Research Article

Journal of Nuclear Technology in Applied Science
Year 2025, Volume-13, Issue-1 (January - December)

www.acspublisher.com

Sorption Study of Cobalt and some Toxic Compounds from Contaminated Water using Natural Material

Salama M.H.M.[1]*; Ibrahim A.M.H.[2]; Ibrahim S.[3]; El-Shahat M.F.[4] and Abdel Azeem S.M.[5]

[1] Siting and Environment Department, Nuclear and Radiological Safety Research Centre (NRSRC), Egyptian Atomic Energy Authority, Cairo, Egypt.
[2] Hot Laboratory Centre, Fuel Technology Department, Egyptian Atomic Energy Authority, Abu-Zabal-Kalubia, Egypt.
[3] Holding Company for Potable Water and Sanitation, Fayoum City, Egypt.
[4] Chemistry Department, Faculty of Science, Ain-Shams University, Cairo, Egypt.
[5] Chemistry Department, Faculty of Science, Fayoum University, Egypt.

ARTICLE INFO

Keywords: *Aminated-banana peel, Cobalt, Chlorophenols, Removal, ICP-OES, HPLC-UV, Tap and river waters.*

doi: 10.48165/jntas.2025.13.2

ABSTRACT

The present work describes raw banana peel (RBP) adsorption characteristics for chlorophenols from tap and river water samples. Also, aminated banana peel (AmBP) was prepared by the oxidative cleavage treatment of raw-BP from carbonyl groups, which were further reacted with ammonia to create new amine and imine groups in BP to give the resulting. FTIR, SEM, and XRD analyses described the derived adsorbents. Prepared AmBP was used for the removal of cobalt (II), the RBP was applied for removing 4-chloro-2-nitrophenol,4-chlorophenol, and 2,4,6-trichlorophenol from tap and river water before quantification with ICP-OES for cobalt and HPLC-UV for chlorophenols. The absorption was maximal at pH 7.0 for cobalt (II), and pH 5.0 for chlorophenols. The shaking time was 30 minutes, and the adsorbent weight was 0.1 g. Desorption was affected by 0.1 mol/l HCl and 50% (v/v) methanol, respectively. Monolayer capacity adsorption by Langmuir isotherm was 8.5 mg/g for cobalt and from 6.5 to 10.5 mg/g for chlorophenols. Removal of the studied pollutants from tap water and river water was applied, and they showed capture ranging from 88.9-108.1 % for cobalt and from 80- 92% for chlorophenols.

Introduction and methodology

The considerably growing industry has enormously increased wastewater discharging processes and degradation in water quality. Pollutants are dangerous to both humans and the healthy environment. They may be organic or inorganic. Organic sources, such as hydrocarbon dyes and pesticides, and inorganic ones, such as heavy metals, play an essential role because of their significance and possible advantages **Ismael et al. (2022)**. Cobalt has a necessary implementation in modernistic technology; it is an element

---

*Corresponding author.
E-mail address: hegazy1967@gmail.com
Received: 23/04/2025 Accepted: 04/06/2025

that naturally occurs in the formation of the earth. It is a composition of vitamin B12, which helps in the output of red blood cells. People and animals need very small quantities to stay healthy. Toxicity of metal can occur when exposed to large amounts of these metals, excessive metal exposures can cause a domain of events in humans including goitre and reduced thyroid activity **Hossain et al. (2012**).

Cobalt can cause poisoning in three ways when ingested in excess, in large quantities into the lungs by inhalation, or by connection with the skin. The United States Environmental Protection Agency (USEPA) has not settled the reference limit for cobalt. Subsequently, it is very important to attempt to remove it from the different sanctuary environments, using new technologies such as natural biomass, which is active, inexpensive, and does not pollute the environment anymore. **Layer et al. (1963); Fickling et al. (1959**).

Similarly, chlorophenols (CPs), which are highly poisonous, poorly biodegradable, and possibly carcinogenic, are known to pollute the environment **Plugarin et al. (2003**). CPs are among the most hazardous and carcinogenic of the 11 phenolic compounds listed as significant pollutants by the US Environmental Protection Agency **EPA (1983**).They are produced commercially for application in many industries, including pharmaceuticals, as intermediates, preservatives, disinfectants, and antiseptics **Lee et al. (1998**)..

Additionally, when water is disinfected with chlorine, several chlorophenols, particularly 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP), likely form, leaving the water with unattractive and lingering organoleptic qualities **Sarrión et al. (2003)**; **Moraisa et al. (2012**).

Adsorption **(Gómez et al., 2012**), solvent extraction (**Jain et al., 2007)** ozone generator **(Brinda Lakshmi et al., 2013**), reverse osmosis **(Manojlovic et al., 2007**), ionic exchange **(Kargari et al., 2015**), and floatation **(Lee et al., 1996**).

However, some of these methods, like ion exchange, can be expensive or leave behind refractory residues, the high cost of properly disposing of the sludge as well as the pricey chemicals required for the elimination of organic contaminants are disadvantages of conventional treatment **Adolfo et al. (2012**); **ICP-OES (2024**).

CPs were mostly quantified by using chromatographic techniques like reversed-phase liquid chromatography (RPLC) (**Nyssen et al., 1987**), equipped with several detectors such as UV (**Li et al., 2008**), fluorescence (**Feng et al., 2009**), electrochemical (**Higashi et al., 2009**), or mass spectrometry (**Sarrion et al., 2002**), additionally, the technique of gas chromatography (GC) was communicated for the quantification of CPs (**Lopez et al., 2004**).

Humic substances, which occur naturally in samples of the environmental matrix may interfere with compounds, which is a problem when HPLC is used in conjunction with detection modalities other than mass spectrometry or fluorescence **(Fickling et al., 1959; Sarrión et al., 2003**).

Several adsorbent materials have been utilized for removing cobalt from water including sediments **(Swelam et al., 2017**), Luffa Cylindrica (**Wang et al., 2014**), citrus lemon leaves powder (**Mokhtari et al., 2020**), and rice straw (**Aksu et al., 2001**). CP removal from water samples was studied using several agro wastes like sawdust **(Jadhav et al., 2004**), and activated carbon derived from pumpkin stems ***(Ekpete et al., 2011*****)**, coconut shells (**Radhika et al., 2006**), pistachio shells (**Tseng et al., 2010**), and rice straw (**Hikal et al., 2022**).

Banana peel (BP), a discarded agro waste, was used to produce bio-adsorbent of environmentally friendly processes (**Kaewsarn et al., 2008**). BP is recognized as a favorable biocompatible adsorbent where it does not produce harmful substances the possibility of using organic sorbents as fuel to generate power or as a fermenting substrate. Additionally, its surface is covered by a variety of chemical groups, such as carboxyl, hydroxyl, and amide groups (**Tseng et al., 1996**).

In our research, the preparations, characterization, and quality of adsorption of BP towards Co and CP were examined. The adsorptive removal efficiency of the aminated-BP adsorbent was evaluated and the material was applied to remove the examined pollutants from water samples.

Experimental setup

Inductively Coupled Plasma-optical emission spectrometry (ICP-OES) with Argon flow model iCAP 6000 Duo, Thermo Scientific, England. The instrument standardizations were made using a stock solution containing 1000 mg/l multi-element certified standard solution obtained from Merck (Darmstadt, Germany). Shimadzu HPLC SIL-20A instrument (Columbia, USA) with auto-sampler and reversed-phase C18 column (35 cm and 0.3 mm i.d.), was utilized for quantification, of the CPs compounds. Metrohm pH meter model 780 (Herisau, Switzerland) was applied for pH adjustment. Elix-Ultra-pure UV water purification instrument (Massachusetts, USA) provided deionized water was used for all preparations. SEM-EDAX spectrometer model FEI Quanta 400F (Oregon, USA) was used for recording the SEM micrograph of BP before and after adsorption under a vacuum of 3 Pa after coating with a thin layer of palladium (Pa) using Emtecsplutter Coater. FTIR spectrometer (Perkin Elmer 2000, UAS) was used to record the spectra of banana peels using the KBr mechanism. Sterlite cellulose acetate membrane disc filter (Kent, USA) with a pore size of 0.45 µm was fitted to a plastic syringe and used to collect the supernatant from the mixture after shaking the sample with the sorbent. IKA headspace mechanical shaker model IKAKS260C (Staufen, Germany), with a speed of 10-300 rpm for shaking the samples.

Glass vials with a volume of 150 mL and Teflon caps for adsorption study,

Reagents

Analytical-grade chemicals were used in this study. A 1000 mg/l standard solution was made using cobalt nitrate supra pure (Merck, Darmstadt, Germany), and a known amount of reagent was dissolved in de-ionized water. The following CPs were acquired from Sigma-Aldrich (Shanghai, China): 4-chlorophenol (4-CP), 4-chloro-2-nitrophenol (nitro-CP), and 2,4,6-Trichlorophenol (TCP). A standard solution of 1000 mg/l of CPs was prepared by dissolving a known amount of methanol (Fisher Scientific, Loughborough, UK). Serial dilutions from the standard were made with deionized water. Acetonitril and methanol (KMF, Germany) was used in the dynamic phase to separate CPs gradually.

Preparation of aminated-BP biosorbent

Raw banana peel with a yellow colour was obtained freshly from a nearby market and then washed using deionized water many times to remove any impurities and unclean adhering. After that, it was cut into small pieces and sunlight dried for 72 h in a clean environment where all humidity was removed; after that, the dried material was ground and sieved with a diameter of 0.5 -1 mm. Coloured pigments were removed by successive shaking of the material with ethanol for 1 hour and then washed with deionized water.

Removing any metallic impurities, the powder was overnight saturated in a solution of 1.0 mol/l of hydrochloric acid. Then, it was filtered through filter paper (Whatman No.1), and then the effluent was acid-free by washing it several times with deionized water. The raw BP was dried at ambient temperature in a dust-free space.

Several amine compounds present in BP such as the amino acids e.g. leucine, valine, phenylalanine, and threonine, proteins, alkaloids, and catecholamines (**Thrower et al., 1989**), would help the adsorption of cobalt and CPs. Besides, BP also contains polyphenolic compounds some of them with carbonyl groups which can be reacted to ammonia to increase the nitrogen-based compound in BP. Therefore, aminated PB was prepared according to the reported method (**Stevenson et al., 1982**), as follows: A 10 g powdered raw BP was put in 100 ml deionized water and magnetically stirred at 20°C. Immediately, 10 ml of 30% (w/v) ammonia solution was dropwise added under vigorous stirring for 1.0 h to give the ammonia adduct. Then, the pH was adapted to 4.0 to facilitate the lake of water molecules from the adduct of the final imine-formatted product. After that, the mixture was filtrated, and the solid portion was washed from the excess reagents with deionized water. Finally, the aminated-BP adsorbent (cleaned brown-coloured) was dehydrated, and for further use, the adsorbent was kept in a dark vessel.

Adsorption study

A batch procedure for adsorption study, 4-CP, nitro-CP, and TCP was carried out individually employing a 50 ml sample of concentration 40 µg/l placed in a glass vial of 150 mL capacity and Teflon caps and 0.1 g sorbent. The solution was adjusted pH at 7.0 ml for cobalt, and 5.0 ml for CPs, and then the solution was at a speed of 230 rpm for 1 hour. The pH within the range of 2.0-9.0 was studied, the shaking time ranged from 1 to 60 min and the concentration was examined from 10 to 100 µg/l.

Also, the sorbent dosage was inspected from 0.03 to 0.5 g. After adsorption, the supernatant was removed by filtration through a cellulose acetate membrane disc filter fitted to a plastic syringe. After that, adsorbed cobalt was desorbed using 5 ml of (0.1 mol^{-1} HCl), while CPs were desorbed using 3 mL of 50 (v/v) % methanol eluent and shaking the solution for 30 minutes, where C_o, C_e and C are the initial, remaining, and concentration of desorbed (µg/l), respectively. Recovery (%) was calculated using equation (1), also, the adsorbed amount at equilibrium (Qe, mg/g) could be calculated by Equation (2):

$$\text{Recovery (\%)} = [C/C_o] \times 100 \qquad (1)$$

$$Q_e = [(C_0 - C) \times V]/m \qquad (2)$$

Where V is the sample volume (L) and m is the adsorbent weight (g).

Quantification of cobalt and CPs

Instrument standardization, a stock solution of 1000 mg/l multi-element certified standard Merck solution, Germany was utilized. The eluate was analysed by ICP-OES technique, analysis of cobalt was performed at 30 sec running time, 0.2 ml/ min flow rate, 14.6 Mpa of a pressure pump, and injection volume of 50 µl.

HPLC-UV technique was operated in the gradient analysis procedure for CPs determination at 20 min running time, flow rate of 0.7 ml/min, 14.6 Mpa pump pressure, column temperature at 40°C, 50 ml injection volume, and UV detection at 220 nm. Water-methanol-acetonitrile tendency elution program used was 50 to 90% in 17 min. The retention time was 5.7, 8.4, and 9.9 min for 2,4,6-TCP, 4-CP, and nitro-CP, respectively. The measuredstandardsolutionsof CPs are shown by the chromatogram in Figure 1.

Water samples

Tap water and river water samples containing cobalt were examined by the siting and environment department of the Nuclear and Radiological Safety Research Centre of the Egyptian Atomic Energy Authority (EAEA). The river water was obtained from the Nile River at a specific location in Abo Zabal City, Egypt, and tap water were obtained from (EAEA at Nasr City site).

The water samples of CPs were studied in tap and river water. Tap water was collected from the chemistry department, at the University of Duisburg-Essen (Duisburg City, Germany), and the river water was obtained from the Ruhr River (Mulheim City, Germany).

All water samples were filtered through a 0.45 µm filter paper, acidified to pH 2.0 with nitric acid, and immediately analysed. A 50 ml portion of each sample was spiked to concentration levels of 3.0 and 5.0 mg/l for cobalt and 2.0 mg/l of individual CP and detected to the recommended pH of 7.0 for Co and 5.0 for CPs. An adsorption procedure was performed, and the desorbed concentration from each analyte was determined using the quantification technique. Each experiment was iterated four times and the average quantity of the obtained concentration was utilized to calculate the recovery (%).

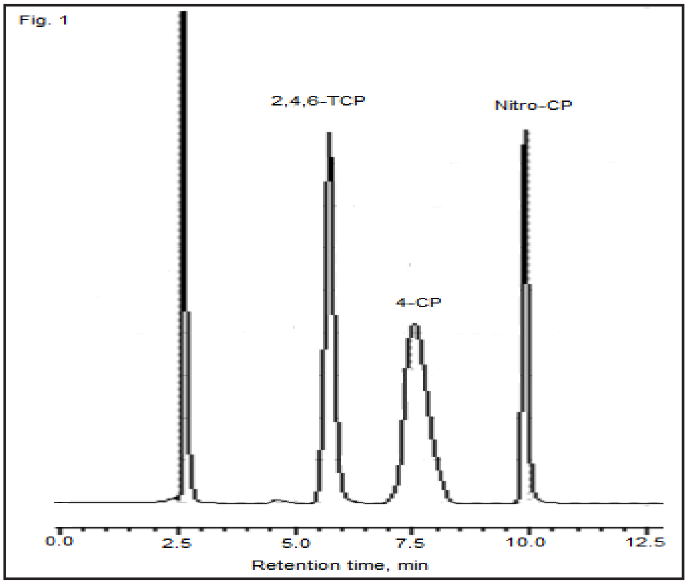

Figure (1): HPLC chromatograms of the measured standards solution of CPs

Results and Discussions

Descriptions of aminated-BP adsorbent

The absorption spectrum of BP and aminated-BP at region 4000-400 cm^{-1} by FT-IR is shown in Figure 2.

For BP, at 3310 cm^{-1} the wide band is attributed to O-H stretching diagnostic for the presence of, higher phenolic constituents in raw banana peel.

At 2933 cm^{-1} the absorption bands are due to S-S groups **(Shamsayei et al., 2018**), while at 1630 $cm^{-1}$the bands can be described as aromatic C=C group **(Mehraban et al., 2020**).

At 1465 and 1422 cm^{-1} the absorption bands may be due to the bending vibration of aliphatic C-H groups, and O-H groups of alcoholic and aliphatic acids, respectively **(Mehraban et al. 2020**).

For aminated-BP, at 1643 cm^{-1}, it can be due to the C=N group, which confirms the oxidative cleavage and addition of amine and imine groups, and a new characteristic absorption band is shown. Also, at 2900 cm^{-1}, a strong band appeared, confirming the excess of the attached groups of NH_2 with the surface after the amination reaction.

Hence, it could be concluded that new –C=O groups were generated in the BP material during the oxidative cleavage reaction, which was converted to imine –C=NH and NH_2 groups during the following amination reaction. The formed nitrogen-rich material adsorption of the studied cations on the adsorbents occurs through the physical adsorption mechanism between the cations (positive charge) and adsorbent molecules (negative charge) because of the combination with the lone pairs of electrons of its oxygen atoms.

The SEM micrographs of raw BP and the progressing am-

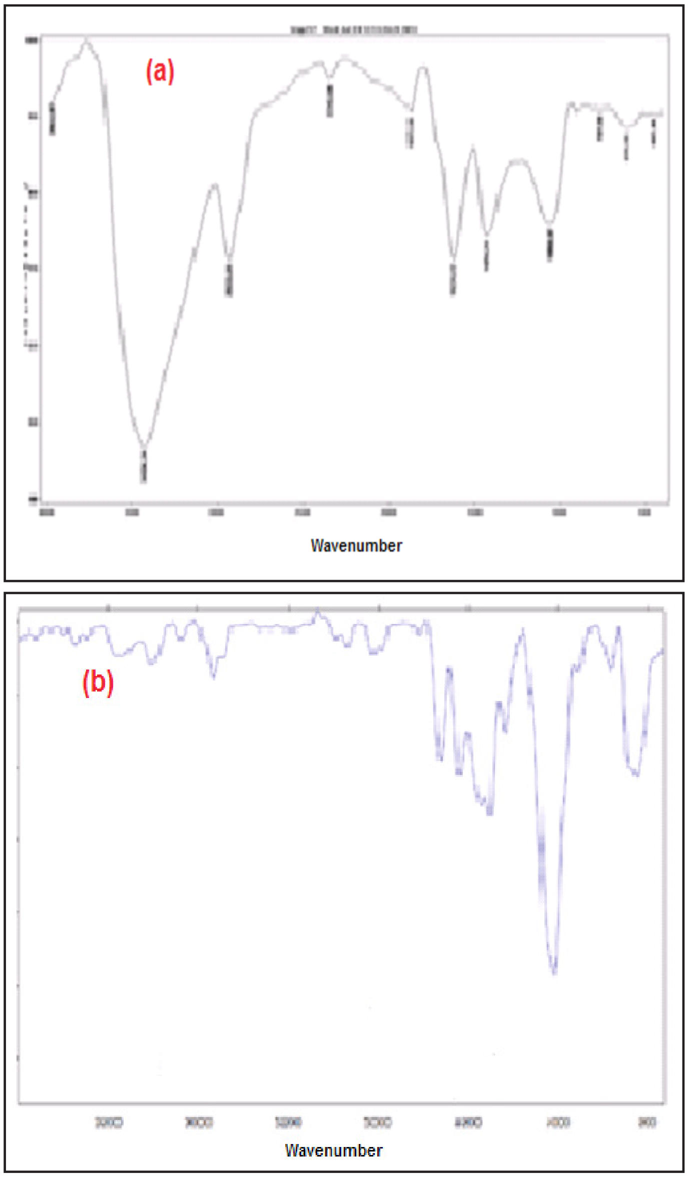

Figure (2): FT-IR spectrum of raw-BP (a) and the aminated-BP adsorbent(b)

inated-BP materials are shown in Figure. 3. BP showed a tubular-like morphology of a hexagonal-shaped structure of a high-porosity surface. The calculated value of the average pore volume on the surface of the particles is 10.2 µm, indicating that the exposed surface area for the adsorption is relatively high. The micrograph of aminated-BP shows that the external surface is an amorphous structure, as shown in Figure. (3-b). In the aminated banana, the density was 0.598 g cm$^{-1,}$ and the moisture content was found to be 20%.

The XRD patterns of both BP and aminated-BP showed a very broad peak at 2θ from 10° to 40°, confirming the amorphous nature of the derived aminated-BP biosorbent.

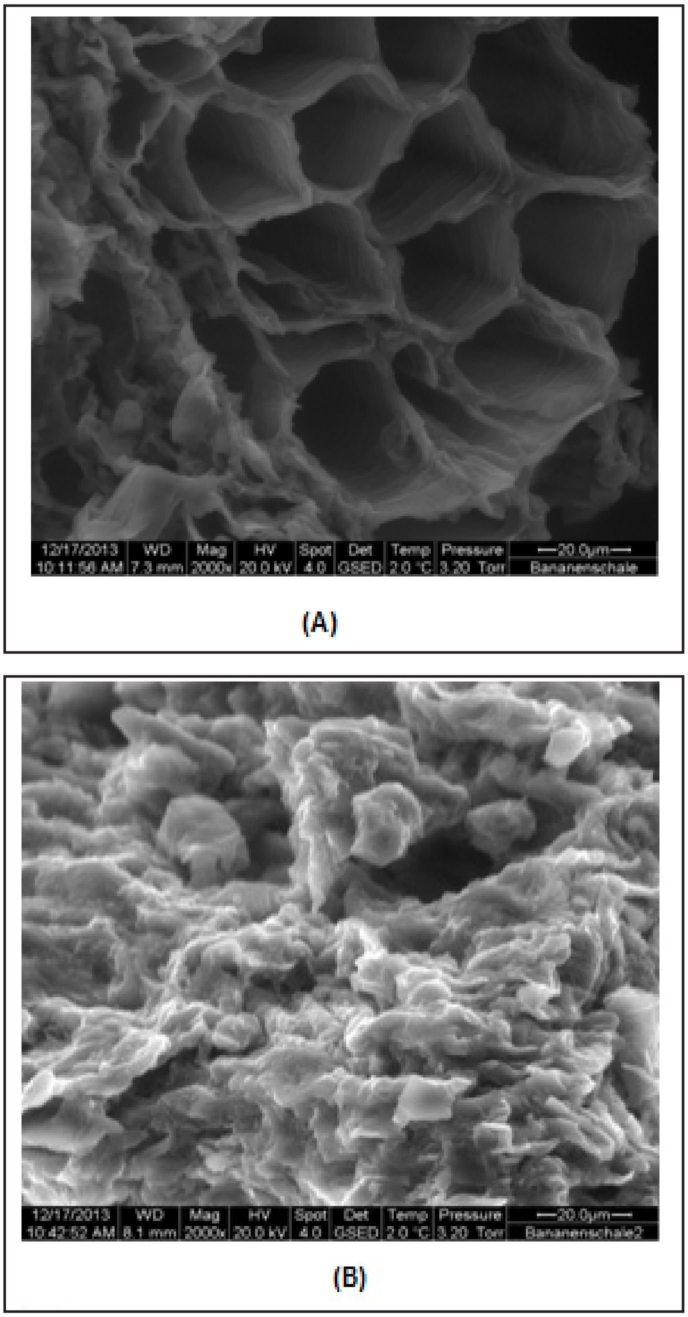

Figure (3): SEM images for BP (A) and aminated-BP (B)

Adsorption removal of Co and CPs

Effect of pH solution

pH effects were studied within the range from 2.0 to 9.0 on the adsorption of Co (II) contaminated-BP and CP onto raw BP, the acquired data are shown in Figure. 4.

For cobalt, the removal (%) increased rapidly with increasing pH from 2 to 5 then reached a maximum value of (79%) at pH 7.0, but at a pH of more than 7.0, removal gradually reduced, which may be due to deposition of metal-hydroxides.

In the case of CPs (Figure 4b), the removal increased rapidly with increasing pH from 2.0 to 4.0, then reached a maximum value around pH 5.0 with a value of 91, 87, and 90 % for 4-CP, 2,4,6-TCP, and nitro-CP, respectively. Highly acidic medium at pH less than 2.0, the removal (%) value was negligible because of the competition of hydrogen ions for the active sites. in the case of 4-CP but strongly decreased with TCP and nitro-CP.

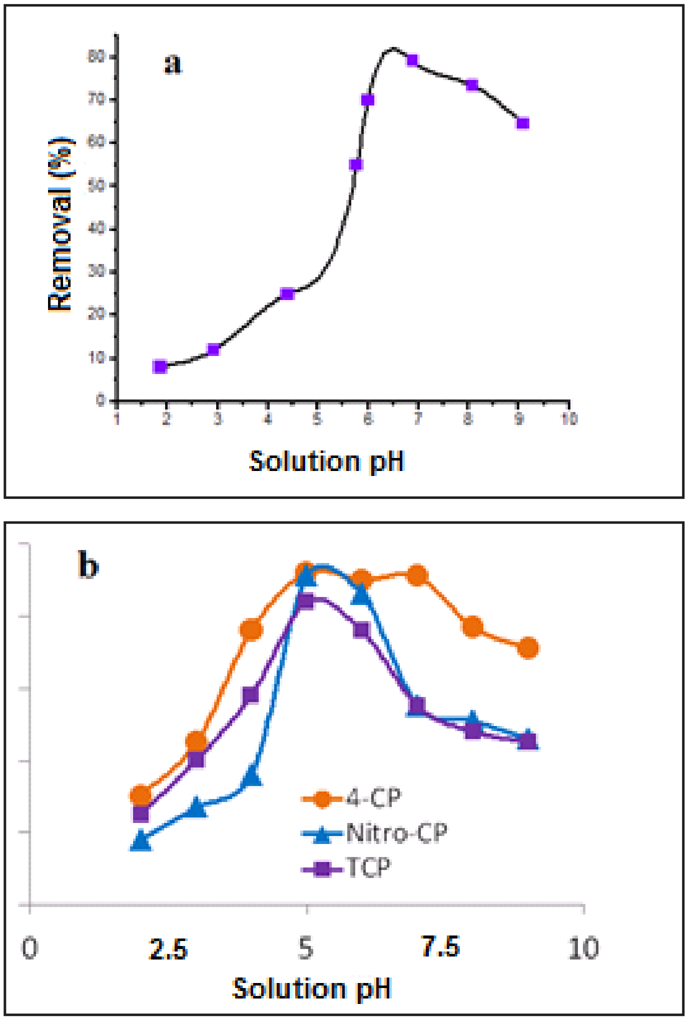

Figure (4): pH effects on the removal of cobalt (a) on aminated-BP and CPs (b) on raw BP adsorbents: sample volume 10 mL, cobalt or CPs concentration 400 µg/l, shaking time 1 h, and sorbent weight 0.1 g influence of equilibrium time

The time of studied shaking ranges from 1–60 min shaking, at pHs 7.0 for Co (II) and 5.0 for CPs samples, respectively, using a shaking speed of 230 rpm as shown in (Figure. 5). Decontamination was rapidly increased and reached equilibrium condition after 25 and 20 min for cobalt and CPs, respectively, indicating fast adsorption process and good accessibility of adsorption sites. So, to ensure the performance of the equilibrium condition a 30 min of shaking time was settled in the following experiments. The dominant adsorption kinetic technique was studied by adequate experimental consequence to the pseudo-first and second-order models (Figure 5). The validity of the pseudo-first-order model could be examined by plotting log ($q_e – q_t$) versus t; the rate of adsorption using this model is expressed by Equation 3:

where q_e and q_t represent the adsorbed number of CPs (μg/g) at equilibrium and at time t (min), respectively.

$$\log (Q_e – Q_t) = \log Q_e - k_1 t/2.303 \qquad (3)$$

(Ramazanoğlu et al., 2022)

Kinetic parameters are shown in Table 1. For Cobalt (II) the degradation results show a linear correlation coefficient (R^2) of 0.984 and q_e values of 31.0 mg/g, while for CPs showed linear correlation coefficients (R^2) from 0.719 - 0.7930, and q_e values from 1.21 - 3.46 mg/g.

A considerable conflict was found with the experimental q_e values from 3.4 to 5.1 mg/g, respectively, showing the uncomfortable characterization of the adsorption kinetics by the pseudo-first-order model.

The pseudo-second-order model is expressed as in Equation (4):

$$t/Q_t = 1/(k_2 Q_e^2) + (1/Q_e)t \qquad (4)$$

(Abbasi et al., 2013)

Where k_2 is the second-order model's rate constant (mg/g min^{-1}); Figure 5 characterizes the engagement of the results with this model. For cobalt, R^2 values are greater than that of the first-order model. Also, q_e has a similarity to the experimental value.

For CPs, the acquired R^2 values from the slope of the degradation equations are higher than those of the pseudo-first-order model, which ranges from 0.992 to 0.999. Moreover, obtained qe values from the second-order model were uncommon, like experimental results ranging from 3.9 to 5.9 mg/g. Thus, the pseudo-second-order model is confirmed as favourable for investigating the kinetic effects experimentally.

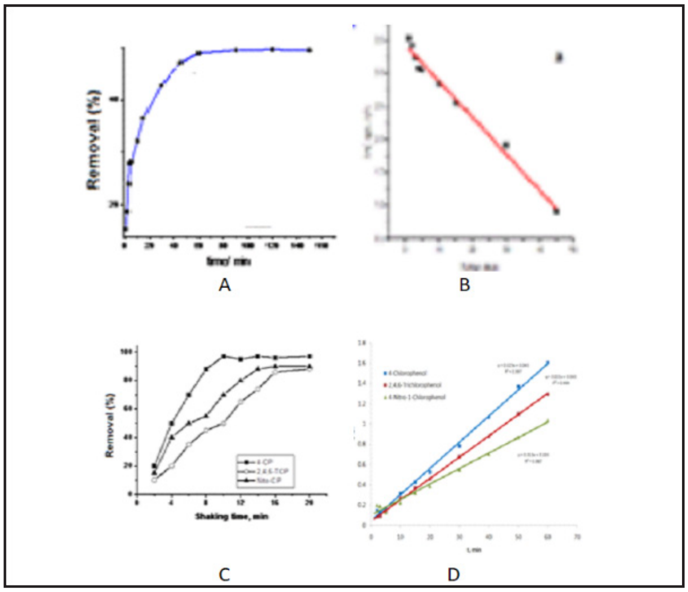

Figure (5): Effect of shaking time on removing cobalt (A) & CPs (C) using the aminated-BP, Pseudo-second-order kinetic model of cobalt at (B) and CPs at (D) sample volume 10 ml, concentration 40 μg/l, and sorbent weight 0.1 g

Table (1): The obtained kinetic data of Adsorption by intraparticle diffusion models first and second-order at 25 °C

Analyte	Adsorbent	Q_{exp} mg/g	Pseudo-first–order			Pseudo-Second–order		
			Q_e mg/g	K_1 mg/g min^{-1}	R^2	Q_e mg/g	K_2 mg/g min^{-1}	R^2
4-CP	Raw-BP	5.1	1.0	0.034	0.470	5.6	0.176	0.995
2,4,6-TCP	Raw-BP	3.4	1.7	0.098	0.948	4.8	0.018	0.981
Nitro-CP	Raw-BP	4.6	2.3	0.057	0.891	5.0	0.033	0.991
Cobalt	Aminated-BP	49.49	31.0	0.127	0.984	50.9	0.005	0.993

Adsorption equilibrium

Adsorption isotherm study enables the evaluation of the equilibrium adsorption capacity of cobalt and CP binding strength to the studied adsorbents. The cobalt adsorption capacity was investigated at concentrations varying from 5 - 50 mg/l and sorbent of 0.1 g for 30 min at 25 °C. Adsorption isotherm showed saturation of the aminated-BP adsorbent of 40 mg/l of concentration, and the calculated experimental qe value was 42.89. In the case of CPs with BP, the adsorption capacity was determined by shaking for 30 min at 25 °C a series of 10 ml samples containing varying concentrations of 0.5 - 10 mg/l and a sorbent of 0.1 g. Extraction isotherm showed saturation of the sorbent was reached at a concentration of 6.0 mg/l with the corresponding experimental qe values of 5.7, 3.6, and 4.3 mg/g for 4-CP, TCP, and nitro-CP respectively. The isotherm profile is shown in Figure. 6. TheLangmuir and Freundlich isotherm models were studied to fit the results. Langmuir isotherms are expressed by Equation (5).

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} K_L} \qquad (5)$$ **Kaewsarn et al. (2008)**

Where: maximum sorbed amount q_{max} of Co (II) and CPs (mg/g) form a complete monolayer. Equilibrium concentration C_e(mg/l) and Langmuir constant K_L related to the affinity of bound with sites to Co (II) and CPs. This model, when matched with the results, supposes a monolayer adsorption technique. The capacity of maximum monolayer adsorption (q_{max}, mg/g) was elaborated from this model.

Freundlich isotherm is an Experimental model established on adsorption on different surfaces, found on somewhat higher linkage grades than the Langmuir model, and more fitting to characterize the adsorption conductance, which shows the importance of surface heterogeneity, as shown in Fig. (6) and Table 2.

$$\ln Q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \qquad (6)$$ **Theng et al. (1966)**

Where Q_e is the adsorption quantity of Co (II) and (mg/g), C_e is the concentration balance of the CP (mg/l), and n and K_F are Freundlich constants correlated to adsorption strength and capability, respectively.

Table (2): Obtained parameters from Isotherms models

Isotherm model	Parameters	Cobalt	Chlorophenols		
Langmuir	Q_{max}, mg/g	8.15	6.5	10.5	7.1
	K_L, L/mg	1.0006	0.145	0.134	0.165
	R^2	0.998	0.851	0.786	0.869
Freundlich	N	0.39	1.08	1.00	1.10
	K_F	2.697	0.733	0.893	1.064
	R^2	0.988	0.992	0.990	0.994

The adsorption isotherm study implies that the adsorption process can be advanced by forming a multilayer covering the interface of the adsorbent. This also considered surface heterogeneity and as long as an exponential division of energetic sites on the surface of the adsorbent. This is regular with the existence of various poisons in the SEM micrographs of the adsorbent.

The adsorption process may initiate with the diffusion of analyte from the bulk of the solution to the adsorbent surface and, after that, to the interior surface to combine with active groups for unlimited gathering in a monolayer or extended to a multilayer style.

The Freundlich constant K_F is 2.697 L/g, which shows a very similar sorbent towards Co (II) during multilayer formation. The maximum calculated capacity (Q_{max}), from the Langmuir model was established as follows, 10.5, 6.5, and 7.1 mg/g for 4-CP, TCP and Nitro-CP, respectively.

The big difference in the capability of adsorption may be due to variations in chemical structure, the number of chlorine atoms, the bonding strength with the BP, and the degree of hydrogen bonding (**Thrower, 1989).**

Nitro-CP has a greater capacity than 4-CP and TCP due to the existence of nitro groups, so the chelating sites are more attainable to nitro-CP and gain a higher adsorption capacity. The Freundlich constant K_F ranged from 0.733 to 1.064 g/l, showing a similar affinity of the sorbent towards all CPs during multilayer formation. Thus, in the early stages of adsorption during the monolayer formation, the difference among the adsorbed CPs was noticeable. The value of the (n) constant was higher than 1.0, which indicates adequate adsorption.

Both values of Freundlich constants specified the favourable adsorption of CPs by BP adsorbent. This conveys the utility of this adsorbent in the enrichment of CPs from too-low concentration samples to achieve quantitative determination by the recommended HPLC technique.

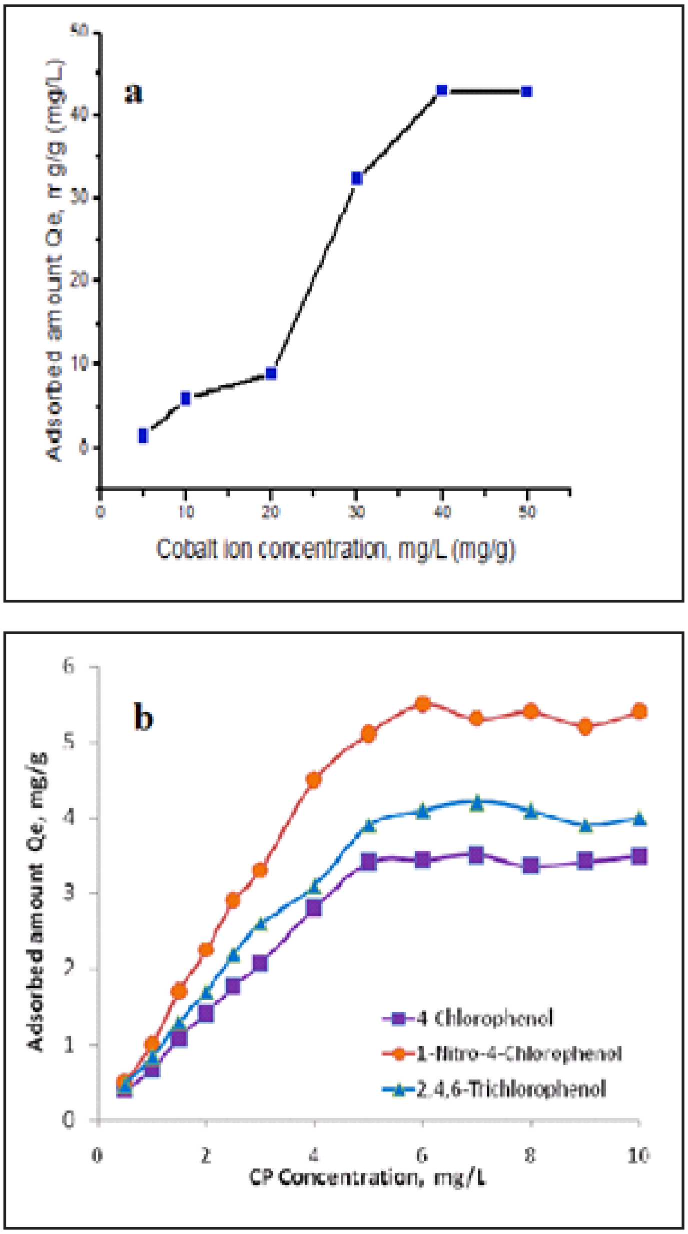

Figure (6): Adsorption isotherm of cobalt (a) onto aminated-BP and CPs (b) onto raw BP adsorbents, respectively: sample volume 10 ml, Concentration: 0.5-10 mg/l of CP , 5-50 mg/l of cobalt and sorbent weight 0.1g

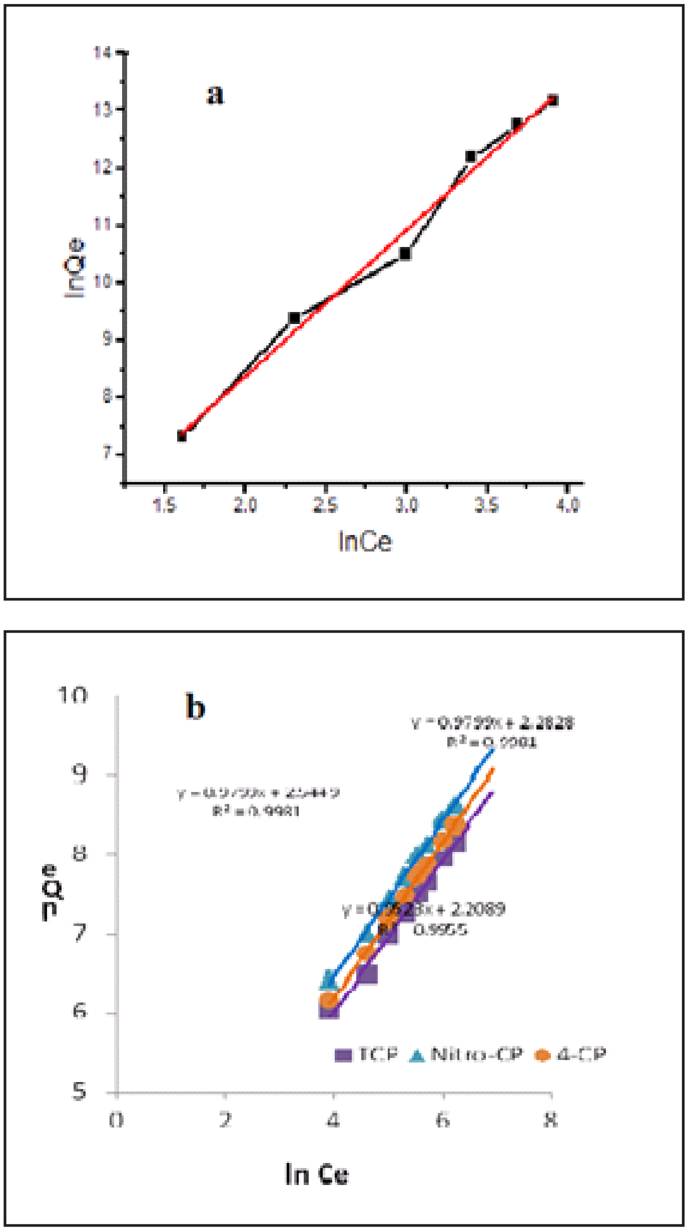

Figure (7): Freundlich isotherm model for cobalt adsorption onto aminated-BP (a) and CP onto BP (b) adsorbents

Adsorbent amount

The influence of sorbent dosage was examined for cobalt and the selected 4-CP compound. Different dosages varying from 0.03 to 0.5 g were tested at pHs 7 and 5, respectively, with a 30 min shaking period. Removal was found to be highly dependent on the amount of sorbent.

Maximum elimination of 91% and 98 % was obtained at sorbent dose ≥ 0.1 g. Further increase in the amount of sorbent was found insignificant. So, the optimal dose was chosen at 0.1 g in the study.

Desorption study

The desorption of cobalt and CPs was examined using varying concentrations of hydrochloric acid and aqueous methanol, respectively.

Hydrochloric acid was inspected from 0.05 to 0.3 mol/l. Results showed excellent cobalt recovery at acid concentrations starting from 0.1 mol/l and above. Thus, 0.1 mol/l concentration was selected for cobalt desorption from aminated-BP.

For CPs desorption, the methanol solution was examined in the range of 5-50% (v/v) using 20 ml with a concentration of 40 µg/l of cobalt or CPs. The recovery gradually increased and reached a maximum value of 90, 88, and 90 % by 50% methanol.

The peaks corresponding to 4-CP and TCP were completely overlapped at a methanol concentration of 25%, but were separated after reaching a 30% concentration. Further concentration of methanol than 50 % (v/v) showed no improvement in recovery data. Thus, a 50 % methanol solution was recommended for desorption. For 4-CP and nitro-CP, the peaks were quantitative and stable.

In contrast, the peak for TCP has become wide board. This could be attributed to stronger binding forces to the adsorbent, resulting in slower TCP release by the eluent. Despite the reduction in peak height, the peak area remained quantitative.

Application to water samples

The addition/recovery tests for cobalt and CPs removal from tap and river water samples were investigated by the presented process, as shown in Table 3.

To demonstrate the practical utility of this procedure, tap and river water samples were analyzed. The levels of 3.0 and 5.0 mg/l of cobalt and 2.0 mg/l of CPs for spiked water samples, using the recommended procedure.

Table (3): Application to water samples

Sample	Adsorbent	Analyte	Spike, mg/L	Found (mean± SD), µg/L	Recovery (%)	RSD (%)
Tap water	Aminated-BP	Cobalt	3.0	2.96± 0.11	98.7	3.4
			5.0	5.40± 0.32	98.1	5.9
River water	Aminated-BP	Cobalt	3.0	2.67± 0.13	88.9	4.8
			3.0	4.65± 0.09	93.0	1.9
Tap water	Raw-BP	4-CP	2.0	1.85± 0.03	92.5	1.6
		2,4,6-TCP	2.0	1.80± 0.05	90.0	2.8
		Nitro-CP	2.0	1.68 ± 0.12	84.0	7.1
River water	Raw-BP	4-CP	2.0	1.71± 0.08	85.5	4.5
		2,4,6-TCP	2.0	1.64± 0.15	82.0	9.1
		Nitro-CP	2.0	1.60± 0.10	80.0	6.3

Cobalt recovery ranged from 88.9-98.1%, with a corresponding RSD value range from 1.9 -5.9%. Thus, the recovery was quantitative, confirming the accuracy of cobalt removal from the examined water samples.

The proposed aminated BP was suggested as a versatile and adequate adsorbent for removing cobalt in several kinds of real-world waters.

For CPs, non-spiked water samples were analyzed in parallel and revealed no detectable cobalt of HPLC peaks for CP. This highlights the inability of the HPLC-UV technique to determine the current CP in the absence of a pre-concentration step.

For spiked water samples at a concentration level of 2.0 mg/l, all CPs had good agreement between spiked and measured analyte amounts.

For tap water, the recovery ranged from 84-92 %. The corresponding RSD (n=4) was found in the range of 1.6-7.1%. For river water, the recovery changed from 80-85 %, and RSD varied from 4.5-9.1%, respectively.

The calculated recovery values for the spiked water were always greater than 80%. Based on these findings, the proposed raw-BP adsorbent could be used to analyze these CP samples.

Comparison with other sorbents

A comparison of the developed adsorbent to other reported materials for cobalt and CPs removal is presented in Table 4.

The adsorption capacity of Am-BP was found higher than raw BP (**Abbasi et al., 2013**; **Ramazanoğlu et al., 2022**), bean peels **(Almhana et al., 2020**), and Citrus reticulate **(Ahamd et al., 2024**) but was less than activated carbon **(Tazik et al., 2023**).

This confirms the developed adsorbent has a good capacity for removing the studied cobalt and CPs from natural water samples.

The equilibration time of the current work is 30 min which is shorter than other reported adsorbents. The removal efficiency of the developed adsorbent was 89 % for cobalt and 88-98.1% for CPs which are comparable to other listed materials.

Thus, the developed Am-BP is considered within the range obtained by other methods. However, the superiority and advantages of the present adsorbent can be due to its being an environmentally safe material, cost-effective, and fast synthesis protocol.

Table (4): Comparison of the adsorption properties of CP and cobalt with other reported adsorbents

Analyte/ Adsorbent	Sample	Adsorption capacity, mg/g	Equilibration time, min	Temperature (°C)	pH	Removal (%)	Ref.
Cobalt	Tap and River water	8.5	30	25	7	92	This work
CPs	Tap and River water	6.5-10.5	30	25	5	89-108	This work
Heavy metals /BP	Environmental water	4.87	60	24	5.5	-	*Ramazanoğlu et al., 2022*
Cobalt/BP	Environmental water	9.02	30	27	5.5	81.0	*Abbasi et al., 2013*
Cobalt/ Broad Bean Peels	Synthetic Wastewater	0.92	90	25	6.0	97.5	*Almhana et al., 2020*
CPs /BP	Environmental water	-	60	25	6.0	91.25	*Ibrahim et al., 2019*
CPs/ Citrus reticulata	Oilfield Produced water	0.72	180	20	1.0	74.43	*Alhamd et al., 2024*
CPs /activated carbon	environmental water	316.1	35	30	3.0	95.35	*Tazik et al., 2023*

Conclusion

Raw-BP was used as an adsorbent for CPs removal from tap and river waters. An aminated-BP was prepared via oxidative reaction followed by ammonia addition that has led to the development of new eco-friendly and environmentally safe adsorbents for cobalt removal.

In the aminated-BP, incorporations of additional amine groups enhanced both the capacity and selectivity of the aminated-BP toward the examined cobalt. The FT-IR test confirmed the chemical modification occurred via C-N and N-H stretching bands and the reduction of O-H and COOH bands.

The SEM image indicated the microstructure is a heterogeneous surface. The XRD pattern showed a nanocrystalline structure.

The adsorption kinetics reached the equilibrium conditions in a 20-minute shaking period and the order of adsorption rate is 4-CP >> nitro-CP>TCP. The adsorption capacity for cobalt was 8.5 mg/g using aminated-BP, the raw BP showed capacities of CPs ranging from 6.5-10.5 mg g^{-1} which is quite sufficient for quantitative adsorption of CPs from real samples, even in contaminated waters they naturally exist at the µg/l or ng/l levels.

Compared to the reported methods, the present approach showed better adsorption capacity and shorter equilibration interval than many reported materials.

The above findings make the use of raw BP as the developed aminated-BP procedure alternative for removing CPs and cobalt, respectively in water samples.

The proposed materials are recognized as easily prepared and low-cost adsorbents for environmental water treatment.

Acknowledgment

Our deep thanks to Prof. Dr. Torsten Schmidt for his great help and all supplements in carrying out part of the experimental work at the Chemistry Department, University of Duisburg-Essen (Germany), and also, part of the exs perimental work at the Siting and Environment Department, Nuclear and Radiological Safety Research Centre (NRSRC), IAEA.

Furthermore, the authors deeply thank all representatives of the Integrated Water Technologies (Iwa Tec) project funded by the DFG authority.

References

- **Abbasi, Z., Alikarami, M.; Nezhad, E.R.; Moradi, F. and Moradi, V. (2013):** Adsorptive Removal of Co^{2+} and Ni^{2+} by Peels of Banana from Aqueous Solution. *Univers. J. Chem.*, 1(3): 90.

- **Adolfo, F.R.; doascimento, P.C.; Bohrer, D.; de Carvalho, L.M.; Viana, C.; Guarda, A.; Nunes, C.A. and Mattiazzi, P. (2016):** Simultaneous determination of cobalt and nickel in vitamin B12 samples using high-resolution continuum source atomic absorption spectrometry. Departamento de Química, Universidade Federal de Santa Maria, RS, Brazil 97111: 900.
- **Ahamd, S.J.; Abbas, M.N.; Jawad, A.; Ibrahim, H.J.T.A. and Abbas, Z.N. (2024):** Removal of phenol from oilfield produced water using non-conventional adsorbent medium by an eco-friendly approach. *Karbala Int. J. Mod. Sci.*, 10(2): 4.
- **Aksu, Z. and Yener, J.A. (2001):** comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents. *Waste Manag*., 21: 695.
- **Almhana, N.M.; Ali, S.A.K.; Al-Najjar, S.Z. and Al-Sharify, Z.T. (2020):** Assessment of Cobalt Ions Removal in Synthetic Wastewater using Broad Bean Peels. *J. Environ. Eng.*, 10(11): 10157.
- **Brinda Lakshmi, A.; Balasubramanian, A. and Venkatesan S. (2013):** Extraction of phenol and chlorophenols using ionic liquid [Bmim]+[BF4]-dissolved in tributyl phosphate. *Clean – Soil, Air, Water*, 41(4): 349.
- ***Ekpete, O.A.; Horsfall, J.M. and Tarawou, T.* (2011):** Evaluation of activated carbon from fluted pumpkin stem waste for phenol and chlorophenol adsorption in a fixed–bed microcolumn, *J. Appl. Sci. Environ. Manage*., 15: 141.
- **Environmental Protection Agency (1981):** part VIII, 40 CFR part 136, p.58.
- **Environmental Protection Agency (EPA) (1984):** method 625, phenols, in Federal Register.
- **Feng, Q.Z.; Zhao, L.X.; Yan, W.; Lin, J.M. and Zheng, Z.X. (2009):** Molecularly imprinted solid-phase extraction combined with high performance liquid chromatography for analysis of phenolic compounds from environmental water samples. *J. Hazard. Mater*., 167(1-3): 282.
- **Fickling, M. M.; Fischer, A.; Mann, B.R.; Packer, J. and Vaughan, J. (1959):** Hammett Substituent Constants for Electron-withdrawing Substituents: Dissociation of Phenols, Anilinium Ions and Dimethyl anilinium Ions. *J. Am. Chem. Soc.*, 81(16): ٤٢٢٦.
- **Gómez, M.; Murcia, M.; Dams, D.; Christofi, R.; Gómez, N.E. and Gómez, J.L. (2012):** Removal efficiency and toxicity reduction of 4-chlorophenol with physical, chemical and biochemical methods. *Environ Technol*., 33: 1055.
- **Higashi, Y. and Fujii, Y. (2009):** HPLC-UV analysis of eugenol in clove and cinnamon oils after pre-column derivatization with 4-fluoro-7-nitro-2,1,3-benzoxadiazole, *J. Liq. Chromatogr. Related. Technol*., 32: 2372.
- **Hikal, W.M.; Said-Al Ahl, H.A.H.; Bratovcic, A.; Tkachenko, K.G.; Sharifi-Rad, J.; Kacaniova, M.; Elhourri, M. (2022):** Banana peels: a waste treasure for a human being, *Evid Based Complement Alternat Med.*, 7616452.
- **Hossain, M.A.; Hao, N.H.; Guo, W.S. and Nguyen, T.V. (2012):** Removal of copper from water by adsorption onto banana peel as bio adsorbent. *Int. J. Geomate*., 2: 227.
- **Ibrahim, S.I.M.; Schmidt, T.C. and Abdel Azeem, S.M. (2013):** Banana Peel as Alternative Bio-sorbent Material for Removal of 2-Chlorophenol from Water. https://www.uni-due.de/imperia/md/content/zwu/banana_peel_as_alternative_bio-sorbent_material_for_removal_of_2-chlorophenol_from_water.pdf
- **ICP-OES (2024):** Determination of Cobalt in Natural Water Using a Flow Injection System After Preconcentration on Activated Carbon. accessed Mar 05.
- **Ismael, M.E.; Mokhtar, A.; Adil, H.; Li, X. and Lü X. (2022):** Appraisal of heavy metals exposure risks via water pathway by using a combination pollution indices approaches, and the associated potential health hazards on population, Red Sea State, Sudan. *Phys. Chem. Earth*, 127: ١٠٣.
- **Jadhav, D.N. and Vanjara A.K. (2004):** Removal of phenol from water using sawdust, polymerized sawdust, and sawdust carbon. *Ind. J. Chem. Technol*., 11: 35.
- **Jain, S. and Jayaram, R.V. (2007):** Adsorption of phenol and substituted chlorophenols from aqueous solution by activated carbon prepared from Jackfruit (artocarpusheterophyllus) peel-kinetics and equilibrium studies. *Sep. Sci. Technol*., 42: 2019.
- **Kaewsarn, P.; Saikaew, W. and Wongcharee, S. (2008):** Dried biosorbent derived from banana peel: a potential biosorbent for removal of cadmium ions from aqueous solution. 18th Thailand Chemical Engineering and Applied Chemistry Conference October 20-21 Pattaya Thailand.
- **Kargari, A. and Khazaali, F. (2015):** Effect of operating parameters on 2-chlorophenol removal from wastewaters by a low-pressure reverse osmosis system. *Desalination*, 55: 114.
- **Layer, R.W. (1996):** The chemistry of imines. *Chem. Rev*., ٦٣(٥): ٤٨٩.
- **Lee, K.C. and Ku, Y. (1998):** Removal of chlorophenols from aqueous solution by anion-exchange resins. *Sep. Sci. Technol*., 31: 2557.
- **Lee, M.R.; Yeh, Y.C.; Hsiang, W.S. and Hwang B.H. (1998):**, Solid-phase microextraction and gas chromatography-mass spectrometry for determining chlorophenols from landfill leaches and soil. *J. Chromatogr*. A., 806(2): 317.
- **Li, J.; Zhao, X., Shi, Y., Cai, Y., Mou, S. and Jiang, G. (2008):** Mixed hemimicelles solid-phase extraction based on cetyltri-

methylammonium bromide-coated nano-magnets Fe_3O_4 for the determination of chlorophenols in environmental water samples coupled with liquid chromatography/spectrophotometry detection. *J. Chromatogr*. A., 1180: 24.

- **Lopez, P.; Roldan, M.L.; Alda, de. and Barcelo, D. (2004):** Simultaneous determination of selected endocrine disrupters (pesticides, phenols, and phthalates) in water by in-field solid-phase extraction (SPE) using the prototype PROFEXS followed by on-line SPE (PROSPEKT) and analysis by liquid chromatography-atmospheric pressure chemical ionisation-mass spectrometry. *Anal. Bioanal. Chem*., 378: 599.
- **Manojlovic, D.; Ostojic, D.R., Obradovic, B.M.; Kuraica, M.M.; Krsmanovic V.D. and Puric, J. (2007):** Removal of phenol and chlorophenols from water by new ozone generator. *Desalination*, 213: 116.
- **Mehraban, M. and Manoochehri, M. (2020):** Determination of chlorophenols in water by liquid chromatography method after magnetic solid phase extraction based on SiO_2/MIL-101@Fe_3O_4 nano adsorbent. *Sep. Sci. Plus,* 3(5): ١٥٠.
- **Mokhtari, N.; Khataei, M.M.; Bahram, M.D.; Monjezi, H. and Yamini, Y. (2021):** Solid-phase extraction and microextraction of chlorophenols and triazine herbicides with a novel hydrazone-based covalent triazine polymer as the adsorbent. *Microchem. J.*, 160: 105634.
- **Moraisa, P.; Stoicheva, T.; Clara, M.; Bastoa, P.; Teresa, M. and Vasconcelos, S.D. (2012):** Extraction and preconcentration techniques for chromatographic determination of chlorophenols in environmental and food samples. *Talanta*, 89: 1.
- **Nyssen, G.A.; Lovell, G.S.; Simon, A.A.; Smith, J.G.; Tolar, B.K. and Wilson, D.J. (1987):** Removal of Trace Levels off Phenols from Aqueous Solution by Foam Flotation. *Sep. Sci. Technol*., 22: 2127.
- **Plugarin, C. and Torres, R.A. (2003):** Electrochemical degradation of p-substituted phenols of industrial interest on Pt electrodes. *Chemosphere*, 50: 97.
- **Radhika, M. and Palanivelu, K. (2006):** Adsorptive removal of chlorophenols from aqueous solution by low-cost adsorbent kinetics and isotherm analysis. *J. Hazard. Mater*., 138: 116.
- **Ramazanoğlu, D.; Mohammed, Z.A. and Maher K.A. (2022):** Extraction of some heavy metal ions from aquatic solution by banana peel-based biosorbents. *Environ. Res. Tec*., 1: 5.
- **Sarrión, M.N.; Santos, F.J. and Galceran, M.T. (2002):** Determination of chlorophenols by solid-phase microextraction and liquid chromatography with electrochemical detection. *J. Chromatogr*. A, 9471: 55.
- **Shamsayei, M.; Yamini, Y. and Asiabi, H. (2018):** Evaluation of highly efficient online yarn-in-tube solid phase extraction method for ultra-trace determination of chlorophenols in honey samples. *J. Chromatogr*. A, 1569: 70.
- **Stevenson, F.J. (1982):** Humus Chemistry A wiley- Interscience publication, New York, USA.
- **Swelam, A.A.; Awad, M.B.; Salem, A.S.M.A. and El-Feky, A.S. (2017):** Biosorption of Cobalt (II) Ions from Aqueous Solution using Rice Strawand its Modification. *J. Sci. Eng. Res*., 4: 121.
- **Tazik, M.; Dehghani, M.H.; Yaghmaeian, K.; Nazmara, S.; Salari, M.; Mahvi, A.H.; Nasseri, S.; Soleimani, H. and Kariri, R.R. (2023):** 4-Chlorophenol adsorption from water solutions by activated carbon functionalized with amine groups: response surface method and artificial neural networks. *Sci. Rep*., 13: 7831.
- **Theng, B.K.G.; Wake, J.R.H. and Posner, A.M. (1966):** NOTE. *Soil Sci*., 102(1): 70.
- **Thrower, P.A. (1989):** Chemistry and Physics of Carbon. Marcel Dekker, Inc., New York.
- **Tseng, R.L.; Wu, K.T., Wu, F.C. and Juang, R.S. (2010):** Kinetic studies on the adsorption of phenol, 4-chlorophenol, and 2,4-dichlorophenol from water using activated carbons. *J. Environ. Manage*., 91(11): 2208.
- **Wang, K.D.I.; Chen, P.S. and Huang, S.D. (2014):** Simultaneous derivatization and extraction of chlorophenols in water samples with up-and-down shaker-assisted dispersive liquid-liquid microextraction coupled with gas chromatography/mass spectrometric detection, *Anal. Bioanal. Chem*., 406: 2123.