsorbents were stored in air tight bottle and were subjected to further characterization and experimentation.

Characterization of synthesized nanomaterials

Field emission scanning electron microscopy & Energy dispersive X-ray analysis

Field emission scanning electron microscope (FESEM: Carl Zeiss, EVO 18 SEM, Germany) was used to define the surface topography and elemental composition ZnO, ZnO@PP. The elemental composition and surface distribution of elements were identified Energy Dispersive X-ray spectroscopy (EDX) of the synthesized nanoadsorbents.

Fourier transform infra-red spectroscopy

The existence of functional groups on the surface of samples was recorded by Fourier transform infra-red technique (FTIR: Shimadzu IR AFFINITY-I, Japan and by making bits of samples mixed with KBr. For FTIR spectrum, pinch of sample (in powder form) was grinded well with KBr salt and bits were prepared from this mixture using disc pressure press. The bits were then analyzed under IR spectrophotometer.

Preparation of heavy metal ion Stock Solution

The stock solutions of 500 mg/L of metal ions including Cu (II), and Cr (VI) were prepared by dissolving 1.91g of cupric nitrate trihydrate [Cu(NO₃)₂.3H₂O] and 1.41g of potassium dichromate (K₂Cr₂O₇), respectively in 1000mL of double distilled water. All reagents were analytical grades and all working solutions were prepared from these stock solutions with double distilled water

Batch mode experimental of heavy metal ions

The entire lab experiments were successfully conducted to optimize various process parameters i.e. pH, metal concentration, adsorbent dose, and contact time for the removal of metals ions with prepared nanoparticles. The experiments were done using 250 mL Erlenmeyer flasks with 50 mL of metal ion solution of required concentration, required contact time and adsorbent dose at a room temperature (27±1 °C) with continuous stirring speed of 180/200 rpm (rotations per minute). Photocatalysis were avoiding by conducting experiments under dark condition in closed shaker. The metals concentration solutions were

estimated by UV-VISIBLE spectrophotometer and metal ions concentration was quantified using atomic absorption spectrophotometer (AAS) before and after the experiment.

Adsorption Isotherm Models

The adsorption isotherm for solid-liquid system is a key factor that is used to explain the how adsorbates interact with adsorbents and adsorption behavior. In the present research three different models viz Freundlich, Temkin and Langmuir models were applied to investigate adsorption behaviour of two metals ions by synthesized adsorbents (Freundlich, 1906; Temkin and Pyzhe, 1940).

Adsorption Kinetic Study

The rate constant of metal ions adsorption onto the nanoadsorbents was determined by three different adsorption kinetic models viz., pseudo-first order (Langergren rate eq.), pseudo-second order and intraparticle model. These models were applied to experimental data at equilibrium time.

Thermodynamic Study

All the thermodynamic parameters Gibb's free energy (ΔG^0), change in entropy (ΔS^0) and enthalpy (ΔH^0) for the adsorption of metal ions have been quantified and determined by the equations (Sahmoune, 2019).

Reusability of Adsorbents

The reuse efficiency of the synthesized nanoadsorbents were also undertaken and then investigated by carrying out several successive cycles for synthetic metal ions removal experiments. After successful completion of batch mode experiments, nanoadsorbents by centrifugation method were separated from the aqueous medium and cleaned with ethanol and distilled water for many times and dried in oven for few hours at 100°C. The regenerated nanoadsorbents were further used for adsorption study.

Results

FTIR spectra of Nanoparticles

Figure 1 fourier transform infrared (FTIR) spectroscopy was done to study the functional groups on the surface and potential binding sites present on the synthesized materials. The FTIR spectrum of ZnO @ Potato Peel (PP) displayed characteristic lower absorption bands at 3400 cm⁻¹ (O-H), 2920cm⁻¹ (C-H), 1635 cm⁻¹ (C-O), and 519 cm⁻¹ (Zn-O), stretching is observed, in Figure 1 than ZnO nanoparticles due incorporation of nanoparticles loaded on to potato peel. The broad absorption band observed around 3420 cm⁻¹. The O–H stretching vibrations associated with hydrogen-bonded hydroxyl groups, indicating the presence of surface –OH functionalities.

In the case of the ZnO nanoparticles, prominent absorption peaks were observed at 519 cm⁻¹ characteristics of Zn-O vibrations stretching. Similarly, the broad band centered at approximately 3420 cm⁻¹ is assigned to O-OH stretching vibrations, confirming the retention of hydroxyl groups after composite formation. Additionally, distinct peaks detected at lower wave numbers in ZnO@PP are characteristic of Zn-O stretching vibrations, thereby ensuring the effective integration of zinc oxide within the potato peel (Kataria and Garg, 2019; Saini et al., 2017).

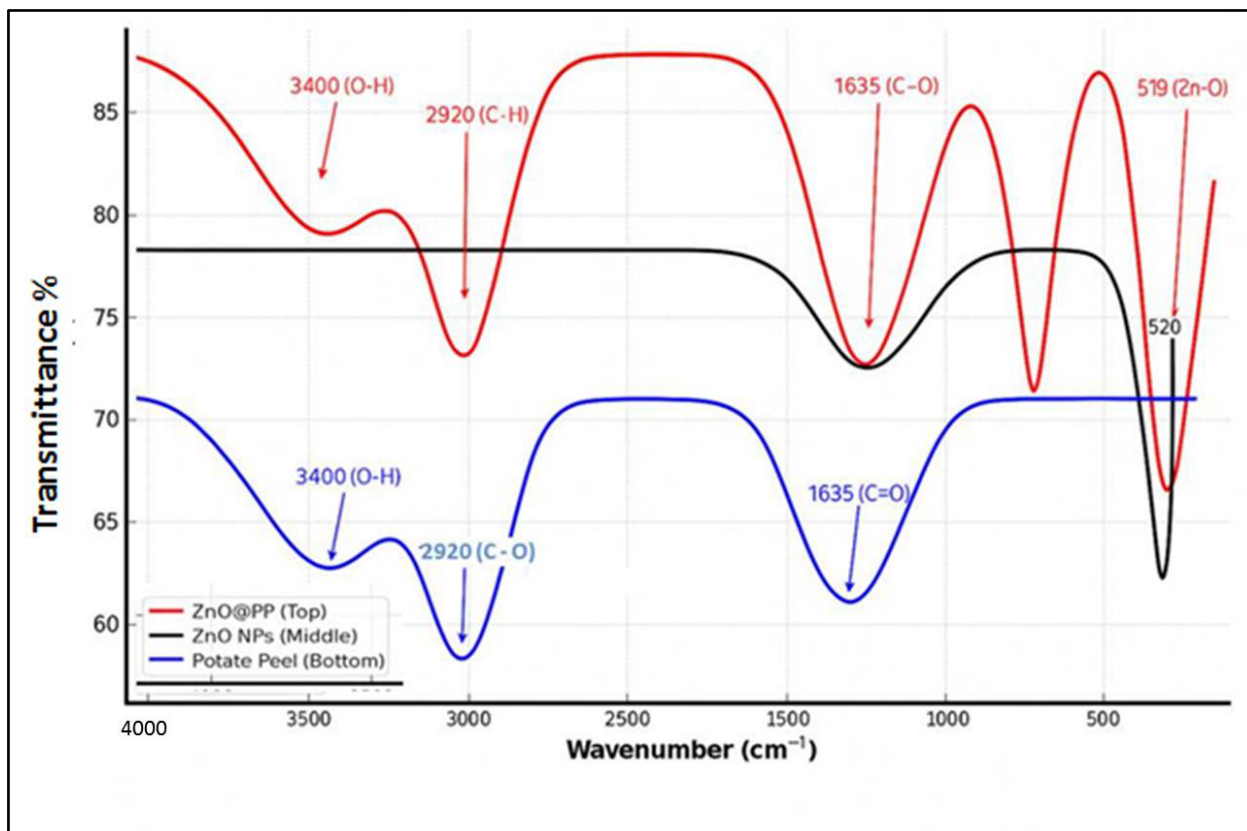


Figure 1: FTIR spectra comparison of Potato Peel, ZnO and ZnO Nanocomposites

SEM and EDX of loaded nanoparticles Analysis

Morphology of potato peel, ZnO NPs and ZnO@PP Nanoparticles morphology was analyzed after loading of Cu^{2+} and Cr^{6+} it clearly shows the entrapment of Cu^{2+} and Cr^{6+} . After its adsorption on these adsorbents, the potato peel surface looks rough, ZnO NPs appears aggregates and ZnO@PP showed altered surface textures along with aggregation of metal ions. Figure 2 (a-f) clearly shows the entrapments of these metals on the surface of Nanoparticles and suggesting thereby the adsorption of metal ions onto potato peel, ZnO NPs, and ZnO@PP nanocomposites.

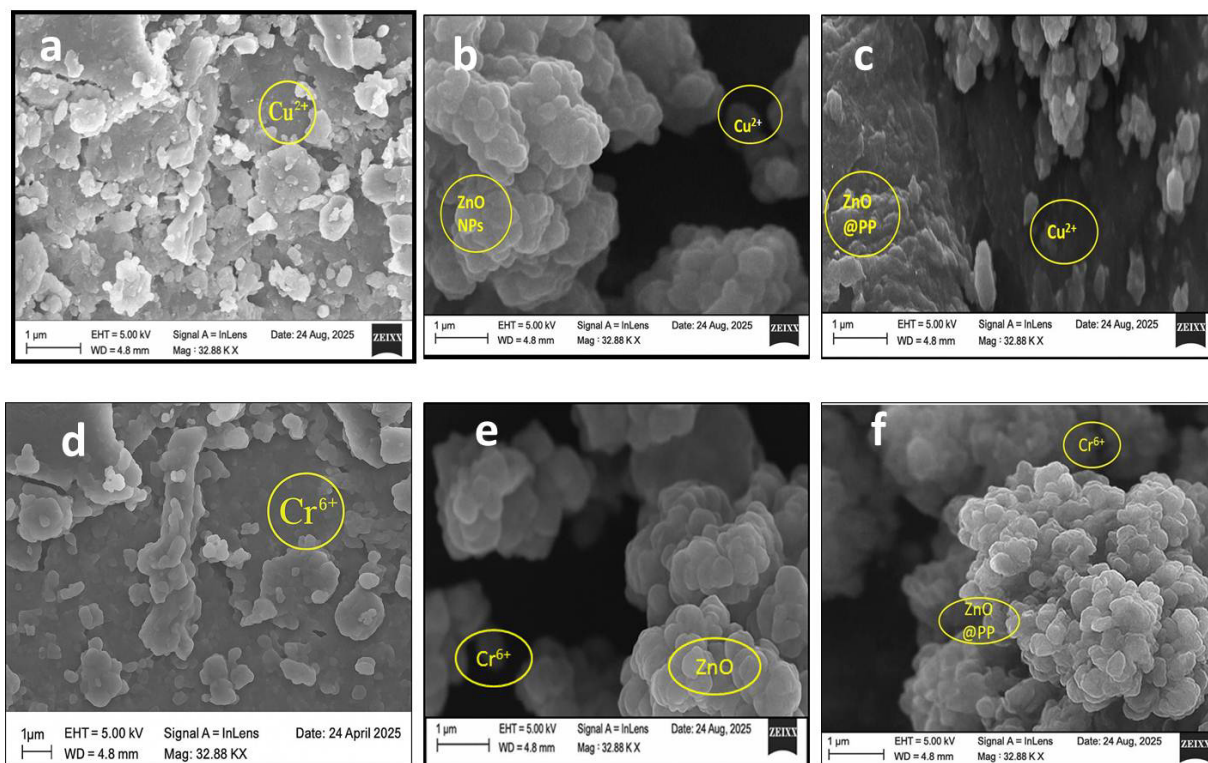


Fig. 2 FESEM images of Cu^{2+} and Cr^{6+} (a) FESEM images Cu^{2+} loaded Potato Peel (b) FESEM images of Cu^{2+} loaded ZnO NPs (c) FESEM images of Cu^{2+} loaded ZnO@PP Nanoparticle (d) FESEM images of Cr^{6+} loaded potato peel (e) FESEM images of Cr^{6+} loaded ZnO Nanoparticle (f) FESEM images of Cr^{6+} loaded ZnO@PP Nanoparticle

To determine the elemental composition of ZnO@PP before and after the adsorption of Cu^{2+} and Cr^{6+} ions, energy-dispersive X-ray (EDX) analysis was carried out. The weight percentages of the elements detected in potato peel, ZnO nanoparticles, ZnO@PP, and the corresponding Cu^{2+} - and Cr^{6+} -loaded samples are presented in Figures 3 (a-e). Examination of the EDX spectra after metal ion uptake revealed the appearance of characteristic peaks corresponding to Cu and Cr in potato peel, ZnO nanoparticles, and ZnO@PP nanocomposites. The presence of these peaks confirms the successful adsorption of Cu^{2+} and Cr^{6+} ions onto the surface of the ZnO@PP material.

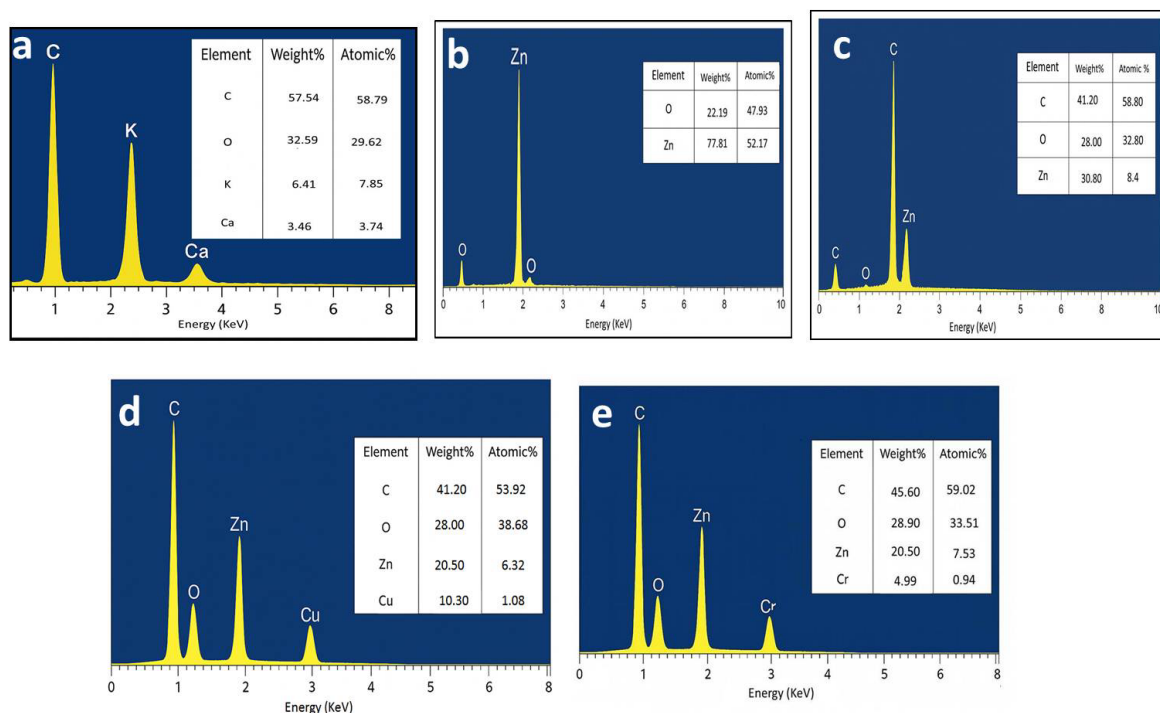


Figure 3: EDX Image (a) EDX Image of Potato Peel (b) EDX Image of ZnO Nanoparticles (c) EDX Image of ZnO@Potato Peel Nanoparticles (d) EDX Image of Cu²⁺ loaded ZnO@PP Nanoparticles (e) EDX Image of Cr⁶⁺ loaded ZnO@PP Nanoparticles

Batch adsorption studies for heavy metal removal from simulated water

Effects of pH variation on metal removal

The adsorption behavior of contaminants on solid surfaces is strongly influenced by the pH of the solution. In the present study, the effect of pH on the removal of Cu(II) and Cr(VI) was examined by varying the solution pH from 2 to 8, as illustrated in Fig. 4 (a-b). The maximum removal efficiency for Cu (II) was observed at pH 7 are 93.82%, 91.82% and 87.82%, respectively for ZnO@PP NPs, ZnO NPs and potato peel, it shows a clear pattern of absorption with increase pH. While for Cr(VI) maximum was observed at pH 5 are 71.44%, 69.88% and 63.78%, respectively for ZnO@PP NPs, ZnO NPs and potato peel. When the pH was increased

to 7 and 8 the removal efficiency decreased to 51.38%, 49.1% and 45.2% %, respectively for ZnO@PP NPs, ZnO NPs and potato peel. These results indicate that more effective in removing Cr(VI) under acidic conditions than under neutral conditions, which can be attributed to pH-dependent surface interactions (Leiva et al., 2021; Prasad et al., 2021). The observed trend can be explained by several mechanisms, including the reduction of Cr(VI) species and the protonation or deprotonation of surface functional groups as the pH changes. A strong relationship exists between the pH of the solution and the surface charge characteristics of the adsorbent, which significantly affects adsorption performance. Under acidic conditions, enhanced protonation of functional groups promotes stronger interactions with Cr(VI), leading to higher removal efficiency compared to neutral conditions (Leiva et al., 2021; Prasad et al., 2021).

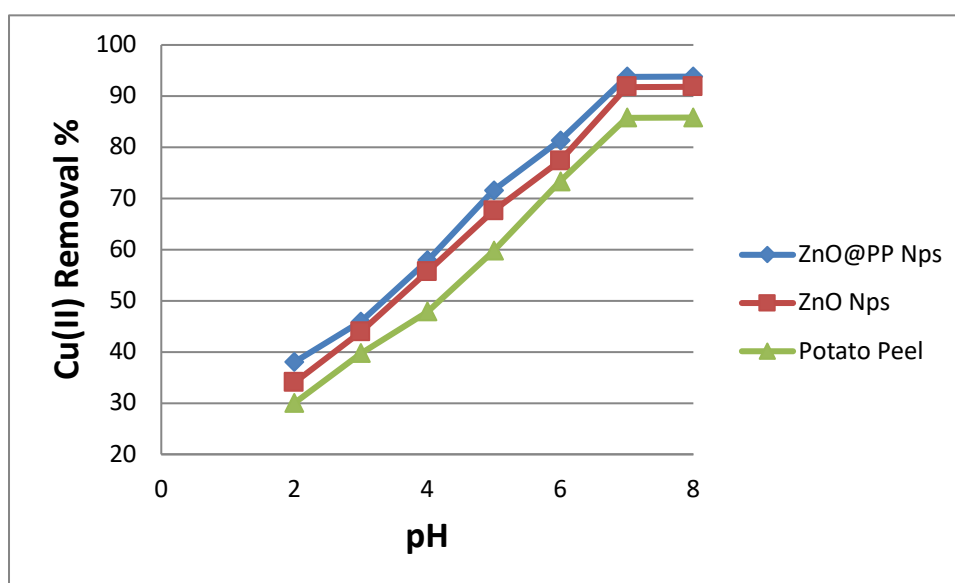


Figure 4 a: Effects of pH on Cu(II) removal using ZnO loaded potato peel nanoparticle, ZnO NPs and potato peel

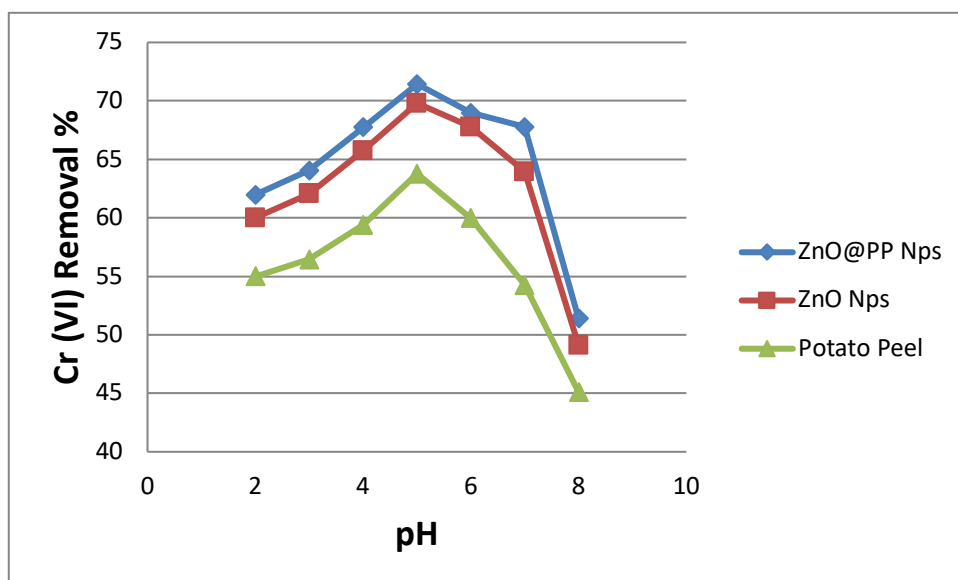


Figure 4 b: Effects of pH on Cr(vI) removal using ZnO loaded potato peel nanoparticle, ZnO NPs and potato peel

Effect of Adsorbent doses

Figure 5a-b illustrates the effect of adsorbent dosage on the adsorption of Cu^{2+} and Cr^{6+} ions using potato Peel (PP), ZnO nanoparticles (ZnO NPs), and ZnO@PP nanocomposites adsorbents over the dosage range of 0.01–0.04 g per 50 mL of solution. The experiments were conducted at pH 7 for Cu^{2+} ions and pH 5 for Cr^{6+} ions. The results clearly show that, for all adsorbents, the removal efficiencies of Cu^{2+} and Cr^{6+} ions increased progressively with an increase in adsorbent dose, indicating the availability of a greater number of active adsorption sites at higher dosages. The adsorption efficiency with ZnO@PP achieving the maximum uptake (51.94–98.6%) for Cu^{2+} and (56.24–71.52% for Cr^{6+} , followed by ZnO NPs (45.95–97.36%) for Cu^{2+} and (52.34–67.72%) for Cr^{6+} followed by PP (39.76–84.4%) for Cu^{2+} and (48.35–65.71%) for Cr^{6+} . Results are supported by Leiva et al., 2021; Prasad et al., 2021.

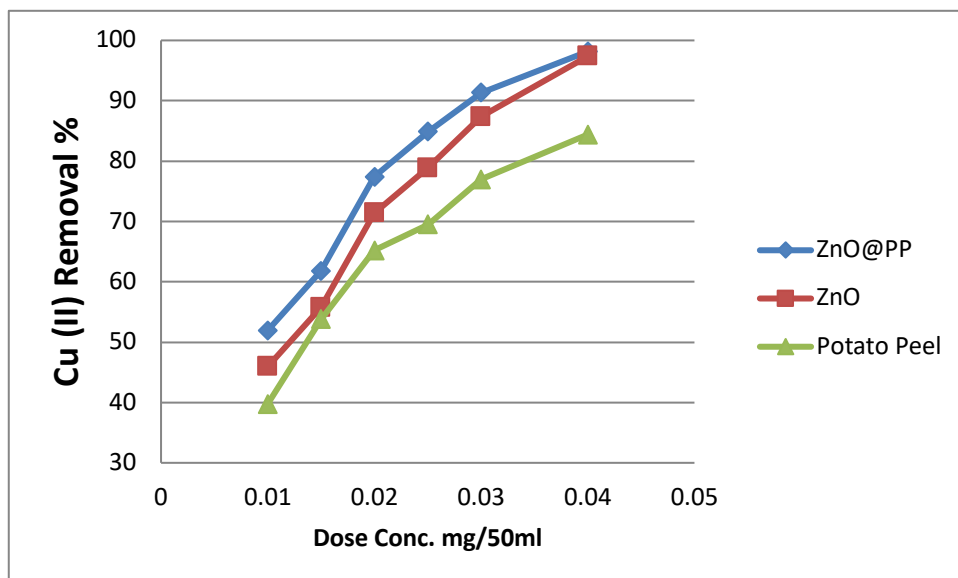


Figure 5a: Effect of dose concentration on Cu(II) removal

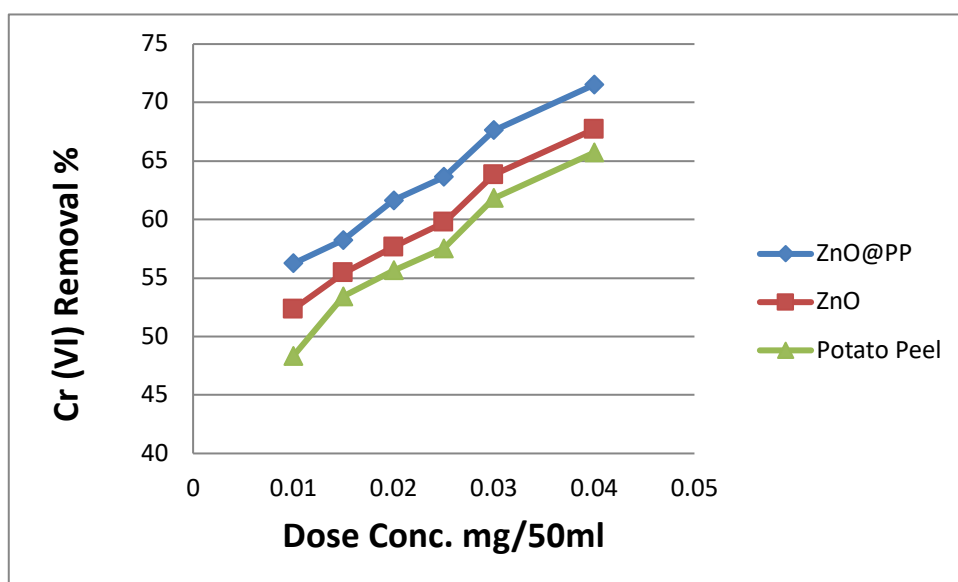


Figure 5 b: Effect of dose concentration on Cr(VI) removal

Effects of different metal concentration on metal ions

The adsorption performance of Cu^{2+} and Cr^{6+} ions onto ZnO nanoparticles, ZnO@PP nanocomposites, and potato peel was examined at varying initial metal ion concentrations of

10, 30, 50, 75, and 100 mg/L, while all other experimental conditions were maintained constant (pH 7 for Cu²⁺ and pH 5 for Cr⁶⁺, adsorbent dose of 0.03 g, contact time of 10–60 min, temperature of 27 °C, and agitation speed of 200 rpm). The findings revealed a noticeable decline in removal efficiency with increasing metal ion concentration for all adsorbents tested.

For potato peel, the percentage removal of Cu²⁺ decreased from 81.7% to 52.65%, while that of Cr⁶⁺ declined from 71.7% to 52.75% as the concentration increased. A similar trend was observed for ZnO nanoparticles, where Cu²⁺ removal reduced from 92.7% to 62.32% and Cr⁶⁺ removal from 79.9% to 55.83%. In the case of ZnO@PP nanocomposites, the adsorption efficiency also decreased, with Cu²⁺ removal dropping from 97.70% to 74.93% and Cr⁶⁺ from 85.10% to 59.93%, as illustrated in Figure 6 (a–b). This behavior can be attributed to the saturation of available active sites on the adsorbent surface at higher metal ion concentrations, as these sites are more readily accessible and rapidly occupied at lower initial concentrations (Leiva et al., 2021; Prasad et al., 2021).

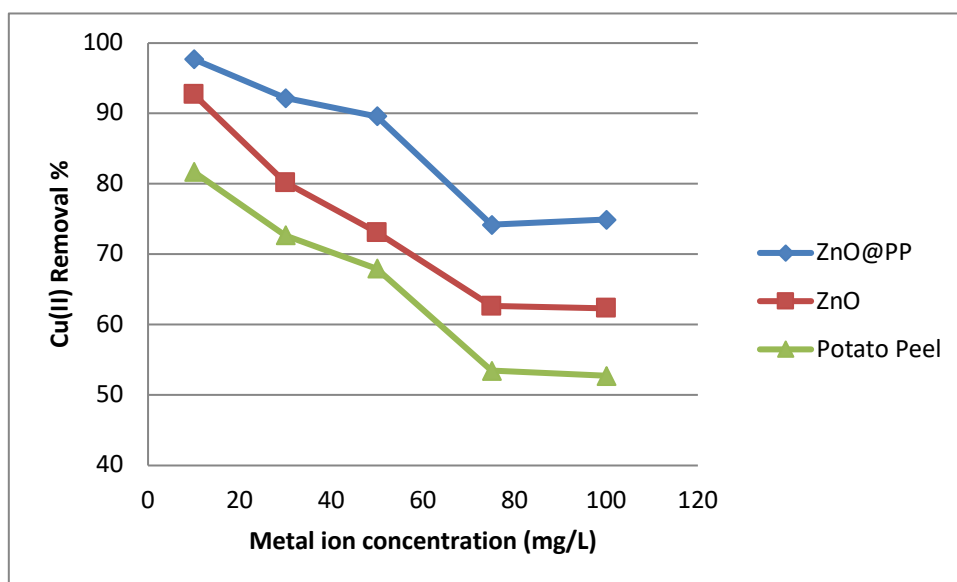


Figure 6 a: Effects metal ions concentration on Cu (II) removal

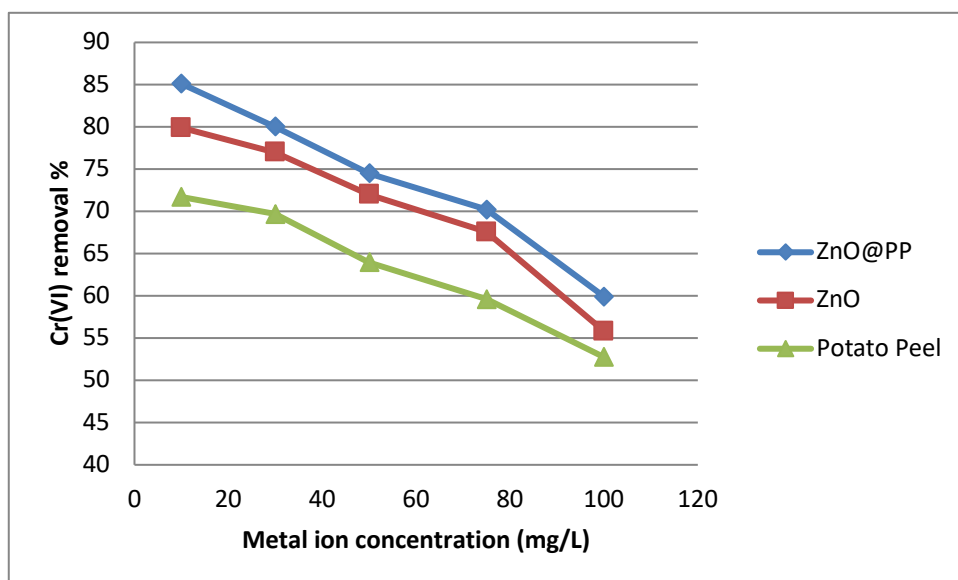


Figure 6 b: Effects metal ions concentration on Cr (VI) removal

Effects of contact time on the removal of metals

The effect of contact time on the adsorption of Cu^{2+} and Cr^{6+} ions by potato peel, ZnO nanoparticles, and ZnO@PP nanocomposites was examined over a time interval of 10–60 minutes, while all other experimental conditions were kept constant. The adsorption profiles showed a rapid increase in metal ion removal during the initial stage for all three adsorbents, followed by attainment of a maximum uptake. This behavior indicates fast interaction between metal ions and readily accessible surface sites at the beginning of the process.

At an initial concentration of 50 mg/L, the potato peel adsorbent achieved maximum removal efficiencies of 78.42% for Cu^{2+} and 64.98% for Cr^{6+} ions. In comparison, ZnO nanoparticles showed slightly higher removals of 80.22% for Cu^{2+} and 68.97% for Cr^{6+} ions. The highest adsorption performance was observed for ZnO@PP nanocomposites, with maximum removal efficiencies of 86.42% and 72.98% for Cu^{2+} and Cr^{6+} ions, respectively, as depicted in Figure 7(a–c). The enhanced removal with increasing contact time can be attributed to the availability of a large number of vacant and active adsorption sites on the adsorbent surface during the initial adsorption period (Leiva et al., 2021; Prasad et al., 2021).

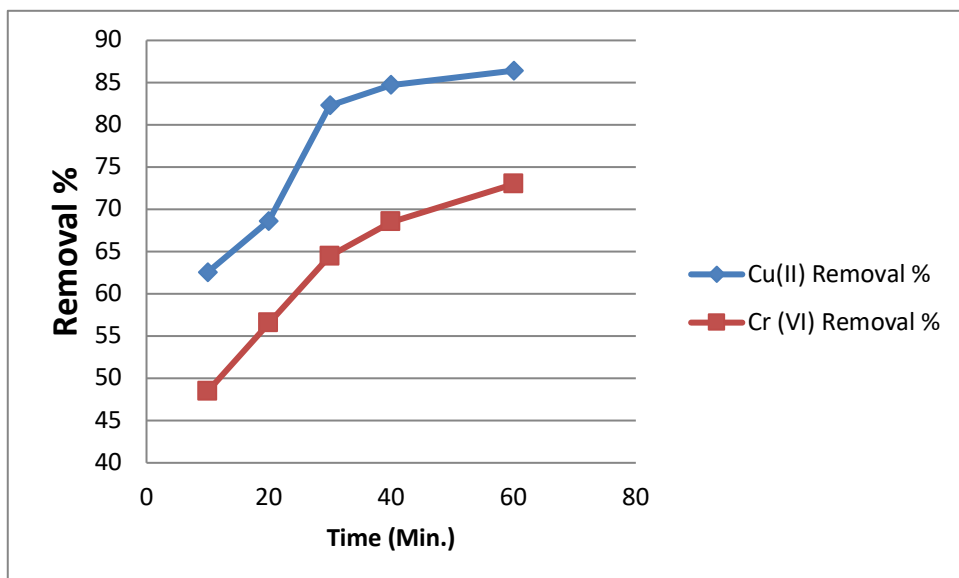


Figure 7a: Effects time on Cu (II) and Cr (VI) removal using ZnO potato peel loaded nanoparticles

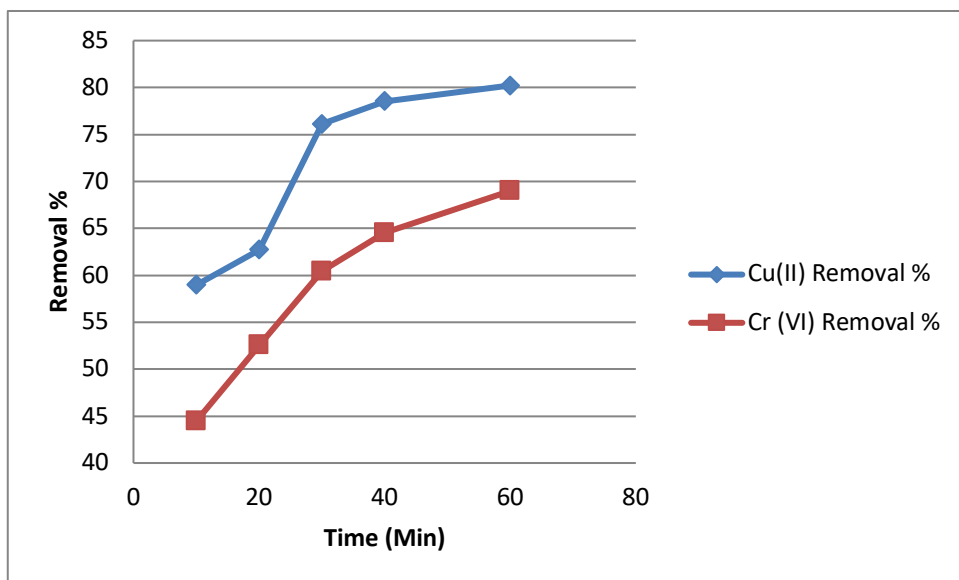


Figure 7b: Effects time on Cu (II) and Cr (VI) removal using ZnO nanoparticles

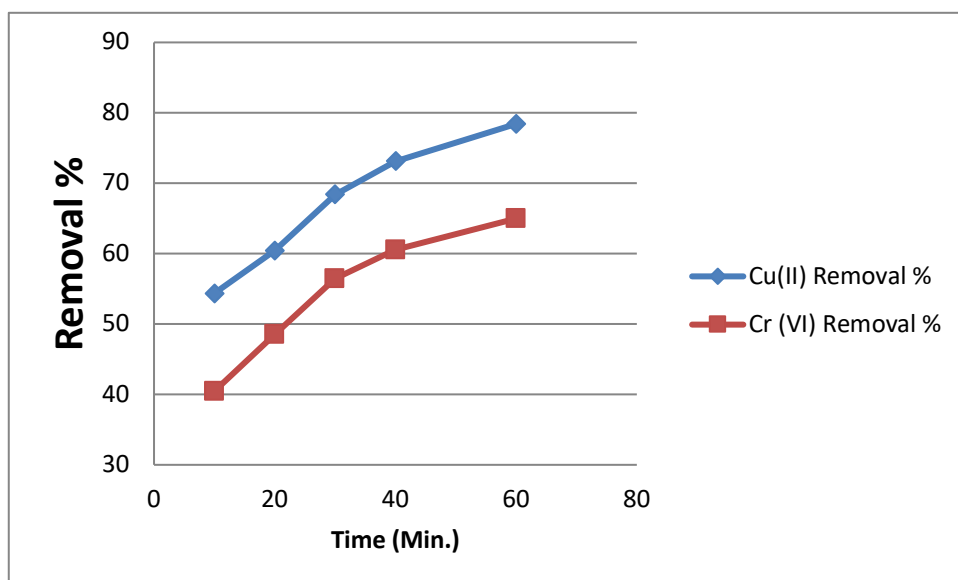


Figure 7c: Effects time on Cu (II) and Cr (VI) removal using potato peel

Temperature variation effects on metal ions removal

Temperature plays a crucial role in the adsorption process, as an increase in temperature enhances ionic mobility and may generate additional active sites on the adsorbent surface due to the weakening or breaking of chemical bonds. Figures 8 (a–c) illustrate the adsorption behavior of Cu^{2+} and Cr^{6+} ions onto potato peel, ZnO nanoparticles, and ZnO@PP nanocomposites over a temperature range of 30–50 °C. The results indicate a clear increase in metal ion removal efficiency with rising temperature for all adsorbents. When potato peel was used as the adsorbent, the removal efficiency of Cu^{2+} increased from 47.98% to 88.40%, while that of Cr^{6+} rose from 38.18% to 68.37%. In the case of ZnO nanoparticles, higher removal efficiencies were observed, with Cu^{2+} and Cr^{6+} removal increasing from 47.98% to 88.84% and from 38.15% to 82.04%, respectively. The highest adsorption performance was achieved using ZnO@PP nanocomposites, where Cu^{2+} removal increased from 47.98% to 94.84% and Cr^{6+} removal from 42.18% to 92.04%. The enhanced adsorption at elevated temperatures can be attributed to improved interaction between metal ions and the active sites on the adsorbent surface. Higher temperatures facilitate greater diffusion and transport of metal ions in the solution, effectively accelerating the adsorption process, as increased thermal energy acts as a driving force for adsorption (Leiva et al., 2021; Prasad et al., 2021).

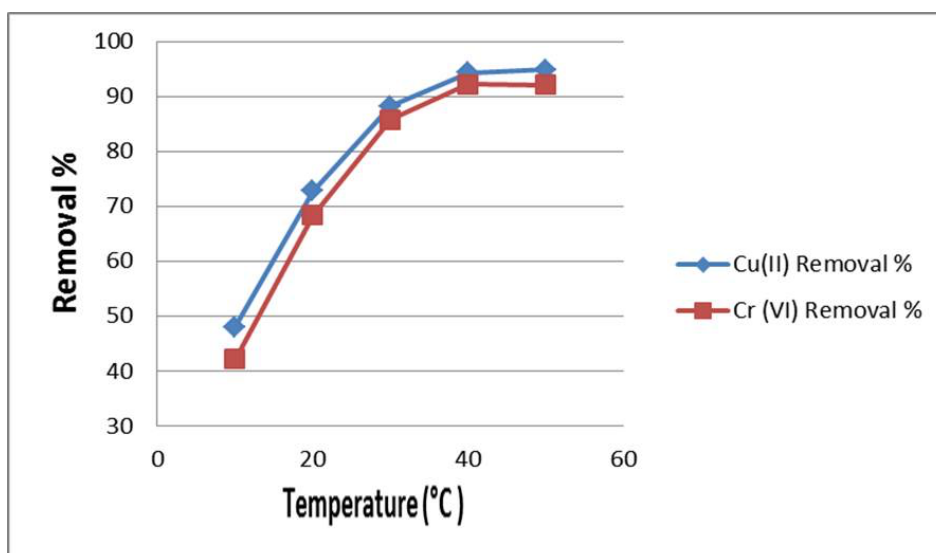


Figure 8 a: Effects temperature on Cu (II) and Cr (VI) removal using ZnO@PP nanoparticles

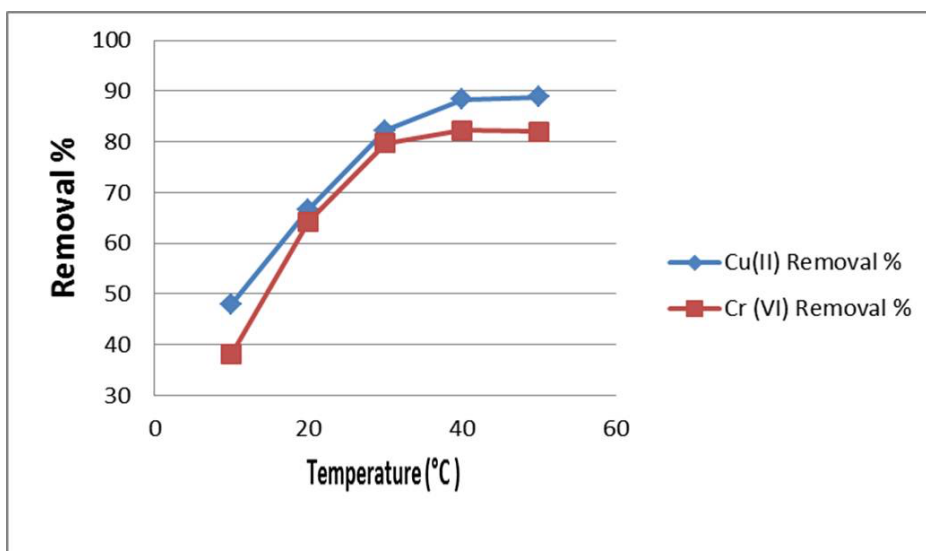


Figure 8 b: Effects temperature on Cu (II) and Cr (VI) removal using ZnO nanoparticles

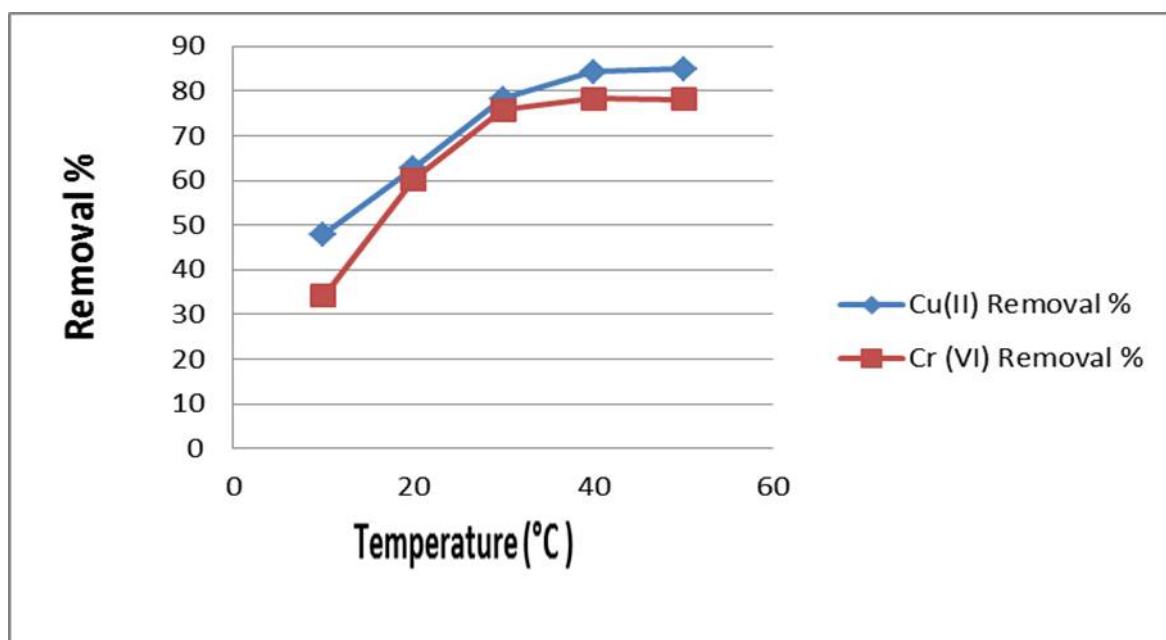


Figure 8c: Effects temperature on Cu (II) and Cr (VI) removal using potato peel

Isotherm modeling

The adsorption characteristics and interactions between metal ions and the surfaces of the adsorbents were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherm models. These models were applied to interpret the equilibrium adsorption data and to understand the nature of the adsorption process.

The linear form of the Langmuir isotherm model is expressed as:

$$C_e / q_e = 1 / (q_{\max} b) + C_e / q_{\max} \quad (1)$$

where $q_{\max}$ (mg g^{-1}) represents the maximum monolayer adsorption capacity and b (L mg^{-1}) is the Langmuir constant related to the affinity between the adsorbent and adsorbate. The Langmuir parameters were determined from the linear plot of C_e/q_e versus C_e . The calculated values of $q_{\max}$, b , and the correlation coefficient (R^2) for Cu^{2+} and Cr^{6+} adsorption onto ZnO@PP , ZnO nanoparticles, and potato peel are summarized in Table 1.

The Freundlich isotherm model, which describes adsorption on heterogeneous surfaces, is given in its linearized form as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (2)$$

Here, K_f represents the Freundlich adsorption constant, and n is the heterogeneity factor indicating adsorption favorability. The parameters K_f and n were obtained from the linear plot of $\log q_e$ versus $\log C_e$. Adsorption is considered favorable when the value of n lies between 1 and 10.

The Temkin and Pyzhev isotherm model accounts for adsorbate–adsorbent interactions and is expressed in linear form as:

$$q_e = B \ln K_T + B \ln C_e \quad (3)$$

where $B = RT/b$, b is the Temkin constant associated with the heat of adsorption, R is the universal gas constant, T is the absolute temperature, and K_T ($L\ g^{-1}$) is the equilibrium binding constant. The Temkin parameters were evaluated from the plot of q_e versus $\ln C_e$, and the corresponding R^2 values and constants are presented in Table 1.

The Dubinin–Radushkevich (D–R) isotherm model (Dubinin and Radushkevich, 1947) was also applied and is represented by:

$$\ln q_e = \ln Q_s - K_D \varepsilon^2 \quad (4)$$

where Q_s ($mg\ g^{-1}$) is the theoretical saturation adsorption capacity, K_D ($mol^2\ kJ^{-2}$) is the activity coefficient related to adsorption energy, and ε is the Polanyi potential, defined as:

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (5)$$

The values of Q_s and K_D were obtained from the intercept and slope of the linear plot of $\ln q_e$ versus ε^2 . The mean adsorption energy E ($kJ\ mol^{-1}$), which provides insight into the nature of the adsorption process, was calculated using the following equation:

$$E = 1 / \sqrt{2K_D} \quad (6)$$

The D–R model was fitted to the experimental adsorption data for both metal ions on ZnO@potato Peel Nanoparticles, ZnO Nanoparticles and Potato Peel to assess the adsorption mechanism and mean free energy. The corresponding D–R parameters and correlation coefficients are listed (table 2).

Table 1: Adsorption isotherms parameters for Cu²⁺ and Cr⁶⁺ adsorption on ZnO@potato Peel Nanoparticles, ZnO Nanoparticles and Potato Peel

Isotherms model Parameters		ZnO loaded potato Peel Nanoparticles		ZnO Nanoparticles		Potato Peel	
		Cu ²⁺	Cr ⁶⁺	Cu ²⁺	Cr ⁶⁺	Cu ²⁺	Cr ⁶⁺
Langmuir	q_{max} (mg/g)	256.4	147.1	211.73	141.88	144.9	119.0
	b (L/mg)	0.0275	0.0025	0.0662	0.0573	0.251	0.084
	R^2	0.986	0.986	0.871	0.963	0.9757	0.999
Freundlich	N	2.22	2.70	2.38	2.56	1.98	2.08
	K_f (mg/g)	67.61	35.48	34.67	17.78	21.88	15.14
	R^2	0.984	0.978	0.982	0.976	0.986	0.982
Temkin and Pyzhev	B	174.19	82.35	156.25	71.43	111.11	90.91
	K_T (L/mg)	1.23	0.35	0.51	0.21	0.35	0.21
	R^2	0.995	0.979	0.968	0.962	0.978	0.972
Dubinin-Radushkevich	Q_s (mg/g)	128.1	99.9	124.8	93.1	100.2	87.9
	K_D (mol ² /kJ ²)	1.23X10 ⁻⁶	2.3X10 ⁻⁶	2.35 X10 ⁻⁷	3.47X10 ⁻⁶	3.45 X 10 ⁻⁷	5.67 X 10 ⁻⁶
	E (kJ/mol)	2.01	1.46	1.46	1.20	1.20	0.94
	R^2	0.958	0.942	0.952	0.938	0.964	0.952

Evaluation of the equilibrium isotherm models revealed that the Langmuir model provided the best fit for the experimental adsorption data of Cu²⁺ and Cr⁶⁺ ions on ZnO@PP nanocomposites. In contrast, adsorption onto tea waste was more accurately described by the Freundlich isotherm compared to the other models examined in this study. The calculated separation factor (RL) values

were found to be within the range of 0 to 1 ($0 < RL < 1$), indicating that the adsorption of both Cu²⁺ and Cr⁶⁺ ions onto ZnO@PP nanocomposites is favorable. Additionally, the Freundlich constant n for both metal ions exceeded unity, confirming multilayer adsorption on heterogeneously distributed active sites of the adsorbents. A comparison of the maximum adsorption capacities of previously reported adsorbents with that of ZnO@PP is presented in Table 2.

Table 2: Comparison of adsorption capacity of synthesized nanomaterials for Cr(VI) and Cu(II)

Sl. No.	Adsorbent material	Target Metal	Maximum adsorption capacity (mg·g ⁻¹)	Reference
1.	Green-synthesized nano iron from tea leaves	Cr(VI)	29.8	Kaur et al., 2021
2.	Eggshell-derived zinc oxide nanoparticles	Cr(VI)	38.32	Gonfa et al., 2022
3.	Orange peel-based nano iron	Cr(VI)	5.37	López-Téllez et al., 2011
4.	Bamboo leaf green-synthesized nano silicon	Cr(VI)	22.93	Sharma et al., 2022
5.	Green-synthesized boehmite nanoparticles	Cr(VI)	59.5	Milanović et al., 2021
6.	Horsetail plant-mediated green-synthesized nano silicon	Cr(VI)	2.55	Ahmed et al., 2016
7.	Fragrant pear peel-derived nano iron	Cr(VI)	26.97	Rong et al., 2020
8.	Green-synthesized nano iron from eucalyptus leaves	Cr(VI)	20.5	Jin et al., 2018
9.	Eggshell-based nanocrystalline chlorapatite	Cr(VI)	63.47	Han et al., 2021

10.	Biocomposite zinc oxide nanoparticles	Cr(VI)	55.56	Khan et al., 2017
11.	Green-synthesized nano zinc oxide from <i>Azolla pinnata</i>	Cr(VI)	60.13	Ou et al., 2022
12.	ZnO@ PP	Cr(VI)	99.88	Current Study
13.	Polyvinyltetrazole-co-PAN	Cu(II)	44.2	Kumar et al., 2016
14.	Cs-aminated multiwalled carbon nanotubes	Cu(II)	28.3	Salehi et al., 2013
15.	NiFe ₂ O ₄	Cu(II)	41.42	Mondal et al., 2017
16.	Co-Fe ₂ O ₃	Cu(II)	22	Chan et al., 2015
17.	GO/PVA	Cu(II)	72.6	Tan et al., 2015
18.	Alumina	Cu(II)	16.88	Delavar et al., 2017
19.	ZnO nanoparticles	Cu(II)	84	Mondal and De, 2022
20.	ZnO nanoparticles	Cu(II)	47.5	Leiva et al., 2021
21.	ZnO@ PP	Cu(II)	128.0	Curent Study

The results demonstrated that the ZnO@PP nanocomposite exhibited a significantly higher adsorption capacity compared to untreated tea waste and several previously reported adsorbent materials. This enhanced performance suggests that ZnO@PP is a promising and efficient adsorbent for the removal of metal ions from simulated wastewater systems.

Thermodynamic studies

The thermodynamic parameters-standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)-for the adsorption of Cu²⁺ and Cr⁶⁺ onto ZnO@potato peel nanocomposites, ZnO nanoparticles, and raw potato peel were evaluated by performing adsorption experiments at various temperatures between 30 and 50 °C. All other experimental parameters were maintained constant throughout the study to ensure accurate assessment of temperature effects on the adsorption process. The following equations were used to calculate the thermodynamic parameters:

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

$$K_d = \frac{C_a}{C_e} \quad (8)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature in Kelvin, K_d is the equilibrium constant, and C_a (mg/L) represents the concentration of metal ions adsorbed on the adsorbent at equilibrium. The values of ΔH° and ΔS° were determined from the slope and intercept of the linear plot of ln K_d versus 1/T. The calculated thermodynamic parameters are summarized in Table 3 (a-c) and Figure 9 (a- f).

Positive ΔS° values for both metal ions indicate an increase in randomness at the solid–solution interface during adsorption. The positive ΔH° values for Cu²⁺ and Cr⁶⁺ ions suggest that the adsorption process is endothermic, with ions being actively absorbed onto the adsorbent surface. Negative ΔG° values observed at higher temperatures confirm that the adsorption is both spontaneous and feasible, supporting the conclusion that the adsorption of Cu²⁺ and Cr⁶⁺ ions onto these adsorbents occurs predominantly via physical interactions (Malkoc and Nuhoglu, 2007).

Table 3 a: Thermodynamic parameters description of Cu(II) and Cr(VI) metals adsorption by ZnO@						
Temp.	Cu(II)			Cr(VI)		
(K)	ΔG°	ΔS°	ΔH°	ΔG°	ΔS°	ΔH°

	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)
283	-1.21	101.87	27.58	0.14	70.50	20.03
293	-1.91			-0.64		
303	-3.87			-5.1		
313	-4.46			-2.02		
323	-4.97			-2.67		

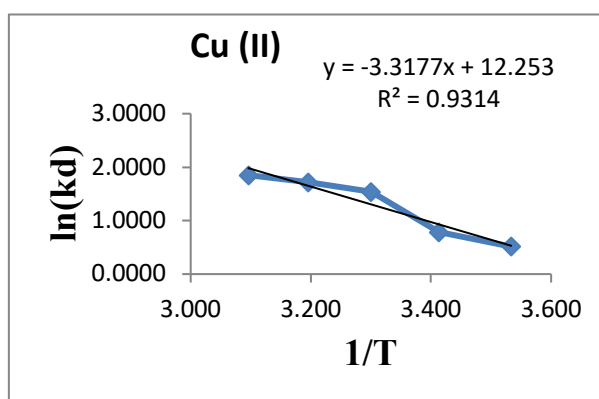


Fig 9a: Thermodynamic plot for Cu(II) removal by ZnO@PP nanoparticles

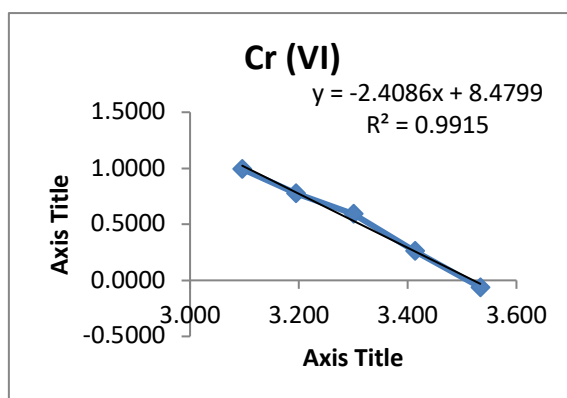


Fig 9b: Thermodynamic plot for Cr(VI) removal by ZnO@PP nanoparticles

Table 3 b: Thermodynamic parameters description of Cu(II) and Cr(VI) metals adsorption by ZnO

Temp.	Cu(II)			Cr(VI)		
(K)	ΔG^0	ΔS^0	ΔH^0	ΔG^0	ΔS^0	ΔH^0
	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)
283	-0.85	80.01	21.81	0.52	65.06	18.85
293	-1.27			-0.25		
303	-2.92			-1.07		
313	-3.38			-1.38		
323	-3.76			-2.15		

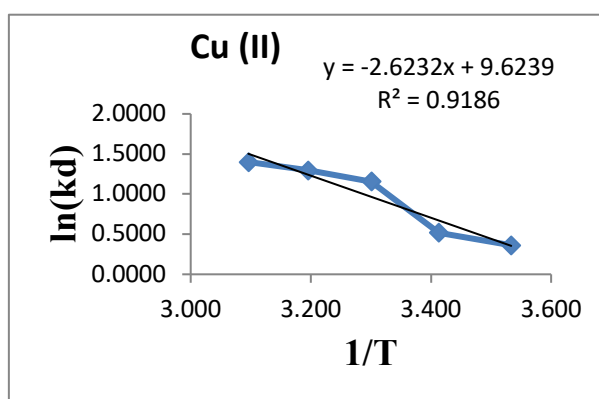


Fig 9c: Thermodynamic plot for Cu(II) removal by ZnO nanoparticles

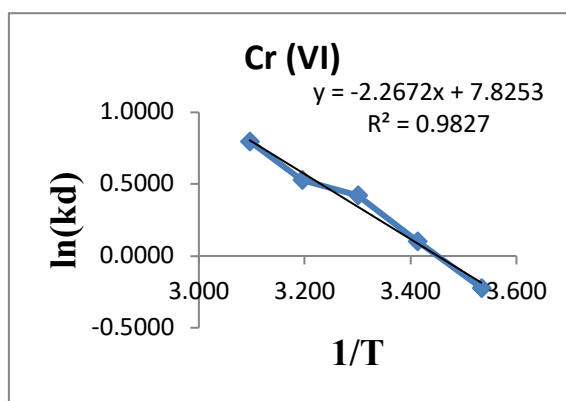


Fig 9 d: Thermodynamic plot for Cr(VI) removal by ZnO nanoparticles

Table 3c: Thermodynamic parameters description of Cu(II) and Cr(VI) metals adsorption by potato Peel						
Temp.	Cu (II)			Cr (VI)		
(K)	ΔG^0	ΔS^0	ΔH^0	ΔG^0	ΔS^0	ΔH^0
	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)	(k J mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(k J mol ⁻¹)
283	-0.41	76.71.12	21.34	0.91	61.80	18.19
293	-1.03			-0.14		
303	-1.94			-0.65		
313	-2.61			-1.11		
323	-3.47			-1.66		

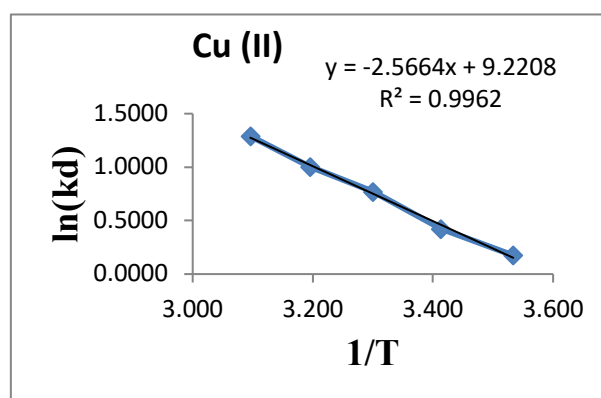


Fig 9e: Thermodynamic plot for Cu(II) removal by potato peel

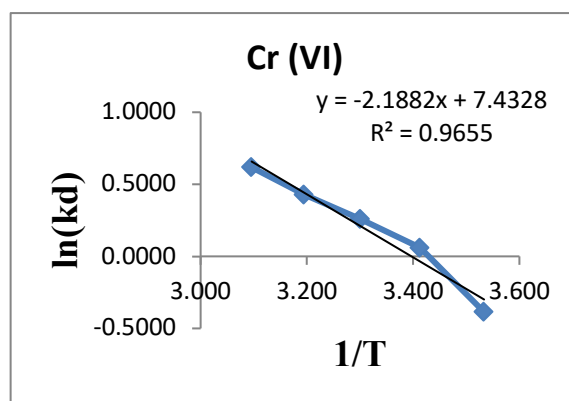


Fig 9 f: Thermodynamic plot for Cr(VI) removal by potato peel

Kinetic isotherm study

The adsorption kinetics of Cu(II) and Cr(VI) onto ZnO@PP nanoadsorbents were studied using two kinetic models: the pseudo-first-order model (Lagergren, 1898) and the pseudo-second-order model (McKay & Ho, 1999). These models helped understand the adsorption rate and identify the key mechanisms controlling the process. The linearized forms of these kinetic equations are given below:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

$$q_t = k_{id} t^{1/2} + C$$

The adsorption capacity at equilibrium is represented by q_e (mg g⁻¹), while q_t (mg g⁻¹) denotes the capacity at time t . The pseudo-first-order and pseudo-second-order kinetic models have rate constants k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹), respectively. Table 4 summarizes the kinetic parameters obtained by fitting experimental data to the linearized models using linear regression. For the pseudo-first-order model, k_1 and q_e were determined from the plot of $\log(q_e - q_t)$ vs t , while for the pseudo-second-order model, parameters were obtained from the plot of t/q_t vs t . The pseudo-first-order model underestimated the equilibrium adsorption capacities $q_e(\text{cal})$ compared to experimental values $q_e(\text{exp})$ for both metals. In contrast, the pseudo-second-order model

showed high regression coefficients ($R^2=0.996-0.999$ for Cu(II) and $R^2=0.992-0.997$ for Cr(VI)) and close agreement between $q_e(\text{cal})$ and $q_e(\text{exp})$. The interparticle diffusion model showed moderate regression coefficients ($R^2=0.964-0.968$), indicating a contribution to metal adsorption. The findings suggest that the pseudo-second-order kinetic model best describes the adsorption kinetics, indicating chemisorption mechanisms involving valence forces and electron sharing/exchange between metals and adsorbents.

Table 4: Kinetic models parameters description of Cu(II) and Cr(VI) metals adsorption

Kinetic Models	Parameters	Cu (II) (mg/ml)			Cr(VI) (mg/ml)		
Pseudo-first Order	k_1 (min^{-1})	0.064	0.058	0.046	0.052	0.046	0.035
	$q_e(\text{cal})$	36.3	56.3	128.07	34.9	56.3	99.88
	R^2	0.999	0.986	0.982	0.982	0.980	0.976
Pseudo-second Order	k_2 (g/mg min)	0.0021	0.0012	0.005	0.0016	0.009	0.0038
	q_e (cal)	37.04	58.82	142.86	35.71	55.56	111.11
	R^2	0.999	0.998	0.996	0.997	0.996	0.992
Intraparticle Diffusion	k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	3.45	5.23	10.23	2.94	4.53	8.12
	C	10.71	15.38	38.45	8.57	12.82	28.57
	R^2	0.964	0.968	0.964	0.964	0.962	0.958
Exp. Data	$q_e(\text{exp})$	56.3	82.3	100.2	53.3	74.5	87.9

4.2.7 Reuse potential of the adsorbents for metal removal

The regenerated ZnO@PP nanocomposites, ZnO nanoparticles, and raw potato peel were reused for the adsorption of Cu²⁺ and Cr⁶⁺ ions for up to three consecutive cycles. During the first adsorption–desorption cycle, ZnO@PP nanocomposites exhibited removal efficiencies of 93.82% for Cu²⁺ and 71.44% for Cr⁶⁺, which were notably higher than those achieved using ZnO nanoparticles and potato peel alone. However, a gradual decline in removal efficiency was observed in subsequent cycles. By the end of the third reuse cycle, the adsorption efficiency of ZnO@PP decreased to 85.82% for Cu²⁺

and 63.78% for Cr^{6+} , as illustrated in Figure 10. These findings indicate that the $\text{ZnO}@PP$ nanocomposite retains considerable adsorption capacity even after multiple regeneration cycles, demonstrating its potential applicability in the treatment of metal-contaminated wastewater. Although ZnO nanoparticles and potato peel also showed a similar decreasing trend in reusability, their retention efficiencies were comparatively lower than those of the $\text{ZnO}@PP$ nanocomposite, as presented in Figure 10 (a–b).

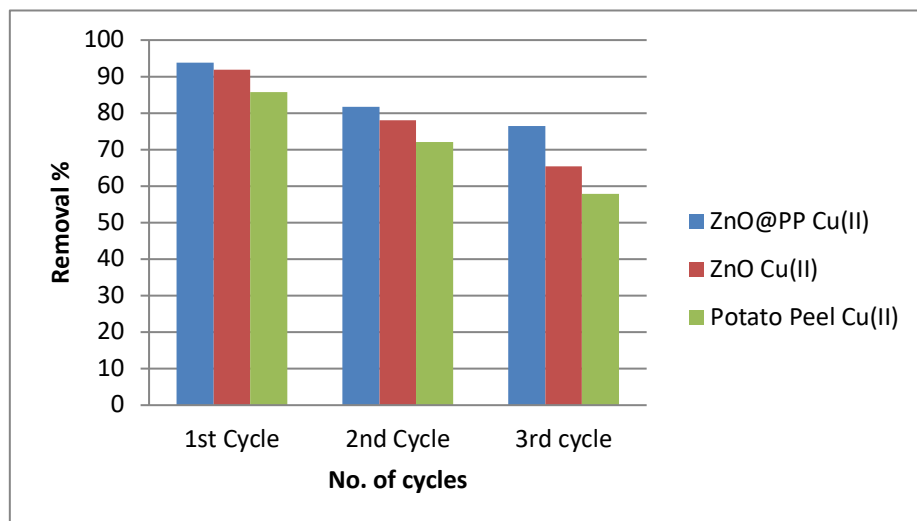


Figure 10a: Reuse efficiency of Nanoadsorbents for Cu(II) metal Removal

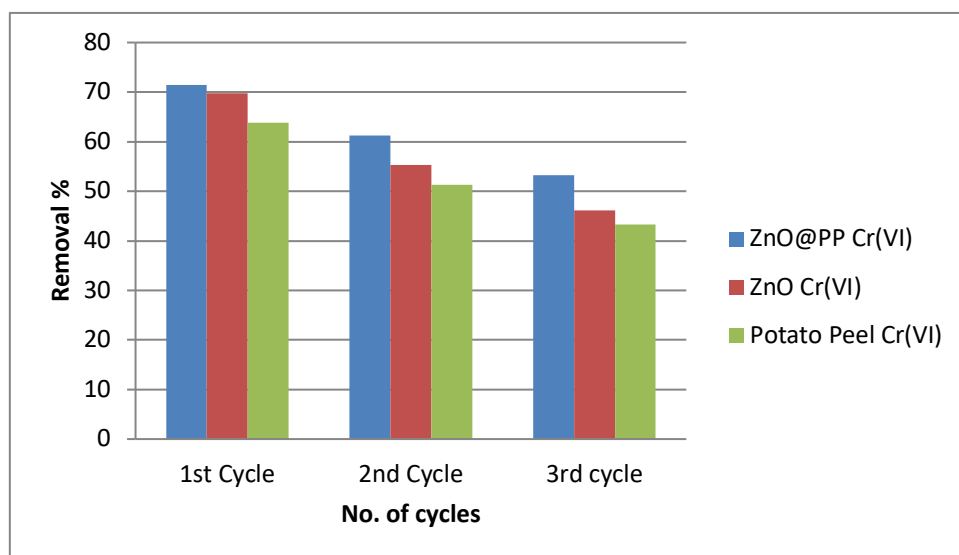


Figure 10 b: Reuse efficiency of Nanoadsorbents for Cr(VI) metal Removal

Conclusions

In this work, ZnO and $\text{ZnO}@PP$ nanoparticles were synthesized successfully using a co-precipitation

approach and exhibited remarkable adsorption capability for copper and chromium under optimized conditions. When compared with previously reported nanoadsorbent materials, the prepared ZnO@PP showed enhanced efficiency for the removal of metal ions from aqueous solutions. The highest adsorption capacities achieved were 128 mg g⁻¹ for copper and 98.88 mg g⁻¹ for chromium. Analysis of equilibrium data revealed a good fit with the Langmuir isotherm model, suggesting uniform monolayer adsorption on a homogeneous surface. Kinetic investigations indicated that the adsorption behavior of both metals followed a pseudo-second-order model, implying that chemisorption is the dominant controlling mechanism. In addition, regeneration studies demonstrated that the ZnO@PP nanoparticles maintained significant adsorption performance over several reuse cycles, confirming their structural stability and reusability. Overall, the results establish ZnO@PP nanoparticles as effective and sustainable nanoadsorbents for the removal of cationic metals from water systems.

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