

# EFFECTIVE REMOVAL OF COBALT FROM AQUEOUS SOLUTIONS USING CLAY AND IRON-SUPPORTED COMPOSITE HYBRIDS

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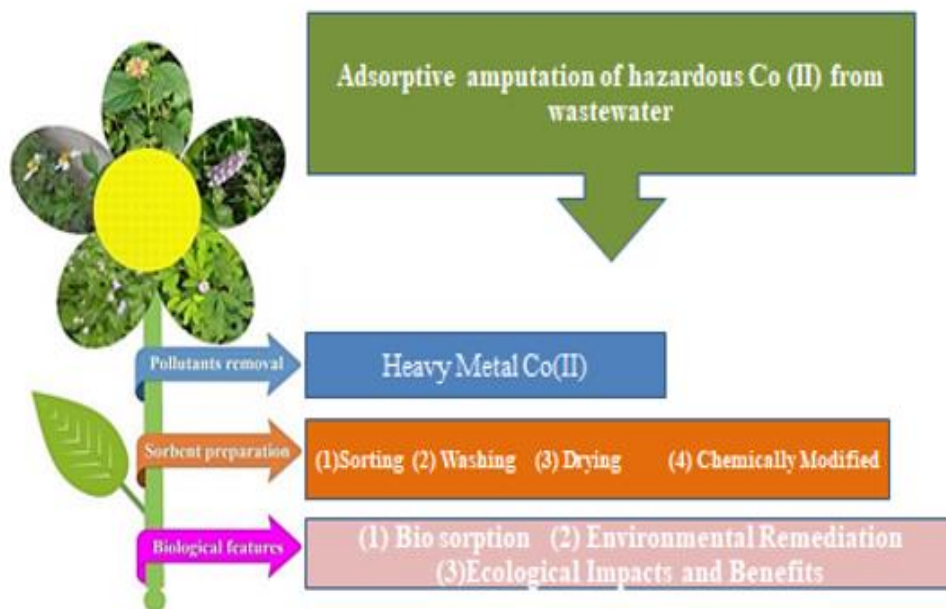
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### Abstract

Water pollution is one of the major and widespread problems throughout the world affecting plants as well as human beings. Heavy metals adsorb readily onto the nonliving biomass of many aquaphytes. Biosorption of heavy metals from aqueous solutions is a technique for the treatment of industrial wastewater. Biosorption of Co (II) metal from the aqueous medium by modified Brassica Napus leaves (BNL) was examined for preliminary pH, initial metal absorption, and contact time. The most favorable sorption circumstances were studied for this metal discretely. The Chemical adaptation of biomass is carried out with an oxidizing agent ( $KMNO_4$ ). The kinetics and equilibrium models were applied to the data. The observed value was analyzed using simple linear regression. Studies showed that pretreatment of biomass dominated over all other clay and iron-supported composite hybrids. The Langmuir and Freundlich equilibrium adsorption models were investigated and observed to fit the data. The Freundlich model gave a better fit than the Langmuir model with an  $R^2$  value of 0.9999. The kinetic study revealed that adsorption was fast in the first 60 minutes and equilibrium was achieved after 120 minutes for heavy metal. Pseudo-second-order reaction model best describes the adsorption process.

**Keywords:** Brassica Napus, Composite Hybrids, Clay and Iron-Supported Biomass, Wastewater,  $KMNO_4$  Pretreatment.

## Graphical Abstract



## 1. INTRODUCTION

Heavy metal pollution arises from different sources as a result of industrial actions and scientific improvement but most commonly is due to the purification of metals. Discharge of the heavy metals in the water bodies because of anthropogenic actions is the most important water pollution source. Most of the metals Cobalt, Zinc, Copper, Nickle, Lead, and Mercury are frequently detected in engineering wastewater that also cause harmful effects on human beings, which instigate battery construction, tanneries, oil refining, smear manufacture, pesticides, dye manufacture, printing, and picturesque industries, etc. (Kadirvelu et al., 2001).

Heavy metals must be removed before discharge because, unlike organic wastes, heavy metals are non-biodegradable build-up in gulps of air tissues and are responsible for various diseases and disorders (Namasivayam and Ranganathan, 1995). Heavy metals are steely-gray, shimmering, and rigid metals. Everyone is unwrapping to the fundamentals of small levels of metals in the atmosphere, stream, and foodstuff.  $2\text{gdm}^{-3}$  of metals in consumption water has been estimated.

Heavy metals have both advantageous and destructive special effects on physical conditions. Important natural sources of metals in the atmosphere are loam, grime, and marine irrigate. Sensitive metal poisoning causes dangerous health hazards in humans like asthma, failure of the heart, and harm to the liver and thyroid (Rengaraj and Moon, 2002).

Many physicochemical techniques urbanized in favor of the eradication of heavy metals from aqueous solutions, such as mining, ion exchange, chemical rainfall, and crust intake partition process. Biosorption is another established technique for the exclusion of heavy metals from aqueous solutions (Perez et al., 2009).

Bio sorption is the potential of dynamic sites on the shell of biomaterials to connect and deliberate metals from even the most adulterated aqueous solutions. The efficiency of biomass depends on factors such as several sites on the biosorbent matter, their ease of access, and their chemical state such as the availability and the resemblance between sites and heavy metals (Volesky, 1999).

The largest advantages of biosorption are the low working rate, chemical capacity to minimize disposal of organic slush, and a large number of competencies in detoxifying very thin effluents (Pan et al., 2006). Physical pretreatment methods such as heat, autoclaving, glacial, ventilation, baking, and substance pretreatment through alkali and organic chemicals showed improvement and diminution in metal bio adsorption (Zubair et al., 2008).

Brassica Napus is a leafy green vegetable belonging to the family Brassicaceae, it's commonly called rapeseed. It is the third largest source of vegetable oil in the world (behind palm oil and soybean oil). Brassica Napus is grown for edible kale-like salad greens. Brassica Napus leaves grow to 100 cm in height with hairless, fleshy, pinnatifid, and glaucous lower leaves which are stalked whereas the upper leaves have no petioles.

The rapeseed pods are green and elongated silique during development that eventually ripens to brown. Brassica Napus is one of the cultivated medicinal food plants in Middle Asia, North Africa, and West Europe. In traditional Iranian medicine, the root parts of this plant were used for therapeutic properties such as a diuretic, anti-scurvy, anti-inflammatory of the bladder, and anti-goat (Hajihashemi et al., 2019).

To find a different, more affordable, and more effective adsorbent material for the sequestration of Co (II) from water, clay, Brassica Napus leaves and iron salt were combined to create composite hybrids. The use of iron salt, also known as magnetic compounds, in the adsorbent manufacturing process enhanced the composite's binding, porosity, and adsorption capabilities.

An amazing adsorbent can be produced by combining the exceptional adsorptive qualities of clay with the functional groups found in biomass, such as leaves of Brassica Napus. The affordability and accessibility of the precursors (Brassica Napus leaves and clay), the use of green chemicals, the lack of energy usage, and the simplicity of the synthetic process were all taken into account during the hybrid's formation. The adsorption properties of the composite hybrids were investigated by altering the solution's pH, contact time, and metal ion concentration.

The purpose of this stuff will be to conclude the effect of element pretreatment and iron support for heavy metals elimination from biomass and to charge the changes in the uptake capacity of metals whether decrease or increase after the pretreatments.

## 2. MATERIALS AND METHODS

### Preparation of Biomass:

Bentonite Clay was collected from the local market of Faisalabad, Pakistan. Brassica Napus leaves are washed repeatedly with water to remove dust, debris, and soluble impurities. Then the leaves were sun-dried for 48 hrs. And ground.

### Pretreatment of Biomass (P-BNL)

Biomass was pretreated with 0.1M  $\text{KMNO}_4$  (10 g of biomass/100 mL of chemical solution) and stirred for 24h at room temperature at 200 rpm by using OCT-DIGITAL 4527-01 shaker. Pretreatment is carried out to assess whether biomass's adsorption ability has increased or decreased. Modified biomass was filtered and washed with distilled water up to natural pH biomass was oven-dried at 60°C. Chemically pretreated biomass of Brassica Napus leaves was reweighed after treatment to establish any mass loss caused by modification. Reweighed biomass was then sieved through Octagon Digital Siever (OCT-Digital 4527-01) to obtain different particle sizes. Biomass having a homogenous particle size of 0.25mm was used for further experiments.

### Characterization of $\text{KMNO}_4$ Pretreated Brassica Napus Leaves

Using Fourier Transform Infrared Spectroscopy (FTIR: Shimadzu Spectrometer, Japan), the functional groups of the biomass were determined. Before analysis, P-BNL and KBr were individually oven-dried for 7 hours at 393K and kept in a desiccator. The P-BNL spectra measured between 4000  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$ . Scanning electron microscopy is used to visualize the surface characteristics of P-BNL.

### Preparation of Composite Hybrids

#### Native and Clay Composite Hybrid (NC-Hybrid)

For the synthesis of NC-Hybrid 20 g of Native biomass and 20 g of bentonite clay were added in 100 mL of distilled water and mixed with the help of a magnetic stirrer (78-1Ghoura Electronic magnetic) at 300 rpm. After stirring the NC composite hybrid and dried in an oven at 60°C for 12 hrs.

#### Pretreated and Clay Composite Hybrid (PC-Hybrid)

For the synthesis of PC-Hybrid 20 g of pretreated biomass and 20 g of bentonite clay were added in 100 mL of distilled water and mixed with the help of a magnetic stirrer (78-1Ghoura Electronic magnetic) at 300 rpm. After stirring the PC composite hybrid filtered and dried in the oven at 60°C for 12 hrs.

#### Iron-Supported Pretreated Clay Hybrid (IPC-Hybrid)

For the synthesis of IPC-Hybrid 20 g of pretreated biomass and 20 g of bentonite clay were added in 100 mL of 0.1M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and mixed with the help of a magnetic stirrer (78-1Ghoura Electronic magnetic) at 300 rpm. After stirring filtered the IPC-Hybrid and dried in oven at 60°C for 12 hrs.

## Iron-Supported Native Clay Hybrid (INC-Hybrid)

For the synthesis of INC-Hybrid 20 g of native biomass and 20 g of bentonite clay were added in 100 mL of 0.1M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and mixed with the help of a magnetic stirrer (78-1Ghoura Electronic magnetic) at 300 rpm. After stirring filtered the INC-Hybrid and dried in oven at 60°C for 12 hrs. Then all these composite hybrids were sieved through Octagon Digital Siever (OCT-Digital 4527-01) to obtain different particle sizes. A composite hybrid having a homogenous particle size of 0.25 mm was used for further experiments.

## Adsorption Experiment

### Preparation of Stock Solution:

The 1000 ppm Cobalt stock solution was prepared in a 1000 cm<sup>3</sup> volumetric flask by dissolving 2.494 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in distilled water and the stock solutions were diluted to prepare the desired concentrations. The aqueous phase pH was adjusted using 0.1M HCl and 0.1M NaOH solutions. Freshly prepared stock solution is used daily. Standard curves for max developed through measurement of absorbance of metal by UV-visible spectrophotometer.

### Batch Biosorption Studies

All glassware used for experimental purposes was washed with 60% (v/v) nitric acid and subsequently rinsed with DW to remove any possible interference by other metals. Biomass concentrations (1g per 100mL), biosorbent particle size (0.25mm), contact time (24h), temperature (30°C), and shaking speed (150-200 rpm) to check the possible maximum removal of metal ions. Control assay accompanied each experiment. At the end of each experiment, flasks were removed from the shaker, and solutions were separated from the biomass by filtration through filter paper.

### Analytical Procedure

Samples were filtered to remove solid particles and then analyzed to determine the ion concentration by UV/Vis spectrophotometer (Model: Analyst 300, Perkin–Elmer). Heavy metal uptake is calculated by a simple concentration difference method. Uptake of metal was calculated from the mass balance equation.

$$q_e = V (C_i - C_e)/m$$

Where  $V$  is the volume of the solution (L),  $C_i$  is the initial concentration (mg/L),

$C_e$  is the final concentration in solution (mg/L) and  $m$  is the mass of the sorbent (g).

% sorption is given as:

$$\% \text{ sorption} = (C_i - C_e)/C_i \times 100$$

### Effect of pH

The impact of pH on metal ion adsorption was investigated over a pH range of 1–5. In this investigation, 100 mL of wastewater was measured into separate conical flasks. 0.1

g of each biomass was then added, and the mixture was shaken at 200 rpm for 24 hrs. HCl was used to alter the pH between 1 and 5. The combination was filtered via Whatman filter paper, and the filtrate's metal ion concentrations were assessed.

### Effect of Contact Time

For a duration of 24 hrs., the impact of contact time on the elimination of metal ions was investigated. For each of the various contact times (0, 15, 30, 60, 120, 240.... and 1440 minutes), 0.1 g of the adsorbents (composite hybrids) were added to a different conical flask holding 100 mL of wastewater. The flask was then closed, put in a rotary shaker, and agitated at 200 rpm. Following each agitation period, the contents of each flask were filtered and examined.

### Kinetic Analysis

The kinetics of adsorption were investigated by examining the adsorptive absorption of heavy metals from wastewater at various time intervals. Heavy metal adsorption kinetics onto composite hybrids modeled using the pseudo-first- and pseudo-second-order model equations. A model's ability to accurately depict the adsorption process can be determined by plotting each model's linearity. The following two equations display the generic expression for the pseudo-first-order equation model:

$$dq/dt = K_1(q_e - q_t)$$

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

Pseudo-second-order chemisorption kinetic rate equations are expressed as:

$$dq/dt = K_2 (q_e - q_t)^2$$

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

### Statistical Analysis

Mean and standard error values were calculated from triplicate sets of experiments. All statistical analysis was performed using Microsoft Excel 2010, Version Office Xp.

## 3. RESULT AND DISCUSSION

This research work used a green product called Brassica Napus leaves, clay (which is inexpensive and readily available), and magnetic particles (which have a propensity to attract environmental contaminants) to create a composite hybrid in the search for an effective adsorbent material for wastewater treatment. The principle of inventive composite hybrids was to know the biosorption capability and then evaluate the adsorption capacity of chemically pretreated biomass. The characteristics of the KMNO<sub>4</sub> pretreated adsorbent were elucidated by using SEM and FTIR.

### 3.1. Effect of Pretreatment

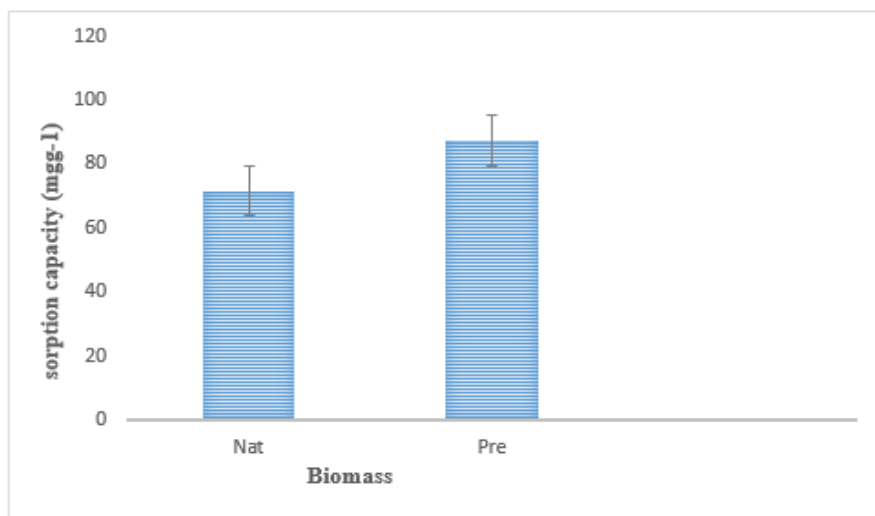
Comparing the result of pretreatment on Brassica Napus leaves, 100 mgL<sup>-1</sup> of Co (II) solution (at the pH of 5) was shaken at 200 rpm with 0.1 g of pretreated Brassica Napus



leaves. One can notice that in Fig. 1 the pretreatment of biomass by  $\text{KMnO}_4$  increased the sorption capacity ( $\text{mgg}^{-1}$ ) of biomass in order:

Pretreated biomass ( $85.75 \text{ mgg}^{-1}$ ) > Native biomass ( $65.32 \text{ mgg}^{-1}$ )

Generally, oxidizing agent treatment is used for metal removal causing an increase in sorption capacity (Ravindran et al., 2017).  $\text{KMnO}_4$  treatment showed a remarkable increase in the sorption capacity of biomass.  $\text{KMnO}_4$  pretreated biomass showed more sorption capacity than native biomass and it was due to the solubility of more mineral matter of biomass, which resulted in more porosity in biomass. According to this property, it is also used in sterilizing wells of drinking water. Overall, it was found that the enzymatic scarifications of biomass were affected by the testing levels of independent variables (pretreatment temperature, duration, and  $\text{KMnO}_4$  concentration). This result was consistent with other investigations conducted by multiple published works. Romero et al., 2018, used  $\text{FeCl}_3$  to pretreat rapeseed straw by varying the temperature, duration, and concentration of the solution.



**Figure 1: Effect of pretreatment on the biosorption of Cobalt using Brassica Napus**

### 3.2 Characterization of $\text{KMNO}_4$ Pretreated Brassica Napus Leaves

Scanning electron microscopy is a dynamic technique for visualizing the microscopic morphology of materials and obtaining information about their size and shape. The P-BNL (Fig. 2 a) surface is rough and coarse. There are a few irregular aggregates on the adsorbent's surface. The surface is made up of non-uniform, heterogeneous particles to which metal ions can attach. Additionally, there are surface holes that can contain metal ions easily. Following treatment with  $\text{KMNO}_4$ , the surface of P-BNL developed a rougher texture and a layer of dense, spherically shaped particles might include elevated levels of K and Mn elements (Reddy and Lee, 2014).

Fourier transform infrared spectroscopy is a method for determining the active sites on the surface of the adsorbent that are available to bind or interact with contaminants and the active sites found in P-BNL were visualized using this technique. FTIR spectroscopy is a useful tool for analyzing chemical structures because it can measure the rotation and vibration of molecules, including those of different surface functional groups like amino, carbonyl, carboxyl, and so on. The vibrations of -OH were indicated by the peaks about  $3420\text{ cm}^{-1}$ , while the vibrations of  $1609\text{ cm}^{-1}$  were related to both -C and -O, as shown in Fig. 2 b. Additionally, the absorption of Si-O-Si was indicated by the peak around  $1115\text{ cm}^{-1}$ . It should be mentioned that adding potassium permanganate to Brassica Napus leaves increased the number of oxygen-containing groups in the mixture (Liu et al., 2020).

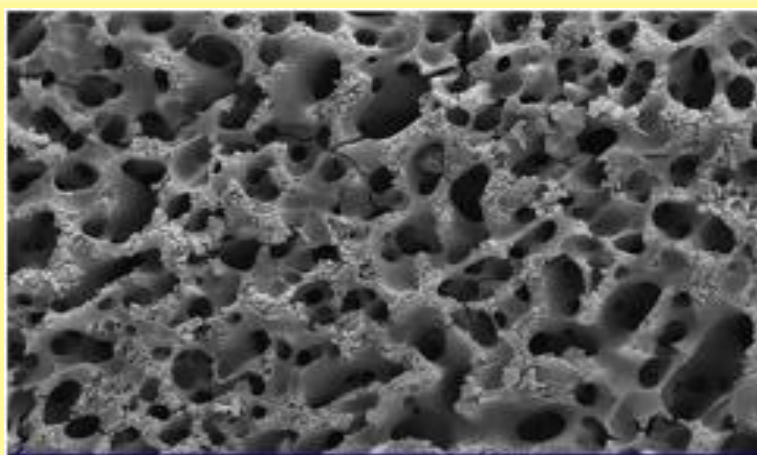


Figure 2: (a) Scanning electron microscopy of P-BNL

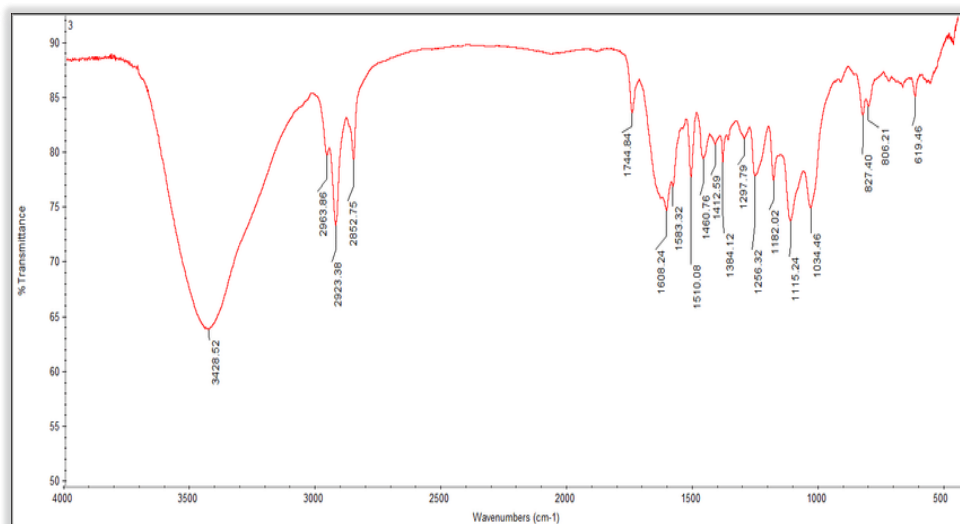


Figure 2: (b) FTIR spectroscopy of P-BNL



## Effect of pH

One of the crucial parameters controlling the metal ion adsorption is the pH of the solution. Under specific conditions, the influence of pH was investigated between 1 and 5 (at room temperature of 32°C, with an ideal contact period of 24h, shaking speed of 200 rpm, and 0.1g of the composite hybrids utilized).

One can see in Fig. 3 that the maximum sorption capacity  $q$  ( $\text{mgg}^{-1}$ ) was achieved at pH 1 for the removal of Co (II) metal ions. Sorption capacity was decreased from (87.39-71.6) > (84.89-63.12) > (82.78-63.8) > (77.16-60.21) > (76.82-57.9) > (74.44-52) > (71.66-51.53) for P-BNL, PC-Hybrid, IPC-Hybrid, INC-Hybrid, Nat, Clay, NC-Hybrid when pH varied from 1-5.

pH of the solution affects the biomass properties, mechanism of adsorption of the metal molecule on the surface of biomass, and metal molecule dissociation (Low et al., 1995). At lower pH, the biomass surface becomes enriched with positively charged ions, as a result, strong electrostatic interactions develop between anionic metal molecules and the positively charged biomass surface.

Moreover, raising pH lessens the competition between protons and metal ions for adsorption sites on the particle surface by lowering the concentration of  $\text{H}^+$ . An additional element that may enhance metal ion adsorption is the rising pH, which promotes metal ion precipitation out of the solution as hydroxides. The decrease in adsorption that was seen after pH 3 was caused by the development of soluble hydroxyl complexes (Jain et al., 2021).

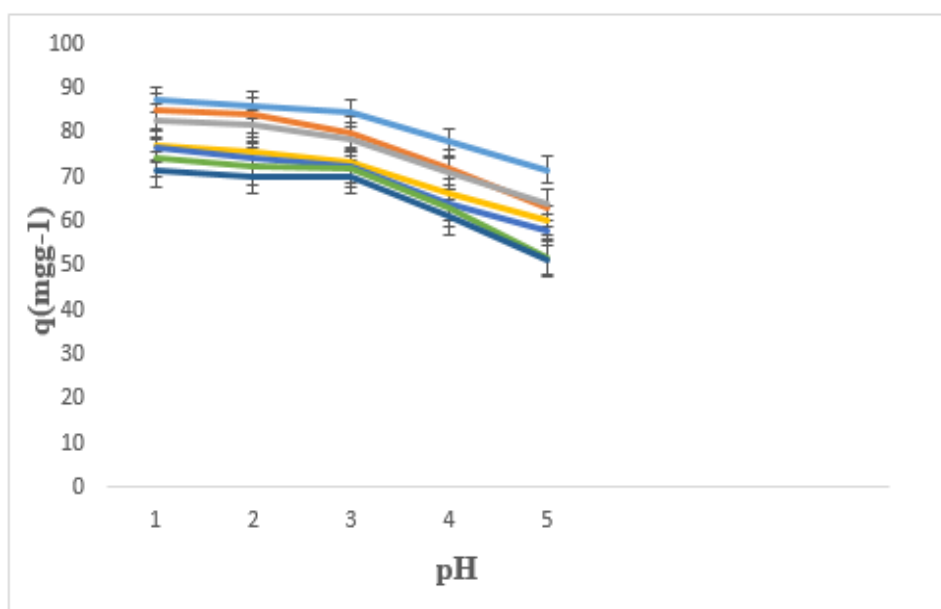


Figure 3: Effect of pH on biosorption of Cobalt using Brassica Napus

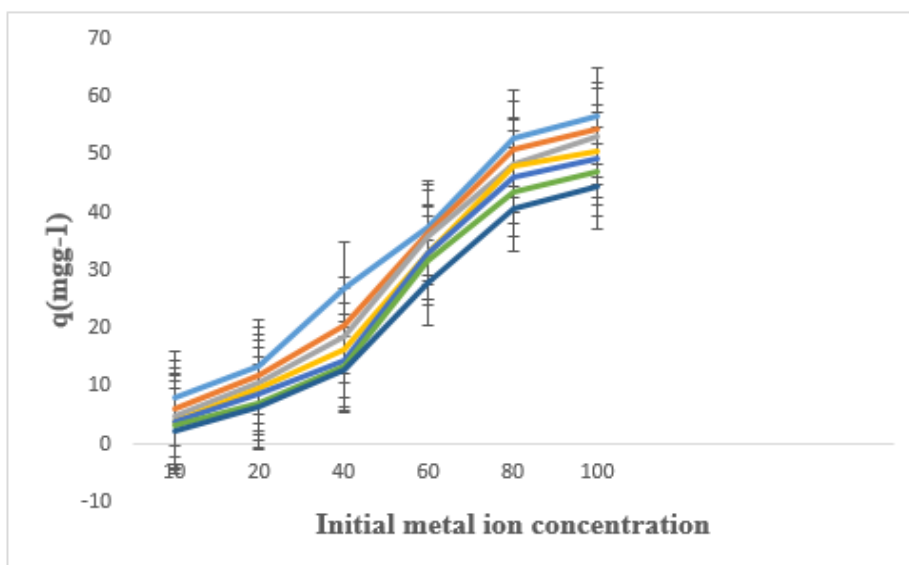
### Effect of Initial Metal Concentration

The effect of initial metal concentration on the elimination of Co (II) metal from the aqueous solutions by different adsorbents was studied at pH 1 by changing the concentration of the system from 10 to 100 mgL<sup>-1</sup>. Results showed that adsorption capability improved with an increase in the initial metal concentration of Co (II) on the biomass and % age removal decreased with an increase in initial metal concentration.

Results shown in Fig 4, in this case, enhancing initial metal concentration from 10 to 100 mg/L resulted as an increase in adsorption capability  $q$ (mg/g) as (7.89-56.68), (6.13-54.24), (4.78-54.09), (4.02-50.58), (3.76-49.22), (3.22-46.99), (2.33-44.54) using P-BNL, PC-Hybrid, IPC-Hybrid, INC-Hybrid, Nat, Clay, NC-Hybrid respectively.

This is explained by the previously mentioned parameters, as it found that adsorbents with additional sorption sites were uncommon. Increasing the initial Co (II) concentration can effectively improve the mass transfer limitation between the solid phase and the aqueous phase, resulting in increased metal ion adsorption.

For the elimination of Ni (II), a similar pattern was seen when using copper oxide nanoparticles (Khalid et al., 2018). Thus, based on previous studies, it can be assumed that the initial metal concentration drives the sorption process.



**Figure 4: Effect of different metal concentrations on biosorption of Cobalt using Brassica Napus**

### Isotherm Studies

The bio adsorption isotherm is the basic constraint in the propose of any adsorption system, as it expresses the relation between the mass of metal absorbed per unit mass of adsorbent and the liquid phase metal concentration. The absorption isotherms of Co

(II) onto different composite hybrids (P-BNL, PC-Hybrid, IPC-Hybrid, NC-Hybrid, and INC-Hybrid) were evaluated by varying the initial metal concentration within the range of 10-100mg/L<sup>-1</sup>, with a constant dosage of biomass as 1g/ for every type of Composite Hybrid biomass.

In order to investigate the biosorption isotherms, two models Langmuir and freundlich were used.

### Langmuir Model

A Langmuir isotherm's properties described in terms of a dimensionless separation factor, or  $R_L$ , which characterizes the kind of isotherm and is defined as follows:

$$R_L = \frac{1}{1 + K_L C_0}$$

Where  $K_L$  is the Langmuir constant (Lmg<sup>-1</sup>),  $C_0$  is the initial metal ion in mg/L, and  $R_L$  is a dimensionless separation factor.

### Freundlich Model

The degree of surface heterogeneity of the adsorbent can be determined using the Freundlich adsorption isotherm.

This expression is provided in linear form as:

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

The Freundlich constant  $k$  represents the relevance of the adsorption capacity. Meanwhile,  $n$  is the Freundlich exponent, which characterizes the attraction between the adsorbent and adsorbate. The removal effectiveness of each adsorbent may also be compared using  $k$ , and the pattern of distribution of site bonding energies qualitatively connected to  $n$ . In Fig. 5 the  $\log q_e$  and  $\log C_e$  plot's intercept and slope are used to determine the values of  $k$  and  $n$  (Salvi and Chattopadhyay, 2017).

To assess each hybrid efficacy, a comparison of its isotherm properties was carried out. The isotherm constants and the correlation coefficients ( $R^2$ ) were discovered. The Langmuir constant (Fig. 6) indicated that Pretreated Brassica Napus biomass (P-BNL) performed well, with  $C_0$  (II) metal uptake with a correlation coefficient value of ( $R^2 = 0.9971$ ). The Freundlich isotherm model well describes the data with high correlation coefficient values (Table 1).

The Freundlich isotherm was initially observed in nature but was later interpreted as the adsorption to heterogeneous surfaces or surfaces supporting sites with various affinities. The experimental values were greater than unity for all adsorbents, demonstrating suitable bio-adsorption and repulsive forces between the adsorbed molecules (Unuabonah et al., 2009).

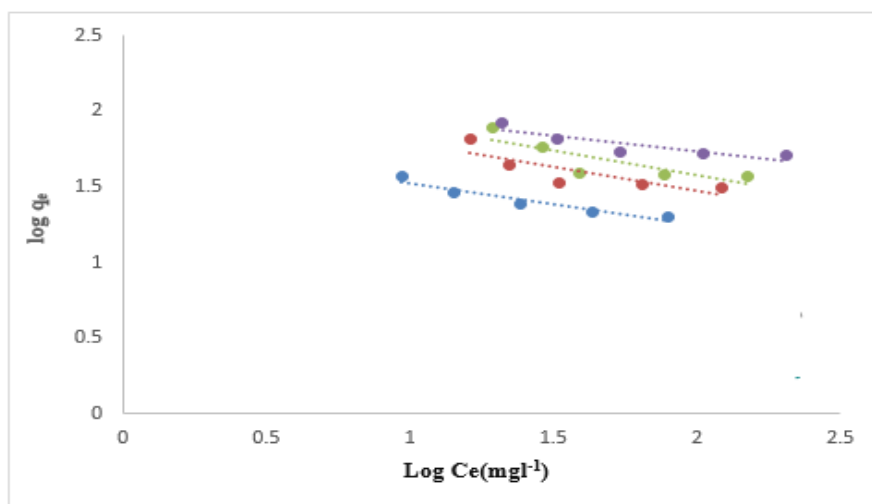


Figure 5: Freundlich isotherm plot for the biosorption of Cobalt using Brassica Napus

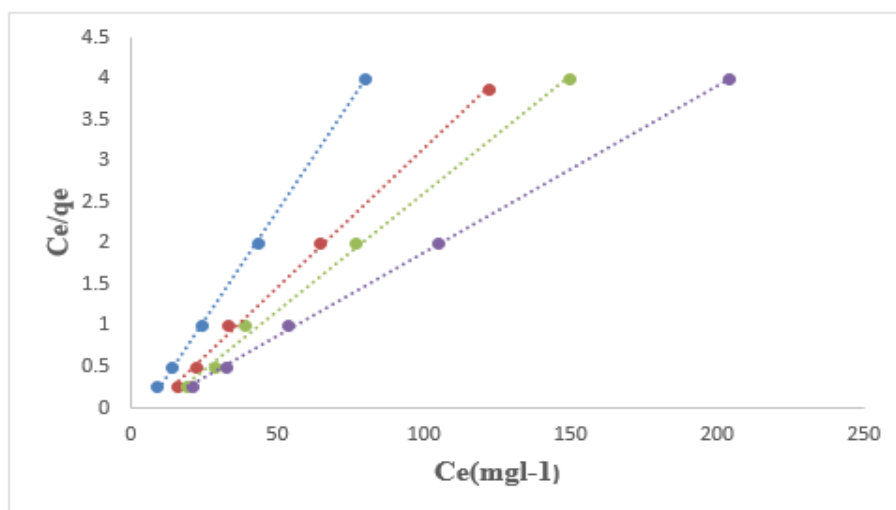


Figure 6: Langmuir isotherm plot for the biosorption of Cobalt using Brassica Napus

Table 1: Coefficient of determination ( $R^2$ ) and adsorption isotherm constants for composite hybrids

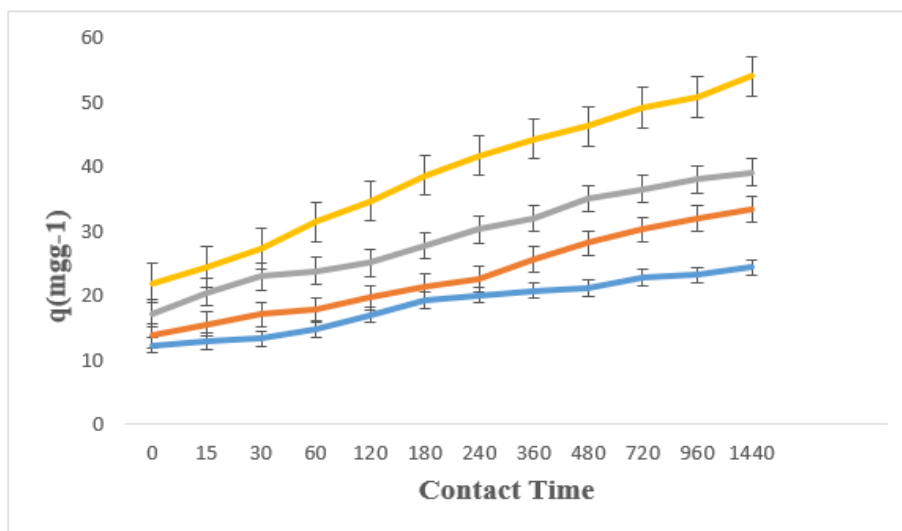
Sr No.	Adsorbents	Langmuir Isotherm Constants			Freundlich Isotherm Constants		
		$q_e$ (mgg <sup>-1</sup> )	$b$ (Lg <sup>-1</sup> )	$R^2$	$k$ (Lg <sup>-1</sup> )	$1/n$	$R^2$
1	P-BNL	18.1031	0.0132	0.9971	9.39211	0.7380	0.9999*
2	PC-Hybrid	16.3576	0.0161	0.9919	9.85723	0.6981	0.9979
3	IPC-Hybrid	13.8866	0.0172	0.9872	13.9991	0.6602	0.9969
4	INC-Hybrid	8.54321	0.0220	0.8087	18.4590	0.5999	0.9649
5	NC-Hybrid	2.5804	0.0401	0.8345	55412.1	0.3354	0.9429

## Effect of Contact Time

The results of an experiment conducted to conclude the equilibrium time are shown in Fig 7. The experiment was carried out at constant concentration and an optimum pH of 1 but with different contact time ranges (0, 15, 30, 45, 60, 120, 240, 480, 1440min). It is apparent that elimination efficiency was very quick during the initial stages of the absorption process followed by a slow increase and then reached equilibrium. The sorption capacity  $q$ (mg/g) was changed during the time range of 0-1440min for P-BNL, PC-Hybrid, IPC-Hybrid, and INC-Hybrid.

Contact time was one of the important parameters for economical wastewater treatment. The % of adsorption increases with contact time until the equilibrium is attained. The most important and fast step is the first step phase at which bulk transport of metal molecules onto biomass takes place in a few minutes due to mixing and adjective flow studies exposed that the majority of metal molecules were detached within the first 60 min. The equilibrium state is attained at 120 min (Altıntig et al., 2021).

The fast adsorption at the initial stage was most likely due to an increased concentration gradient between the adsorbate in solution and adsorbate in adsorbent as there must be an increased number of vacant sites available in the beginning. As contact time increased, more and more functional groups participated in the adsorption of metal molecules until it reached equilibrium (Okareh and Adeolu, 2015). Hannachi et al., 2013, reported that a contact time ranging from 2h to 4h was enough to achieve equilibrium.



**Fig 7: Effect of contact time on biosorption of Cobalt using Brassica Napus**

## Kinetic modeling

The kinetic data helps in tracing the rate-determining phase of the transport mechanism and is utilized to identify the ideal processing parameters for large-scale batch or continuous operations. This study tried to fit the available sorption data using pseudo-

first- and pseudo-second-order kinetic models. To evaluate the biosorption kinetics of cobalt metal two kinetic models were used to fit the experimental data obtained on different composite Hybrids. Based on the fitted data values in Fig. 8 and 9, Compared to the pseudo-first-order reaction model, which was considerably scattered (nonlinear), it is evident that the pseudo-second-order reaction yields very good straight lines.

### **Pseudo first order-Lagergren model**

The pseudo-first-order kinetic model (Lagergren model) is generally expressed as follows:

$$dq/dt = K_1(q_e - q_t)$$

Where  $q_e$  is the amount that solute adsorb at equilibrium per unit mass of biosorbent ( $mgg^{-1}$ ),  $q_t$  is the quantity of solute adsorbed at any given time ( $t$ ) and  $k_1$  is the rate constant. Applying the boundary conditions and simplifying results in the equation given below

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

The calculation of " $k_1$ " can be done using the slope of the linear plot between  $\ln(q_e - q_t)$  vs. ' $t$ ' for different adsorption factors, such as pH, temperature, adsorbate concentration, adsorbent dose, and particle size (Tekin and Açıkel. 2022).

### **Pseudo-second-order kinetic model**

The fitness of the sorption data was assessed taking into account the data using a pseudo-second-order reaction model. The pseudo-second-order kinetic rate equation can be written as follows:

$$dq/dt = K_2 (q_e - q_t)^2$$

Where  $k_2$  is the rate constant of second-order adsorption ( $g\ mg^{-1}\ min^{-1}$ ),  $q$  is the absorbed amount ( $mgg^{-1}$ ),  $q_e$  is the adsorption capacity ( $mgg^{-1}$ ) in the equilibrium. Next Equation takes on the form of further simplifications and integration for boundary conditions with  $t=0$  to  $t > 0$  and  $q_t=0$  to  $q_t > 0$ . The integrated and linearized form of Eq is

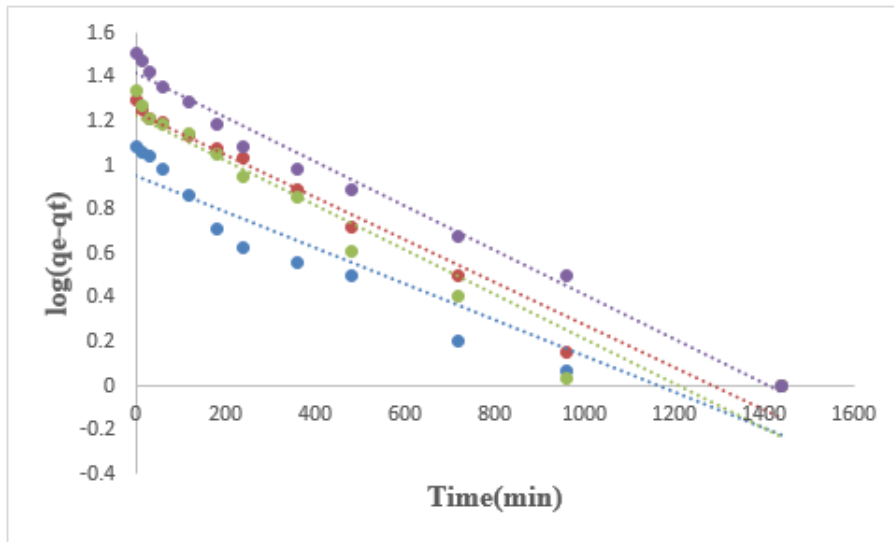
$$t/q_t = 1/k_2 q_e^2 + 1/q_e(t)$$

The values for  $q_e$  and  $k_2$  are determined from the linear relationship shown by the plot of  $t/q_t$  vs  $t$  in Fig. 8. Straight lines were obtained by plotting for P-BNL, PC-Hybrid, IPC-Hybrid, and INC-Hybrid. The second-order rate constants,  $k_2$  and  $q_e$  determined from the slope and intercept of the plots.

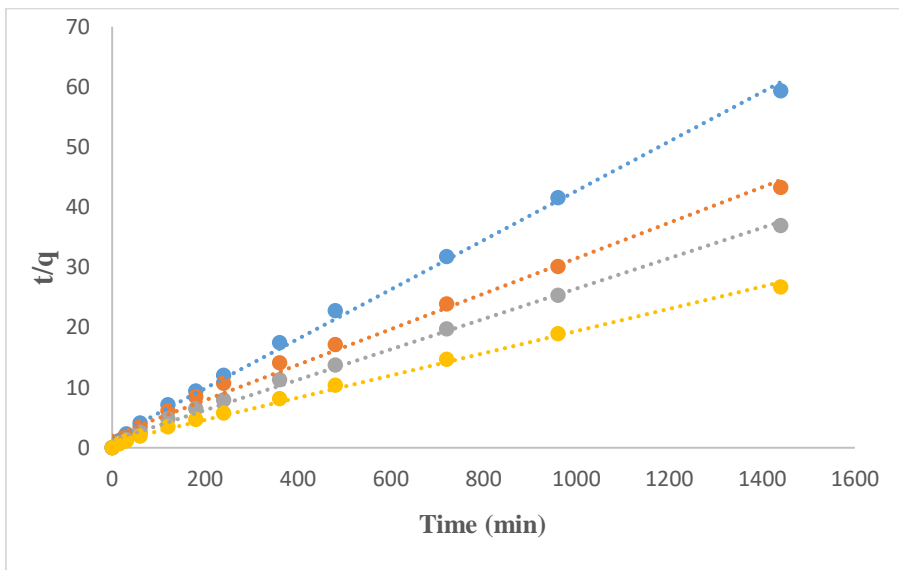
From the regression coefficient values ( $R^2$ ) depicted in Fig. 8 in the case of the pseudo-first-order kinetic model, the plots were not linear over the whole-time range representing that more than one mechanism is mixed up in absorption. The calculated  $q_e$  values obtained from this kinetic model did not show good agreement with the experimental one. This finding suggested that the biosorption system did not follow the pseudo-first-order biosorption rate expression for all initial concentrations of metal.



In the case of the pseudo-second-order kinetic model, the values of  $K_2$  and  $q_e$  calculated from intercepts  $1/k_2q_e^2$  and slopes ( $1/q_e$ ) of the plots of  $t/q_t$  versus  $t$ , which showed high regression coefficient values and a good agreement between calculated and experimental  $q_e$  values indicating the applicability of the pseudo-second-order kinetic model for biosorption of Co (II) metal. The same results were found in the work described by (Onursal et al., 2023).



**Fig 8: Pseudo 1<sup>st</sup> order plot for the biosorption of Cobalt using Brassica Napus**



**Fig 9: Pseudo 2<sup>nd</sup> order plot for the biosorption of Cobalt using Brassica Napus**

## CONCLUSION

Heavy metals are highly dangerous elements with a high potential to pollute water resources that can be accumulated and concentrated in living tissues along the food chain. Removal of toxic contaminants from wastewater is one of the most important environmental issues.

Since all heavy metals are non-biodegradable, they must be removed from the polluted streams for the environmental quality standards to be met. Conventional methods are limited by technical and economic barriers, especially when the concentration of metals in the wastewater is low (under 100 ppm).

These methods have several disadvantages like high operating costs, low selectivity, incomplete removal, and production of large quantities of wastes. Biosorption, which is a property of certain types of inactive, dead microbial biomass to bind and concentrate metals from even very dilute aqueous solutions, is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural waters.

In this study, leaves of *Brassica Napus* leaves were chosen as a biosorbent for the removal of Co (II) metal from aqueous solutions. Based on operating conditions like pH, initial metal ion concentration, and contact time, it is clear from the analysis of the result that *Brassica Napus* leaves, when transformed into composite hybrids, have a great potential for the uptake of cobalt (II) ions from the industrial effluent. Modeling data obtained from isotherms indicated that the Freundlich model gave a better fit than the Langmuir model with an  $R^2$  value of 0.9999.

This suggests that there may be homogeneous or heterogeneous sites on plantain waste adsorbents suitable for the adsorption of large amounts of Co (II). Kinetic study revealed that adsorption was fast in the first 60 minutes and equilibrium was achieved after 120 minutes. The suitability of a pseudo-second-order chemical reaction for the sorption of metal onto composite hybrids was apparent.

The results revealed that leaves of *Brassica Napus* biomass is effective, potential, and best beneficial biosorbent for the removal of metal from aqueous solutions. Consequently, the composite hybrids made from *Brassica Napus* can absorb heavy metal ions from industrial wastewater, which presents a use for the in-situ treatment of heavy metals.

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