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Adsorptive removal of Nickel(II) and Chromium(III) from aqueous solutions onto egg shell powder

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Abstract

In the current research work, eggshell powder was utilized as an adsorbent for the adsorptive removal of Ni (II) and Cr (III) in a batch process. Eggshells were purchased from a local market in Peshawar, Pakistan. For the adsorption of the adsorbate Ni (II) and Cr (III) from the aqueous solution, the biosorbent, i.e., Egg Shell Powder, was utilized. Different parameters, such as pH, contact time, initial concentration, and adsorbent dose, were optimized. The value of qe and % removal was determined using the optimal conditions. The optimum pH for the adsorption of both Ni (II) and Cr (III) was found to be 4 and 9, respectively. The optimum contact times for Ni (II) and Cr (II) were 40 and 30 minutes. The optimum adsorbent dose for Ni (II) and Cr (III) was 0.2 & 0.1g. The (q_e) was determined for Ni (II) and Cr (III) at 25 °C with the increase in concentration of adsorbate. The optimum initial concentration for Ni (II) and Cr (III) was found to be 20 ppm and 40 ppm, respectively.

Keywords: metal oxide, adsorption process, environmental remediation, aqueous solution, low-cost biosorbent.

Remoção adsorptiva de Níquel(II) e Cromo(III) de soluções aquosas utilizando pó de casca de ovo

Resumo

No presente trabalho de pesquisa, o pó de casca de ovo foi utilizado como adsorvente para a remoção adsorptiva de Ni(II) e Cr(III) em processo em batelada. As cascas de ovo foram obtidas em um mercado local de Peshawar, Paquistão. Para a adsorção dos adsorvatos Ni (II) e Cr (III) a partir de soluções aquosas, o biossorvente, isto é, o pó de casca de ovo, foi empregado. Diferentes parâmetros, tais como pH, tempo de contato, concentração inicial e dose do adsorvente, foram otimizados. Os valores de qe e da porcentagem de remoção (% de remoção) foram determinados utilizando as condições ótimas. O pH ótimo para a adsorção de Ni(II) e Cr(III) foi de 4 e 9, respectivamente. Os tempos ótimos de contato para Ni(II) e Cr(III) foram de 40 e 30 minutos. A dose ótima do adsorvente para Ni(II) e Cr(III) foi de 0,2 e 0,1 g, respectivamente. O valor de (q_e) foi determinado para Ni(II) e Cr(III) a 25 °C, com o aumento da concentração do adsorbato. As concentrações iniciais ótimas para Ni(II) e Cr(III) foram de 20 ppm e 40 ppm, respectivamente.

Palavras-chave: óxido metálico, processo de adsorção, remediação ambiental, solução aquosa, biossorvente de baixo custo.

1. Introduction

Metal is a material that, when freshly prepared, polished, or fractured, shows a lustrous appearance and conducts electricity and heat relatively well. Metals are typically malleable or ductile. They can also show magnetic behavior. Most of the metals are paramagnetic or ferromagnetic, while a few of them are diamagnetic, such as Ag, Au, and Al. Examples included Sodium (Na), Lithium (Li), Chromium (Cr), Iron (Fe), Iridium (Ir), etc (Ahmed; Abu-Elsaad, 2024; Liu et al., 2021; Pomahoba, 2017). Heavy metals are metals with relatively high densities, atomic weights, or atomic numbers.

Their density is greater than 5 g cm^{-3}, and their atomic mass is usually greater than 40 a.m.u (atomic mass unit). They are present in low concentration in earth crust (Ali; Khan, 2018; Duffus, 2001). While Cadmium (Cd), Arsenic (As), Lead (Pb), Nickel (Ni), Mercury (Hg), and Vanadium (V) are heavy metals found in wastewater (Balali-Mood et al., 2021). Heavy metals are naturally occurring elements, but can be found throughout the Earth's crust. In non-industrial areas, heavy metals source are automobiles and structures with metallic components (Angon et al., 2024). Heavy metals chiefly establish chemically bound in carbonate, sulfate, oxide, or silicate rocks, or also occur in their metallic, elemental form. Heavy metals are introduced into the environment from two main sources, namely natural sources and anthropogenic sources. Their natural sources included weathering of metal-bearing rocks and volcanic eruptions, while their anthropogenic sources included various industrial and agricultural activities (Bello et al., 2023).

Heavy metals are considered to be usual pollutants in urban dust and runoff. Heavy metals are thrown away into the aqueous waste stream from various sources such as battery manufacture, pharmaceutical, mining, tanneries production of paints, pigments, and also include the ceramics and glass industries. Heavy metals are notable environmental pollutants owing to their toxicity, persistence in the environment, and bioaccumulative nature. Usual harmful effects caused by heavy metals include reduced growth and development, nervous system damage, cancer, and organ damage, etc. (Hwang et al., 2016).

Heavy metals like lead and mercury may cause the development of autoimmunity (where a person's immune system attacks the harmless cells of its own body. When the body does not properly metabolize heavy metals, they become toxic and accumulate in soft tissues (Sharif et al., 2024). Heavy metals are disorganizing metabolic functions in two ways: when heavy metal enters the human body, they start disturbing various functions in vital glands and organs such as the heart, brain, kidneys, bone, liver, etc. They displace essential nutritional minerals from their original place, hindering their biological function while the body requires these nutritional minerals for various physiological and biochemical functions (Ungureanu; Mustatea, 2022).

Ni is a silver-white metal and can be found in many oxidation states (ranging from -1 to +4). It is the 24th most abundant element in the earth crust, and extraordinarily, its concentration is rising. Ni is a member of the outer transition elements belong to group VIIIB and found in a combined state with other elements in ores. Ores have two important groups, i.e., laterites (oxides or silicate ores, e.g., garnierite $(NiMg)\ 6Si_4O_{10}(OH)_8$) and sulphides, pentlandite $(Ni, Fe)_9S_8$. Nearly 1.5 % nickel is found in a combined state with copper, cobalt, and other metals (Barceloux; Barceloux, 1999). There are two main sources by which Ni is launched into the environment. From two main sources, namely natural sources and anthropogenic sources. The natural sources of Ni emission include forest fire, windblown dust, volcanic emission, vegetables, weathering of rocks and soil. Anthropogenic sources included paints, batteries, and electroplating discharge, mining, and production of stainless steel (Harasim, 2018).

Ni in licit level is not dangerous, but when it go outstrip from its licit level, it leads to serious problems in both plants and animals, including human being e.g. lead to cancer of the lung, nose, and bone when its concentration is high. Nickel at high levels also influences the metabolism of essential metals such as Mg (II), Ca (II), Fe (II), Zn (II), or Cu (II). They may also lead to enzyme inhibition when they replace other metal ions in enzymes and proteins (Genchi et al., 2020). Cr is considered the 22nd most abundant element in earth crust. Its atomic number is 24, and it is the first element in group 6. They are found in a wide range of oxidation states. Common oxidation states of Cr comprise $^{+3}$ and $^{+6}$. They rarely exist in $^{+1}$, $^{+4}$, and $^{+5}$ oxidation states (Gul et al., 2025).

Chromium has three stable states of isotopes, i.e., Cr^{52}, $Cr^{53,}$ and Cr^{54}. While Cr^{52} is most stable among them due to the natural abundance of 83.789%. Chromium exists in the form of ores, i.e., iron chromium oxide $FeCr_2O_4$.and chromite. Cr behave paramagnetic above 38 °C (Shah et al., 2024). Chromium (III) is a natural element that can be found in nature, such as rocks, animals, plants, soil, volcanic dust, and gases. Meanwhile, when weathering of rocks occurs, then Cr is discharged into the environment, while volcanic eruption may also cause the discharge of Cr into the environment (Amir et al., 2024). Cr (III) in authorized level is not dangerous, but when exceeded/outstrip from its authorized level, it becomes harmful to living things. Chromium at high concentrations can damage DNA. When Cr enters the bloodstream, it starts damaging the blood cells by causing oxidation reactions.

Kidney and liver failure can also be caused by this oxidative damage. In dyes, paints, and leather tanning, Cr is present, and when it leaks to soil and water, it can cause environmental pollution, etc. (Kashif et al., 2023). Heavy metal pollutants are dangerous, and their presence in water bodies can cause serious health problems. nowadays removal of heavy metals is the main focus of scientists to save the environment from its harmful effects. For the treatment and removal of heavy metals, many methods have been developed. Usual methods used for removing metal ions from aqueous streams are chemical precipitation, reverse osmosis, solvent extraction, lime coagulation, filtration, and ion exchange (Kashif et al., 2024).

In Ultrafiltration, pressure-driven membrane operations with porous membranes are used for the removal of heavy metals. Wastewater treatment and water reuse systems use this technique. Using this technique, the amount of treatment chemicals and labor requirements can be reduced. It also has certain drawbacks, like it needs more electricity, requires replacement of membranes, and may need pre-treatment (Kashif et al., 2024). The ionic components (heavy metals) are separated using selective semipermeable ion membranes in this method. Application of a high voltage between the two electrodes leads to migration of cations and anions towards their respective electrodes. Because of the alternate spacing of cation and anion permeable membrane, dilute salts and concentrated cells of concentrated solutions are formed. The formation of metal hydroxides, which clog the membrane, is a disadvantage of this method (Khan et al., 2025).

It involves the exchange of ions between the ions present in the dilute solution and the ions held by electrostatic forces on the exchange resin. Adsorption of organic matter, chlorine, and bacterial contamination, corrosion, High cost, and also partial removal of certain ions is disadvantage of this method (Khan et al., 2025). Chemical precipitation For heavy metal removal from inorganic effluent it is the most widely used. By the addition of precipitating agents such as alum, lime, iron salts, and other organic polymers, precipitation of metals can be accomplished. They also involve chemical reactions of metal cations in wastewater with precipitating agents. Use of large coagulants and formation of sledge is a drawback of this method (Kalsoom et al., 2025).

It destabilizes colloidal particles by adding a coagulant. The addition depends upon the treating material. Most commonly used coagulants are alumina, ferrous sulphate, and ferric chloride. The coagulant forms hydroxides and oxides upon reaction with impurities and waste material. Quite expensive and disturbs the natural composition of water, which comes under the drawback of this method (Trus et al., 2023). Phytoremediation employed use of certain plants to clean up water contaminated with metals, sediment, and soil. Regeneration of the plant for further bio sorption and is a time-consuming process and comes under its drawbacks (Madhav et al., 2024). In reverse osmosis, is Heavy metals are separated by a semi-permeable membrane at a pressure greater than the osmotic pressure caused by the dissolved solids in wastewater in this process.

Restoration of the membrane and usage of extensive power are major drawbacks of this method. Adsorption is the best method to remove toxic metals from wastewater. The adsorption process occurs when a liquid or gas solute accumulates on the surface of a solid. The adsorption process involves the removal of substances from a liquid to solid surface and is both a chemical and physical process. Adsorbent is referred to as the solid surface upon which absorption occurred and the sticking material is referred to as the adsorbate. The adsorption process is widely used in industrial applications such as the purification of water, activated charcoal, and synthetic resins. While at the molecular level, the adsorption process occurs due to attractive interactions between a surface and the species being adsorbed (Hussain et al., 2021).

Physical adsorption is due to intermolecular (van der Waals) forces of attraction between molecules of the adsorbent and the adsorbate; chemical adsorption involves chemical interaction between the adsorbed substance and the solid. Large sludge production, time-consuming, low absorption, and the expenses of adsorbents are among its drawbacks. The method involves a solid phase (bio-sorbent) and a liquid phase (solvent) containing a dissolved species to be adsorbed (Aljamali et al., 2021). For the removal of heavy metals, many biosorbents have been used (Igwe & Abia, 2006). For the removal of copper, zinc, and lead with qe values of 10.37, 15.59, and 46.69 mg $g^{-1,}$ respectively, aquatic plant *Myriophyllum spicatum* was used as bio sorbent (Milojković et al., 2014).

The seaweed Darville potato rum is used as a bio-sorbent for Ni removal with a qe value of 1.13 mg g^{-1}. *Trichoderma viride* was employed for the removal of Ni(II) from aqueous solution with qe 47.6 mg g^{-1}. Protonated Rice Bran was used to remove Ni(II) from aqueous solution with qe 102 mg g^{-1}. Similarly, biomass of *Oscillatoria* sp. was employed to remove Co(II) from aqueous solution with qe 30.12 ± 0.10 mg g^{-1}. Biosorption of Co(II) from aqueous solution was carried out by using *Acinetobacter baumannii* and

Pseudomonas aeruginosa with qe values of 8.8 and 5.7 mg $g^{-1,}$ respectively. Low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent, and possibility of metal recovery are the major advantages of this method (Fiset et al., 2008).

Heavy metal contamination of water resources has emerged as a serious environmental and public health challenge due to intensified industrial activities such as electroplating, leather tanning, mining, metal finishing, and pigment production. Among these contaminants, Ni(II) and Cr(III) are frequently detected in industrial effluents and can accumulate in aquatic environments, leading to toxic, carcinogenic, and bioaccumulative effects upon prolonged exposure. Although Cr(III) is considered less toxic than Cr(VI), elevated concentrations still pose ecological and health risks, while Ni(II) is associated with allergic reactions and carcinogenicity. Conventional treatment technologies, including chemical precipitation, membrane filtration, and ion exchange, are often limited by high operational costs, energy consumption, and secondary waste generation, particularly when treating wastewater containing low concentrations of metal ions.

Adsorption has gained increasing attention as an efficient and economical alternative for heavy metal removal; however, the high cost of commercial adsorbents restricts large-scale implementation. Consequently, the development of low-cost, sustainable, and environmentally friendly adsorbents derived from waste materials has become a research priority. Eggshell waste, an abundant byproduct of the food industry, is primarily composed of calcium carbonate and exhibits surface characteristics favorable for metal ion adsorption. Utilizing eggshell powder as an adsorbent not only provides an effective approach for removing Ni(II) and Cr(III) from aqueous solutions but also supports waste valorization and sustainable environmental management. Therefore, this study aims to investigate the adsorption performance of eggshell powder toward Ni(II) and Cr(III), highlighting its potential as a cost-effective and eco-friendly material for wastewater treatment application

2. Materials and Methods

2.1 Instruments, glassware, and reagents

Various chemicals and reagents used in the present research work include $Ni(NO_3)_2.6H_2O$, $Cr(NO_3)_3.9H_2O$, Dimethyl Glyoxime (DMG) solution, Ammonia (33%), NH_4Cl, HCl (37%), NaOH (98%), and Na_2 EDTA. Glassware and apparatus used in the current study included beakers, test tubes, funnels, conical flasks, pipettes, graduated cylinders, spatulas, cork, cylinder, stand, thermometer, pestle, and mortar.

2.2 Equipament

The instruments used in the current research comprised, UV visible Spectrophotometer with path length of 1 cm, Quartz cell (S2100 UV Spectrophotometer, UNICO, USA), digital balance, (ATX 224, Shimadzn, Japan), Orbital shaker (KJ-201bs Oscillator, South Korea), hot plate and magnetic stirrer, (MS-300Hs, Scientific Ltd, South Korea), Digital pH meter (3505, Jenway, UK), Oven (IdO-030E, Diahan Lab Tech Co Ltd, South Korea) and Heavy duty electric grinder.

2.3 Preparation of adsorbent

Collection and pretreatment: Egg shells were brought from a local market in Peshawar, Pakistan. The shells of eggs were washed with tap water for cleaning purposes, after being washed with warm water, and then dried in the sunlight. For complete drying, the shells were placed in the ground under the sunlight for 2 days. The dried shells were ground 2-3 times using a heavy-duty electric grinder to make their powder.

2.4 Adsorption study

2.4.1 Preparation of adsorbate solutions

2000 mg L^{-1} and 3000 mg L^{-1} of stock solutions of $Ni(NO_3)_2$ and $Cr(NO_3)_3$ were prepared by adding 2.018 g and 3.47 g, respectively, in 100 mL of distilled water. Dilute solutions were prepared using the dilution formula 1.

$$C_cV_c = C_dV_d \qquad (1)$$

2.4.2 Determination of adsorbate concentration

2.4.2.1 Spectrophotometric determination of Ni(II)

For the spectrophotometric determination of Ni (II), an already reported method was employed. For this purpose, a series of Ni(II) solutions was prepared (10, 20, 30, 40, 50, and 60 ppm). A 50 mL volumetric flask contained 7 mL of adsorbate solution, 2 mL of buffer solution (pH 9.5), and 1 mL of 0.5% dimethyl Glyoxime (DMG) solution (prepared by dissolving 0.5 g of DMG in 100 mL of Ethanol). The solutions were mixed thoroughly and were allowed to stand for five minutes at room temperature. The absorbance of mixed solutions was measured at 530 nm (Topuz et al., 2017).

2.4.2.2 Spectrophotometric determination of Cr (III)

A series of sample Cr(III) solutions were prepared (5, 10, 15, 20, 25, and 30 ppm). 5 mL of each prepared Cr(III) solutions were taken in a test tube and 5 mL of 0.5 % freshly prepared Na_2 EDTA was added to the test tube (dissolve 0.5 g of Na_2 EDTA per 100 mL of distilled water). Put the test tube in a beaker with boiling water placed on a hot plate for 10 min. The test tube was made cool, and absorbance was find against 552 nm (Dawra; Dabas, 2024).

2.5 Factors affecting batch biosorption

2.5.1 Effect of pH on the aqueous solution

For obtaining optimum pH, 20 mL of selected adsorbate solutions (each having a concentration of 20 ppm) were taken in seven separate 100 mL volumetric flasks with pH 3, 4, 5, 7, 9, 10, and 11. For the adjustment of pH, 0.1 M HCl solution and 0.1 M NaOH were prepared. An adsorbent dose of 0.2 g was added to each flask and was shaken at 120 rpm for 1 h using an orbital shaker. The concentration of selected adsorbates was determined in the same way as discussed in section 2.5.2. The amount of selected adsorbates adsorbed per unit mass of adsorbent (q_e) was measured using the formula (2) (Lewis, 1988):

$$Q_e = (C_i - C_f/W)*V \qquad (2)$$

Where: Ci and Cf are the initial and final concentrations of the selected adsorbates before and after adsorption, respectively. V is the volume of selected adsorbates in liter and W is the weight of selected adsorbent in milligrams (mg). % adsorption was determined as formula 3:

$$\%\ \text{adsorption} = (Ci - Cf/Ci)*100 \qquad (3)$$

For obtaining the optimum value of pH, the result was plotted as pH vs qe and % adsorption.

2.6 Effect of adsorbent dose

For this purpose, 20 mL of selected adsorbate solution (each having a concentration of 20 ppm) was taken in seven separate 100 mL volumetric flasks with an adsorbent dose ranging from 0.1 to 0.7 g, maintaining the optimized pH 4 and pH 9 for Ni(II) and Cr(III), respectively. The mixture was shaken in an orbital shaker at 120 rpm for 1 h. The rest of the procedure was the same as discussed in the section 2.5.3.1. For obtaining the optimum value of adsorbent dose, the result was plotted as adsorbent dose (g) vs qe and % adsorption (Prasetyo, 1992).

2.7 Effect of contact time

For the optimum value of contact time, 20 mL of adsorbate solution (each having a concentration of 20 ppm) was added in seven separate 100 mL volumetric flasks with optimum adsorbent dose 0.2 and 0.1 g for Ni(II) and Cr(III), respectively. The optimum pH for Ni(II) and Cr(III) was 4 and 9, respectively. The solutions mixture was shaken for different periods of time, i.e., 10, 20, 30, 40, 50, 60, and 70 min, while the speed of the orbital shaker was kept constant, i.e., 120 rpm. The remaining procedure was the same as mentioned in section 2.5.3.1. For the optimum value of contact time, the result was plotted at initial concentration (ppm) vs q_e and % adsorption (Prasetyo, 1992).

2.8 Effect of initial concentration

For obtaining the optimum value of initial concentration, 20 mL of selected adsorbates solution with different concentrations (10, 20, 30, 40, 50, 60, and 70 ppm) were taken in seven different volumetric flasks (100 mL). Adsorbent doses of 0.2 and 0.1 g, contact time of 40 and 30 min, and pH of 4 and 9 were selected as optimized values of operation for Ni(II) and Cr(III), respectively. The selected mixture was shaken on an orbital shaker at a speed of 120 rpm. The rest of the procedure was the same as discussed in 2.5.3.1. To get the optimum value of initial concentration, the result was plotted as initial concentration (ppm) vs q_e and % adsorption (Prasetyo, 1992).

3. Results

3.1 Spectrophotometric determination of Ni(II)

The spectrophotometric determination of Ni(II) was performed using an already reported method. For this purpose, various solutions of selected adsorbate with known concentrations (10, 20, 30, 40, 50, and 60 ppm) were prepared (Figure 1). For the spectrophotometric determination of Ni(II) solution, 0.5% DMG and pH 9.5 buffer solution were mixed in a suitable proportion already mentioned, in a 50 mL volumetric flask. The absorbance was determined at 530 nm. The results illustrated that the increase in concentration led to an increase in absorbance. The unknown concentration of adsorbate Ni (II) was found using a straight line equation, i.e., y = mx + c, where y is absorbance, m is slope, and c is intercept. The slope m and correlation coefficient (R^2) obtained were found to be 0.0008 and 0.994.

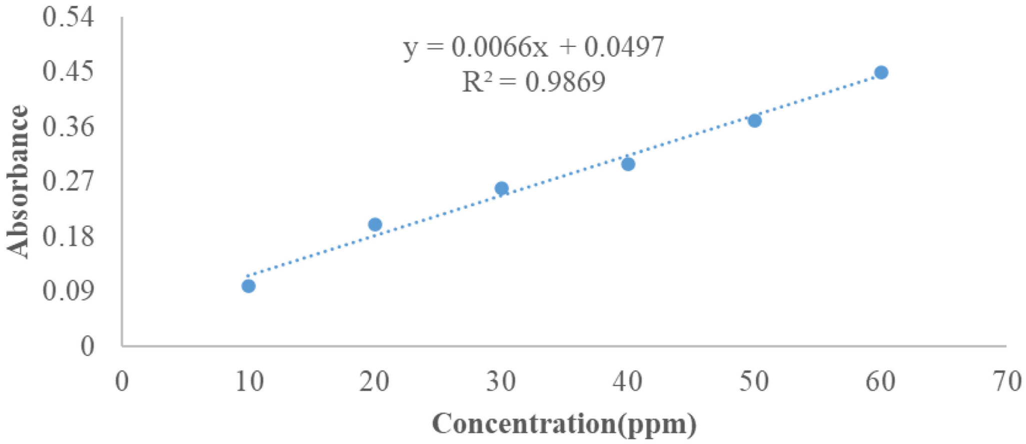

Figure 1. Spectrophotometric determination of Ni(II). Source: Authors, 2025.

3.2 Spectrophotometric determination of Cr(III)

The Spectrophotometric determination of Cr(III) was made using an already reported method with little modifications (Rekka et al., 2007). To determine the concentration of Cr(III) solutions of various concentrations (10, 20, 30, 40, 50, and 60 ppm) were prepared (Figure 2). 5 mL of Cr(III solution was taken in a flask and 5 mL of prepared 0.5% Na_2EDTA solution (dissolving 0.5 g Na_2EDTA in 100 mL water) were added to it to make a total of 10 mL mixture. The absorbance was measured at 552 nm. The results showed that absorbance increases with an increase in concentration. The concentration of adsorbate Cr(III) was found using a straight line equation, i.e., y = mx + c, where y is the absorbance, m is the slope, and c is called the intercept. The slope m and correlation coefficient (R^2) obtained were found to be 0.0003 and 0.9331, respectively.

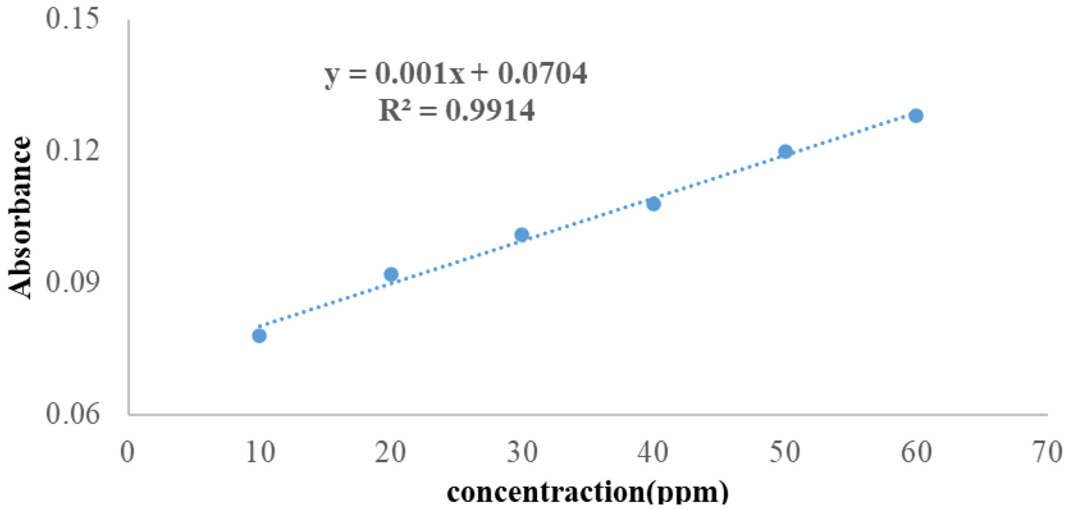

Figure 2. Spectrophotometric determination of Cr(III). Source: Authors, 2025.

3.3 Factors affecting biosorption experiments

3.3.1 Effect of pH

The influence of pH on the adsorption of Ni(II) and Cr(III) onto the shells of Egg was studied over the pH range of 3, 4, 5, 7, 9, 10, and 11 (Table 1). The result showed that the adsorption of Ni(II) and Cr(III) depends upon pH. In the case of Ni(II), an increase in pH leads to an increase in absorption capacity and reach to maximum level at pH 4. At higher pH values, there is reduced competition between hydrogen ions and metal ion which enhances the adsorption capacity of the adsorbent for metal ions. While in the case of Cr(III), the absorption capacity also increases with an increase in pH and attained maximum level at pH 9.

Table 1. Effect of pH on the adsorption of Ni(II) and Cr(III).

s.no.	pH	Ni(II)		Cr(III)	
		q_e (mg g^{-1})	% Adsorption	q_e (mg g^{-1})	% Adsorption
1	3	3.234	32.348	3	30
2	4	8.537	85.378	4.5	45
3	5	8.083	80.833	8.5	85
4	7	6.946	69.469	5.5	55
5	9	5.431	54.3181	4.5	45
6	10	3.916	39.166	3	30
7	11	1.643	16.439	2	20

Source: Authors, 2025.

The entire surface of the adsorbent is converted into a positive charge that leads to a strong interaction that can be depicted from (Figure 3 A and B). The result was plotted as pH vs q_e and % removal.

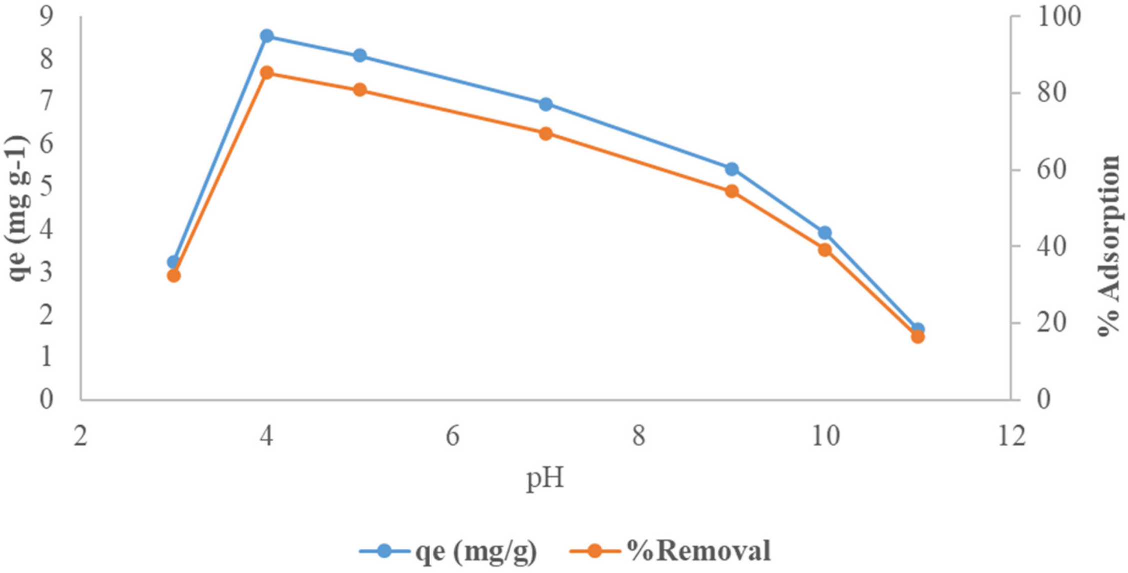

Figure 3. Effect of pH on the adsorptive removal of (A) Ni(II). Source: Authors, 2025.

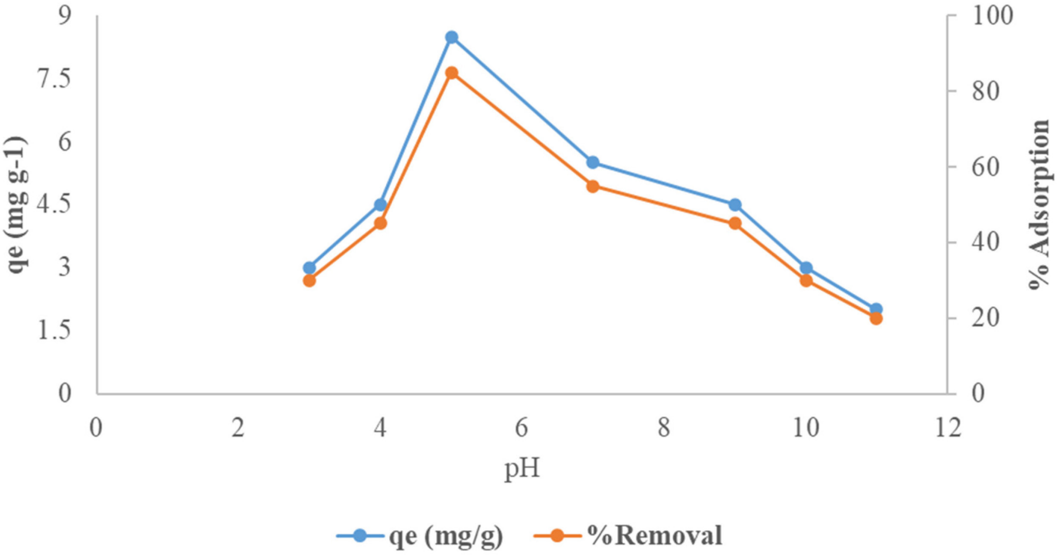

Figure 3. Effect of pH on the adsorptive removal of (B) Cr(III). Source: Authors, 2025.

3.4 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Ni(II) and Cr(III) was studied using different eggshell dosages in the range of 0.1 g to 0.7 g (Table 2). It was confirmed that adsorption of Ni(II) is maximum at an adsorbent dose of 0.2 g; there was no prominent change observed in % adsorption as the adsorbent dose was further increased, which can be credited to the fact that the saturation point was reached. For Cr(III), the optimum value of adsorbent dose was 0.1 g, at which there have been maximum number of active sites for the adsorbent. These optimum values of adsorbent dose were selected for more experiments as depicted in (Figure 3 A and B). The result was plotted as adsorbent dose vs qe and % adsorption.

Table 2. Effect of adsorbent dose on Ni(II) and Cr(III).

s.no	Absorbent dose (g)	Ni(II)		Cr(III)	
		qe (mg g^{-1})	% Removal	qe (mg g^{-1})	% Removal
1	0.1	8.462	84.621	7.5	75
2	0.2	3.473	69.469	2.75	55
3	0.3	2.063	61.893	1.5	45
4	0.4	1.168	46.742	0.875	35
5	0.5	0.631	31.5901	0.5	25
6	0.6	0.273	16.439	0.166	10
7	0.7	0.126	8.863	0.071	5

Source: Authors, 2025.

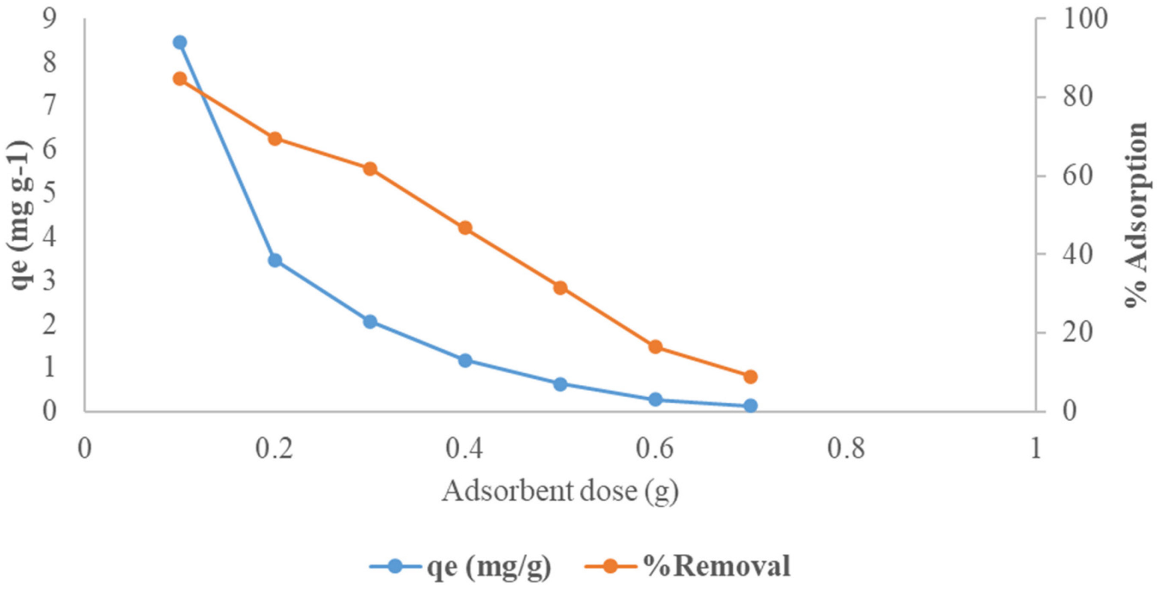

Figure 4. Effect of adsorbent dose on the adsorptive removal of (**A**) Ni(II). Source: Authors, 2025.

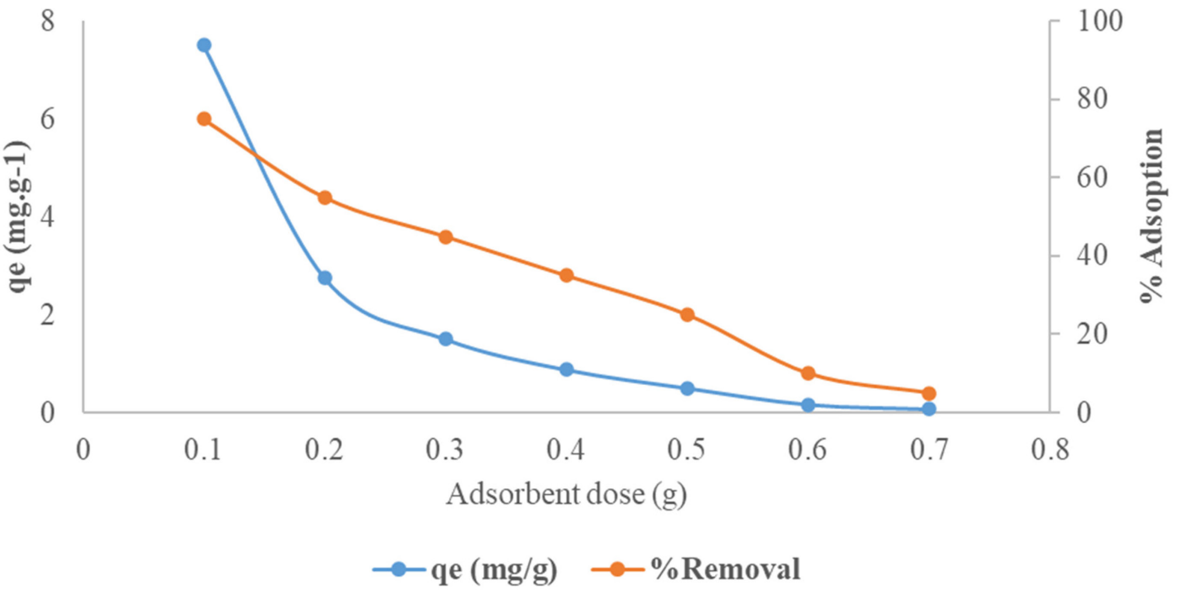

Figure 4. Effect of adsorbent dose on the adsorptive removal of (**B**) Cr(III). Source: Authors, 2025.

3.5 Effect of contact time on adsorption

Contact time is one of the effective factors in the batch adsorption process. To analyze the influence of contact time on the adsorption of Ni(II) and Cr(III), different contact timings were selected, ranging from 10 min to 70 min. The result depicted that the adsorption of Ni(II) increases with an increase in contact time and reaches a maximum value at a contact time of 40 min for Ni(II), and the optimum contact time for Cr(III) is 30 min. Beyond these optimum values, the saturation limit is reached, and there is no further effect on the adsorption activity. Contact times of 40 min and 30 min were selected for Ni(II) and Cr(III), respectively, for imminent experimental parameters as shown in (Figure 4 A and B). The result was plotted as contact time vs qe vs % adsorption.

Table 3. Effect of contact time on Ni(II) and Cr(III).

s. no	Contact time	Ni(II)		Cr(III)	
		qe (mg g^{-1})	% Removal	qe (mg g^{-1})	% Removal
1	10	2.5	25	6.871	68.712
2	20	3.5	35	6.416	64.166
3	30	5	50	7.628	76.288
4	40	8.5	85	6.795	67.954
5	50	7	70	6.568	65.681
6	60	4.5	45	3.992	39.924
7	70	1	10	3.310	33.106

Source: Authors, 2025.

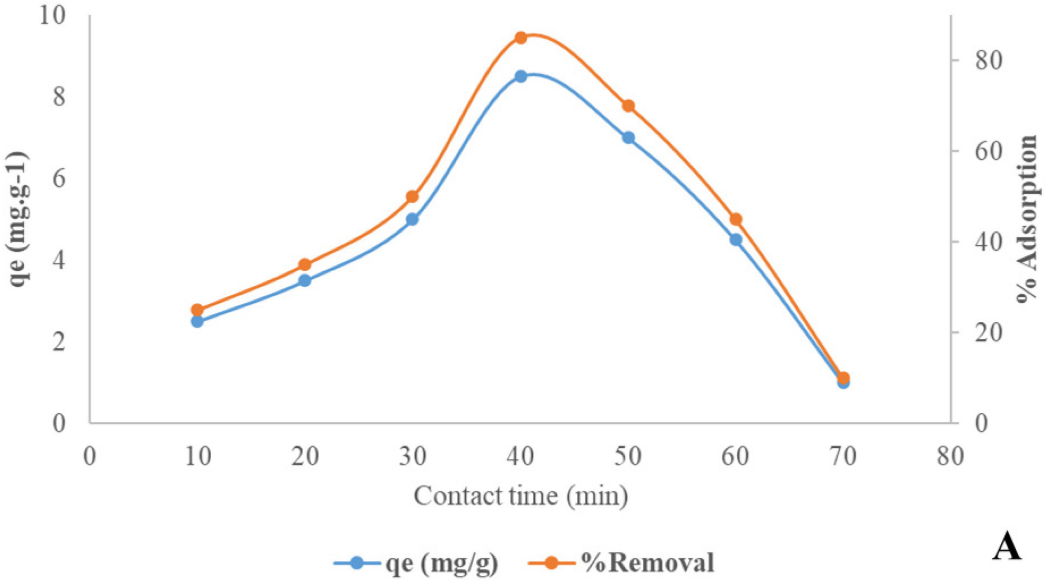

Figure 5. Effect of Contact time on the adsorptive removal of (**A**) Ni(II). Source: Authors, 2025.

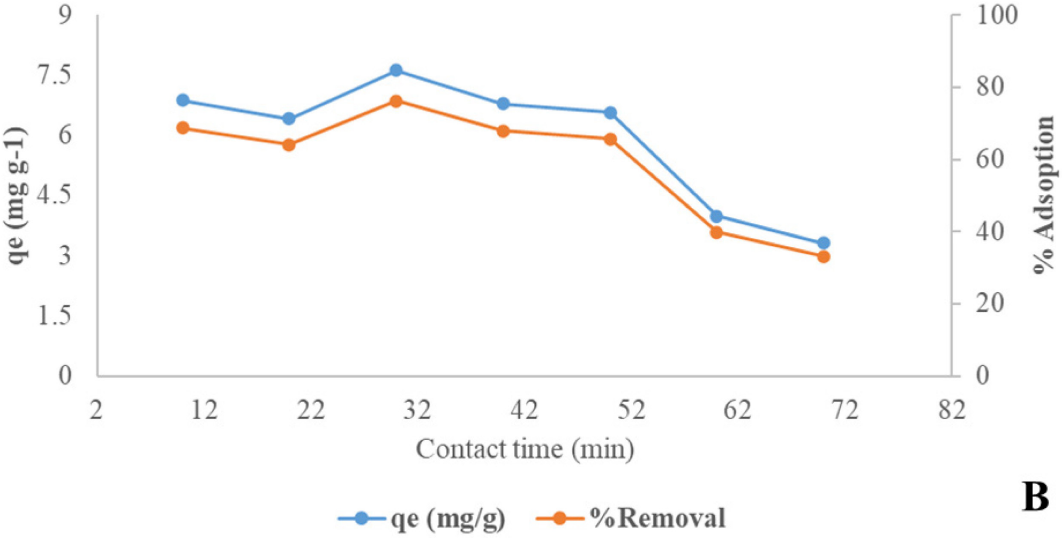

Figure 5. Effect of Contact time on the adsorptive removal of (B) Cr(III). Source: Authors, 2025.

3.6 Effect of initial concentration

Adsorption of Ni(II) and Cr(III) with different initial concentration have been investigated. For the experiment, different initial concentrations (10, 20, 30, 40, 50, 60, and 70 ppm), optimized conditions of pH, adsorbent dose, and contact time were selected. The optimum values for Ni(II) and Cr(III) were 20 and 40 ppm, respectively (Table 4). The adsorption capacity increases substantially with an increase in initial concentration, due to an increase in the number of available active sites. Beyond the optimum values, the saturation point is reached at which metal ions are left unabsorbed in solution.

Table 4. Effect of initial concentration on Ni(II) and Cr(III).

s. no	Initial concentration (ppm)	Ni(II)		Cr(III)	
		qe (mg g^{-1})	% Removal	qe (mg g^{-1})	% Removal
1	10	4.5	45	9.068	90.681
2	20	5.5	55	8.007	80.075
3	30	8.5	85	7.7045	77.045
4	40	3	30	6.871	68.712
5	50	2	20	4.674	46.742
6	60	1	10	3.3106	33.106

Source: Authors, 2025.

Hence, 20 and 40 ppm were selected as optimum initial concentrations for Ni(II) and Cr(III), respectively. The results were plotted as initial concentration vs qe vs % adsorption (Figure 6 A and B).

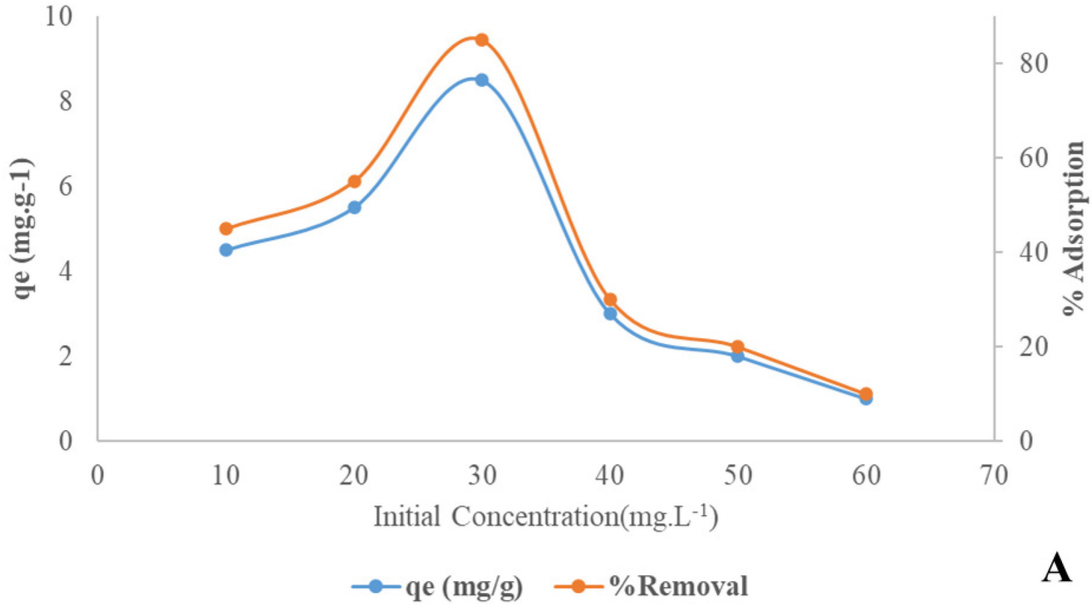

Figure 6. Effect of initial concentration on the adsorption of (**A**) Ni(II). Source: Authors, 2025.

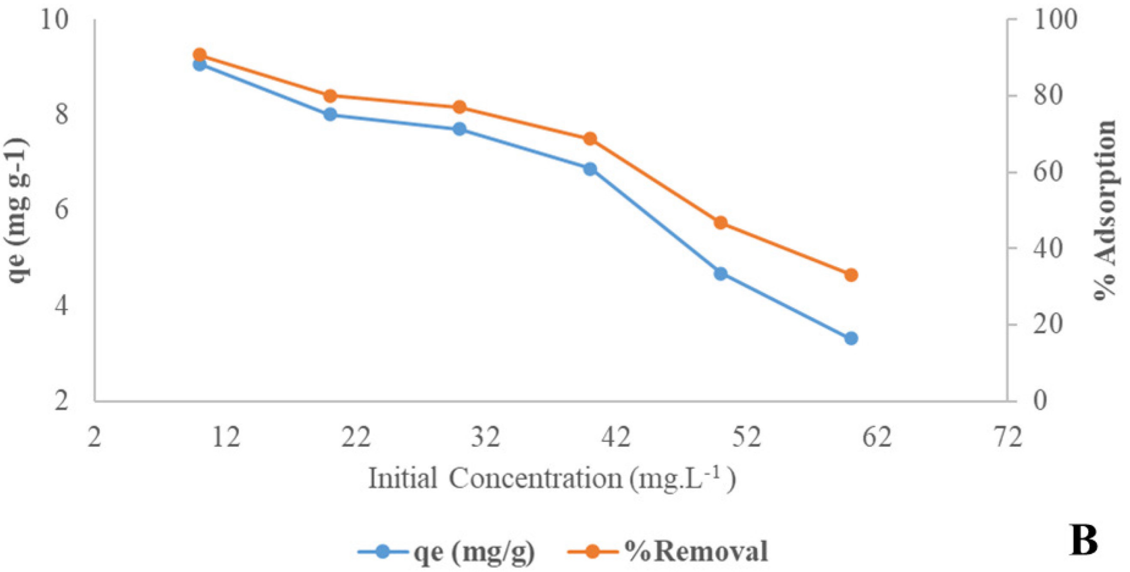

Figure 6. Effect of initial concentration on the adsorption of (**B**) Cr(III). Source: Authors, 2025.

4. Discussion

The adsorption behavior of Ni(II) and Cr(III) onto eggshell powder was strongly influenced by solution pH, which governs both metal ion speciation and the surface charge of the adsorbent. The optimum pH of 4 for Ni(II) adsorption may be attributed to favorable electrostatic interactions between Ni^{2+} ions and negatively charged functional groups, primarily carbonate and hydroxyl groups, present on the eggshell surface. At lower pH values, competition between hydrogen ions and Ni(II) for active adsorption sites reduces metal uptake. In contrast, at higher pH values, partial precipitation of nickel hydroxide may occur, limiting true adsorption. In contrast, the optimal adsorption of Cr(III) at pH 9 can be explained by reduced competition from protons and enhanced surface complexation, as well as possible formation of hydrolyzed chromium species that exhibit stronger affinity for the eggshell surface (Abatan et al., 2020).

The contact time studies indicated rapid adsorption during the initial phase, followed by equilibrium attainment within 40 min for Ni(II) and 30 min for Cr(III). This behavior suggests that adsorption initially occurs on readily available external surface sites, after which intraparticle diffusion and site saturation become rate-limiting. The relatively short equilibrium times reflect the porous nature of eggshell powder and the high accessibility of active sites, indicating efficient interaction between the metal ions and the biosorbent. Similar rapid adsorption kinetics have been reported for other calcium carbonate–based biosorbents, supporting the suitability of eggshell powder for practical wastewater treatment applications (Shi et al., 2009).

The increase in removal efficiency with increasing adsorbent dosage is attributed to the greater availability of surface area and active binding sites. However, beyond the optimum dosages of 0.2 g for Ni(II) and 0.1 g for Cr(III), the adsorption efficiency showed minimal improvement, likely due to particle aggregation and overlapping of adsorption sites, which reduces effective surface area. Furthermore, the observed increase in adsorption capacity (q_e) with rising initial metal ion concentration can be explained by the higher concentration gradient, which enhances mass transfer and promotes greater interaction between metal ions and the adsorbent surface. The identification of optimal concentrations (20 ppm for Ni(II) and 40 ppm for Cr(III)) indicates efficient utilization of available adsorption sites before saturation occurs (Al-Ghouti et al., 2010).

Overall, the adsorption performance of eggshell powder demonstrates its potential as a low-cost, sustainable, and effective biosorbent for the removal of Ni(II) and Cr(III) from aqueous solutions. The differences in optimal conditions for the two metal ions highlight the role of metal-specific chemistry and adsorption mechanisms. These findings support the feasibility of eggshell waste valorization for heavy metal remediation and contribute valuable insight into environmentally friendly wastewater treatment strategies.

5. Conclusions

The results of this study clearly demonstrate the pivotal role of solution chemistry in governing the biosorption efficiency of eggshell powder for the removal of Ni(II) and Cr(III) from aqueous media. The adsorption behavior exhibited a strong dependence on pH, with optimal removal efficiencies achieved under acidic conditions (pH 4) for Ni(II) and alkaline conditions (pH 9) for Cr(III), reflecting the influence of metal speciation and surface charge interactions. Deviations from these optimal pH ranges resulted in a marked reduction in adsorption performance.

Adsorbent dosage was identified as another critical factor influencing metal uptake. Increasing the mass of eggshell powder enhanced the removal efficiency up to an optimal dosage of 0.2 g for Ni(II) and 0.1 g for Cr(III), beyond which no significant improvement was observed, likely due to site saturation and particle aggregation effects.

The adsorption process exhibited rapid kinetics, with equilibrium attained within 40 min for Ni(II) and 30 min for Cr(III), highlighting the operational efficiency and practical applicability of eggshell powder as a biosorbent. Furthermore, adsorption capacity increased with rising initial metal concentrations, reaching maximum uptake at 20 mg L^{-1} for Ni(II) and 40 mg L^{-1} for Cr(III), followed by a decline at higher concentrations, indicating limitations associated with the finite number of available active sites.

Overall, these findings underscore the potential of eggshell powder as a sustainable, low-cost, and efficient biosorbent for the remediation of heavy metal–contaminated waters. The valorization of this abundant agro-industrial waste aligns with circular economy principles and offers an environmentally friendly strategy for wastewater treatment and resource recovery. Future studies focusing on regeneration, reuse cycles, and application in complex effluents are recommended to validate its large-scale applicability further further.

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7. Authors' Contributions

Ajmal Shah and Balqees Khan: conceived and designed the study and contributed equally to this work. *Nimra Ali*, *Saroosh Wazir*, and *Maaz Ahmad*: carried out the experimental work and collected the data. *Adnan Khalid*: provided technical support and methodological guidance. *Ume Aiman*: performed data analysis and interpretation. *Amna Yousaf*: assisted in materials preparation and experimental support. *Syed Adnan*: contributed to manuscript review, editing, and validation of the results. All authors discussed the results, critically revised the manuscript, and approved the final version for publication.

8. Conflicts of Interest

No conflicts of interest.

9. Ethics Approval

Not applicable.

10. References

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