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Phenol Adsorption from Water Using Raw and Quaternized Waste Sorbents: Isotherm, Kinetic, and Thermodynamic Analysis

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Abstract

This study evaluates the adsorption of phenol from aqueous solutions using raw and quaternized peels derived from *Cucumis metuliferus Thunb*. (RTP/QTP) and *Aframomum melegueta* (RAP/QAP), abundant agricultural wastes in Kenya's Ruiru Sub-County. Phenolic pollutants from industrial effluents and agricultural runoff pose severe risks to aquatic ecosystems and human health, including toxicity, carcinogenicity, and bioaccumulation. Traditional remediation techniques such as incineration, advanced oxidation, and membrane filtration are costly, energy-intensive, and prone to secondary pollution, limiting their feasibility in developing regions. In contrast, these zero-cost biosorbents leverage natural lignocellulosic structures, with quaternization—employing epichlorohydrin, propylene oxide, and polyDADMAC—introducing quaternary ammonium groups to boost porosity, surface charge, and affinity for anionic phenolics via enhanced electrostatic interactions and hydrogen bonding.

Raw peels were processed into powders (< 1 mm), while modified versions underwent epoxy activation and amination. Batch adsorption experiments optimized critical parameters: pH 4 (maximizing protonation), contact time 30–60 min, sorbent dose 0.03–0.05 g/20 mL, initial concentrations 5–60 mg/L, and temperature 298 K. Quaternized sorbents excelled, achieving 95.95% phenol removal (QAP) and q_{max} of 17.61 mg/g, outperforming raw counterparts by 2-4-fold. Langmuir isotherms ($R^2 > 0.90$) confirmed monolayer chemisorption, pseudo-second-order kinetics ($R^2 > 0.89$) indicated chemisorption control (K_2 up to 0.124 g/mg/min), and thermodynamics revealed exothermic (ΔH° -10 to -18 kJ/mol), spontaneous (ΔG° negative), entropy-increasing processes favoring low temperatures. Regeneration via 0.5 M HCl sustained > 50% efficiency over five cycles, with Ruiru River spiked samples showing 20–29% removal despite matrix effects. These findings affirm quaternized peels as sustainable, regenerable sorbents for phenolic wastewater treatment, promoting waste valorization and circular economy principles in resource-scarce settings.

1. Introduction

Phenolic compounds like phenol and p-nitrophenol (PNP) contaminate waterways primarily through industrial discharges from petrochemical plants, dye factories, and pesticide applications, as well as agricultural runoff [1]. These substances inflict acute toxicity on aquatic life by disrupting metabolic processes and reproduction, while chronic human exposure leads to dermal irritation, hepatic damage, and heightened cancer risks [2]. In Kenya's Ruiru Sub-County, where intensive farming and local commerce prevail, river systems face elevated phenolic loads, necessitating accessible purification strategies.

Established remediation techniques, including chemical incineration, biological degradation, and advanced membrane separation, incur steep energy expenses and frequently generate secondary pollutants or struggle with dilute concentrations [3]. Surface binding of contaminants to solid media offers a simpler, more flexible option that operates effectively across diverse conditions and avoids toxic

residues [4]. Nevertheless, reliance on costly engineered carbons restricts adoption in resource-limited settings [5].

Discarded fruit rinds from common Kenyan market produce emerge as ideal, no-cost bases for natural binding agents, featuring sturdy fiber matrices primed to trap organic toxins. Rinds sourced from horned melons (*Cucumis metuliferus Thunb*.) and grains-of-paradise pods (*Aframomum melegueta*), plentiful in Ruiru locales, enable conversion of daily waste streams into practical water treatment resources.

Basic rinds deliver moderate performance owing to sparse pores and reactive spots; targeted chemical upgrades using epoxy linkers and cationic polymers install positive charges, expand internal voids, and amplify draws on deprotonated phenolics [6]. Comparable enhancements applied to other plant discards have markedly amplified uptake rates in documented cases.

This investigation appraises unmodified and upgraded horned-melon or *Cucumis metuliferus Thunb* (RTP/QTP) alongside grains-of-paradise or *Aframomum melegueta* (RAP/QAP) rinds for phenol and PNP extraction via controlled batch trials, refining variables such as solution acidity, mixing duration, material dosage, pollutant levels, and thermal settings. Spectral readings at signature wavelengths feed into binding equilibrium models, reaction velocity equations, and energy balance assessments, with reuse trials and field water tests gauging real-world viability [7]. Anticipated results highlight enhanced rinds achieving peak loads near 17 mg/g, reaction-controlled dynamics, and efficient revival through mild acid rinsing over repeated applications.

2. Experimental

2.1 Sample collection and Preparation of Raw Peels

Fresh peels of *Cucumis metuliferus Thunb* peels (RTP) and *Aframomum melegueta* peels (RAP) were collected from local markets in Ruiru Sub-County, Kenya, during the peak harvest season (March 2025). The peels were obtained from ripe, undamaged fruits sourced from subsistence farms in the region to ensure representativeness of locally available agricultural waste. RTP peels were manually separated from mature *C. metuliferus* fruits, while RAP peels were stripped from dried *A. melegueta* pods.

The collected peels were thoroughly washed with tap water to remove dirt and residues, followed by rinsing with distilled water. Excess water was removed using filter paper, and the peels were cut into small pieces (approximately 1–2 cm^2). The pieces were dried in an oven at 60°C for 24 hours until constant weight was achieved, then ground using a laboratory blender to pass through a 1 mm sieve. The powdered raw peels (RTP and RAP) were stored in airtight plastic containers at room temperature until use.

2.2 Preparation of Quaternized Peels

Quaternized peels (QTP and QAP) were prepared via etherification with epichlorohydrin and propylene oxide, followed by amination with polyDADMAC to introduce quaternary ammonium groups for enhanced

adsorption. Exactly 10 g of dried RTP or RAP powder was mixed with 100 mL of methanol in a 250 mL round-bottom flask. Then, 20 mL of epichlorohydrin and 10 mL of propylene oxide were added dropwise under constant stirring at 50°C for 4 hours to form epoxy-activated peels.

The mixture was cooled, filtered, and the solid residue was washed successively with methanol and distilled water. The epoxy-activated peels were then suspended in 100 mL of 20% polyDADMAC solution (adjusted to pH 10 with 0.1 M NaOH) and stirred at 60°C for 6 hours to complete quaternization. The resultant QTP and QAP were filtered, washed repeatedly with distilled water until neutral pH, and dried at 50°C for 12 hours. The quaternized powders were sieved (< 1 mm) and stored in desiccators.

2.3 Chemicals, reagents and solvents

All the reagents utilized in this investigation were of analytical grade and came from Sigma Aldrich and all solutions were made using distilled water. The phenol and *p*-Nitrophenol (PNP) had a purity of 98%. More chemical substances used included: propylene oxide (99.5%), polyDADMAC (65%), epichlorohydrin (99%), methanol (98%), hydrochloric acid (37%), ammonium acetate (98%) and sodium hydroxide (98%). Distilled water was used to formulate stock solutions with a 1000 g/L concentration of phenol and PNP while required concentrations were constituted by serially diluting the stock solutions. Solutions of 0.1 M NaOH or 0.1 M HNO_3 were exploited to modify the pH.

2.4 Instrumentation

The PNP concentration in water was obtained using a double beam UV-VIS spectrophotometer (Model Specord 200, Analytik Jena) at maximum solution wavelength of 318 nm.

2.5 Batch sorption experiments

On a Lab-line mechanical reciprocating shaker model, sorption tests were executed by utilizing 100 mL plastic screw-cap bottles at a speed of 170 revolutions per minute. Model solutions made in ammonium acetate buffer had their pH values altered using dropwise additions of 0.1 M solution concentration of either sodium hydroxide or hydrochloric acid to values between 2 and 10. Each of the mixtures received known masses of the adsorbent before being given time to equilibrate. The resultant mixes were filtered by utilizing Whatman No. 42 filter paper, and the amount of phenol and PNP at maximal wavelengths of 270 and 318 nm in each filtrate was analyzed by employing a UV-VIS (Model Specord 200, Analytik Jena) spectrometer. The maximal wavelengths were arrived at by scanning phenol and PNP samples on the UV-VIS instrument prior to actual analysis.

2.6 Optimization of adsorption parameters

Influence of parameters: contact time, pH, initial PNP concentration, amount of sorbent and temperature on uptake efficiency of the raw and quaternized sorbents was done by maintaining other parameters stable while changing the one under investigation. Variation of process parameters was done as follows; solution pH (2–10), contact time (1–180 min), sorbent dose (0.005–0.06 g), initial PNP concentration (5–60 mg/L) and temperature (15–90˚ C) in 20 mL aqueous solution.

Thermodynamics studies were done by introducing 0.03 g of the modified sorbent in a plastic bottle containing 20, 35, 40 and 50 mg/L phenolic compound. The mix was stirred thoroughly in a water bath shaker for 60 mins equilibrium time at different temperatures of 288, 298, 308, 318, 338, 348, 363 K and 373 K. This was followed by filtration of the mixture and UV-VIS spectroscopic analysis of the filtrate's phenol or PNP concentration.

2.7 Kinetic studies

The mechanism of phenol and PNP uptake by the raw and quaternized adsorbents was ascertained using the results from the kinetic investigations that were fitted into pseudo first order and pseudo second order rate kinetics. A 20 mL phenol and PNP containing 20 mg/L of phenolic compound were separately transferred into 100 mL plastic bottles at optimum pH and sorbent dose. On a mechanical shaker, the mixture was stirred for 10–180 minutes. Volumes of the solution were taken out after every 10 minutes, filtered and then the quantity of phenol and PNP eliminated was measured. Equations 1 and 2 were used to examine the obtained data after it had been fitted into the Lagergren pseudo-first and Ho's second order models [8].

$\text{Log}\ (q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303}\right)$ Eq. 1

$\frac{t}{q_t} = \frac{1}{K\ 2q_e^2} + \frac{1}{q_e} t$ Eq. 2

2.8 Regeneration studies

The raw and quaternized adsorbents, 1.0 g of each were weighed separately into batches of 200 mL plastic screw cap bottles containing 100 mL of either phenol or PNP solution at a concentration of 20 mg/L. The uptake was executed at optimum conditions already determined for phenol and PNP. The mixtures were stirred for one hour on a mechanical shaker, then filtered, and the amounts of phenol or PNP adsorbed were determined using UV-VIS spectroscopy. Each phenolic compound; phenol and PNP was analyzed at its respective wavelength of maximum absorption. The adsorbent loaded with either phenol or PNP was separately dried and 50 mL of 0.5 M HCl was introduced and shaken for 60 mins to strip the attached phenol or PNP. The procedure was done in five different cycles.

2.9 Analysis of environmental water samples

Environmental samples of water were taken from Ruiru River in Ruiru Sub County and tested for phenol and PNP levels. The river is representative since it's in an area that is heavily cultivated and productive tropical zone owing to the fact that the residents practice subsistence agriculture in addition to the area having heightened commercial activities. The analyte solutions were made by separately spiking with 5 mg/L of phenol and PNP to the samples, the concentration is within the range of phenol and PNP levels reported in environmental water samples. 20 mL of spiked phenol and PNP solutions were introduced into 100 mL screw cap bottles containing 0.03 g of quaternized adsorbents. The adsorption was conducted under predetermined phenol and PNP optimal conditions. The mixtures were stirred for an hour on a mechanical shaker, then filtered, and the quantity of the phenolic compound was identified by

UV-VIS spectroscopy. Each phenolic compound; phenol and PNP was analyzed at its own wavelength of maximum absorption.

3. Results and Discussions

3.1 Optimization experiments

Optimization studies were done on both phenol and PNP as discussed in the following sections.

3.1.1 Impact of pH on uptake of of phenol by the prepared adsorbents

The implication of pH was explored by independently weighing batches of 0.03 g of the sorbents into screw cap bottles holding 20 mL of the model solutions containing 30 mg/L of phenol and changing the solution's pH to the necessary range of 2–10. The mixes were then equilibrated for 60 minutes at 170 rpm and 298 K. The outcomes are displayed in Fig. 1.

The outcomes in Fig. 1 unveil that the percentage removal was high at acidic pH values. A maximum removal percentage of 76.09, 85.38, 62.73 and 95.95 for RTP, QTP, RAP and QAP respectively at pH 4 was observed. Farther increment of pH was coupled with diminishing percentage uptake [9]. The enhancement of phenol solubility and the hike in -OH ion concentration raise the barrier to the negatively charged phenolate ions' ability to diffuse, which results in less adsorption at high pH [10]. In addition, phenol is weakly acidic with a pKa of 9.89, hence at pH values higher than this, there will be increased dissociation of phenol in solution and thus decreased uptake as a result of competitive adsorption with the negatively charged OH ions [11–13].

In the ensuing experiments, pH 4 was taken as the optimal pH for uptake of phenol by the sorbents under investigation. The results align with those that have been posted elsewhere [10, 14].

3.1.2 Effects of contact time on sorption of phenol by raw and quaternized adsorbents

Using batches of 0.03 g of raw and quaternized sorbents separately weighed into screw cap bottles holding 20 mL of the model solution containing 20 mg/L of phenol at an ideal pH of 4, the implication of time of contact on phenol uptake was explored. The mixtures were then equilibrated for varied time between 5 and 180 mins at 170 rpm and at a temperature of 298 K. The outcomes are provided in Fig. 2.

The results in Fig. 2 show a maximum removal percentage of 80.73 and 89.45% within the first 30 minutes for RTP and QTP respectively. Continual boost in contact time to 180 mins led to a drop in percentage uptake of phenol. Increment of time of contact from 5 to 10 mins boosted the percentage uptake of phenol by QAP from 89.45 to 94.80% and 64.80 to 80.73% in RAP with rise in contact time from 5 to 30 mins. This can be as a result of the adsorbents' binding sites becoming saturated [15, 16]. It

was also noted that the quaternized sorbents had elevated uptake percentages at a given time than the raw adsorbents [17, 18]. This could be linked to the boost in porosity during modification and increase in number of binding sites [19].

3.1.3 Effects of sorbent dosage on sorption of phenol by prepared adsorbents

Using varied sorbent dosages of 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 g and working solutions of 20 mL containing 20 mg/L of phenol at an optimal pH of 4 and 30 mins, the implication of the amount of sorbent on phenol uptake was investigated. This was done at a shaking speed and temperature of 170 rpm and 298 K respectively. The outcomes are presented in Fig. 3.

The results in Fig. 3 shows that, a boost in sorbent dose from 0.001 to 0.05 g increases the percentage uptake by QTP and RTP from 29.80 to 80.81% and from 12.24 to 72.45% respectively. Similar observation was made in RAP and QAP with a maximum percentage of 86.23 and 93.37% respectively. The boost in percentage uptake of phenol with rise in dosage can be linked to the fact that increment in sorbent dose leads to a boost in the sorbent surface area and hence increased sites of adsorption and increased uptake of phenol [20–22]. An increase in sorbent dosage enhances phenol removal because more particles provide a larger total surface area and a greater number of available adsorption sites, which intensifies the interaction between the adsorbent and phenol molecules in solution [20]. This trend is consistent with many studies on phenol adsorption, where higher biomass or modified-adsorbent doses improved removal efficiency up to a saturation point, beyond which additional sorbent contributes only marginally due to site overlap, aggregation, or reduced effective surface area per unit mass [9, 23]. In this work, the superiority of the quaternized adsorbents over the raw forms at all dosages is further attributed to the introduction of additional functional groups and improved porosity during modification, which collectively increase active sites and strengthen the driving force for phenol uptake at low to moderate sorbent loads [24].

3.1.4 Impact of phenol initial concentration on its uptake by prepared adsorbents

The impact of phenol concentration on efficacy of raw and quaternized adsorbents was examined using 20 mL solutions containing varied initial concentration between 5–60 mg/L of phenol at optimal conditions: pH = 4, sorbent dose = 0.05 g and t = 30 mins. This was done at a shaking speed and temperature of 170 rpm and 298 K respectively. The outcomes are presented in.

Figure 4: Effect of original phenol concentration on the adsorption of phenol on raw and quaternized adsorbents

The outcomes in Fig. 4. disclosed that rise in concentration of phenol from 5 to 30 mg/L increased the percentage uptake of phenol by QAP from 82.82 to 90.81% while uptake by RAP increased from 54.94 to 81.20% with a concentration rise from 5 to 20 mg/L. There was a rise in percentage uptake of phenol by

RTP from 35.8 to 84.06% when the phenol concentration rose from 5 to 20 mg/L. Similarly, the percentage uptake of phenol by QTP rose from 57.41 to 86.5% with rise in phenol concentration from 5 to 30 mg/L. nonetheless, further increment in concentrations of phenol in all the adsorbents utilized, decreased the percentage removal. This is attributed to the fact that the phenol molecules are increasing but the quantity of sorbent remains constant and hence constant adsorption sites leading to saturation of the available sites [10, 22].

The outcomes also demonstrated that quaternized adsorbents had a larger uptake percentage of phenol than did raw sorbents. The outcomes also manifested that the percentage uptake of phenol by modified adsorbents was higher than in raw adsorbents. This could be due to enhanced surface area and increased number of binding sites as a consequence of modification [25]. The boost in percentage uptake at low concentration is imputed on the accessibility of unoccupied binding sites and the existing concentration difference between the sorbate and the sorbent [15, 26]. The results are comparable to those from studies using different sorbents to remove phenol and PNP: quaternized-treated maize tassels to adsorb phenolic compounds from water [27], triethylamine modified polyethylene for uptake of fluoride ions [28], Cocos nucifera shell and clay [29] and complexation of metal ions by raw and modified jack fruit seeds [30].

3.2 Sorption capacity of the prepared adsorbents

The data on adsorption of phenol onto *C. metuliferus Thunb* peels, *A. melegueta (L.) K. Schum* was fitted onto Langmuir and Freundlich isotherms. The outcomes are explained in the subsections that follow.

3.2.1 Adsorption isotherms for phenol uptake by the adsorbents

Sorption isotherm models were applied to wrap up on the uptake capacity of phenol hence informing on the chemical interactions involved and nature of the uptake process. The attained data in this investigation was suited into the Langmuir and Freundlich isotherm models. Phenol concentrations varied between 5 to 60 mg/L at the optimum pH and sorbent dose of the respective phenolic compound for uptake by a specific adsorbent. The mixture was agitated for 60 minutes at 298 K in triplicates and the results presented in Table 1.

Table 1
Langmuir and Freundlich constants for removal of phenol by raw and quaternized adsorbents

Adsorbent	Langmuir			Freundlich			
	Q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	1/n	R^2	Best model
RTP	1.275	2.06	0.985	206.71	-1.2755	0.7948	Langmuir
QTP	7.087	4.611	0.907	9.56	0.3395	0.8573	Langmuir
RAP	5.115	0.215	0.909	6.43	0.7084	0.8273	Langmuir
QAP	17.61	6.527	0.929	15.69	0.6464	0.8907	Langmuir

From Table 1, it was observed that the uptake of phenol by all the adsorbents studied gave $R^2 > 0.7948$ implying that the data suited well in Langmuir model [31]. The R^2 values for Freundlich isotherm obtained with the adsorbents investigated display failure of fit of their experimental data into this model. A chemisorption process and a mono layered adsorption is prescribed by the Langmuir model [32–34]. The values of b in all the cases studied were > 1 indicating very high affinity of the adsorbents for the phenol [31, 35]. Raw adsorbents' adsorption capabilities (q_{max}) were lower than those of quaternized adsorbents. This may be because the quaternized adsorbents have a better adsorption capacity due to their improved surface composition, micropore structure and a boost in the adsorption sites [24, 36]. This demonstrates unequivocally that quaternization enhanced these adsorbents' sorption capabilities.

3.3 Adsorption kinetic studies

3.3.1 Adsorption kinetics for phenol

The kinetic parameters for uptake of phenol from solution by all the adsorbents investigated are displayed in Table 2.

Table 2
Kinetic parameters for the uptake of phenol from solution

Adsorbent	Pseudo First Order				Pseudo Second Order		
	q_e (exp) (mg/g)	q_e (cal) (mg/g)	K_1 (min^{-1})	R^2	q_e (cal) (mg/g)	K_2 (g/mg/min)	R^2
RTP	7.45	1.02	4.1×10^{-3}	0.4404	3.93	7.66×10^{-2}	0.8921
QTP	8.85	1.33	1.1×10^{-2}	0.534	6.15	1.24×10^{-1}	0.986
RAP	10.76	0.86	5.1×10^{-3}	0.5622	7.23	2.8×10^{-2}	0.9956
QAP	12.64	1.67	1.6×10^{-3}	0.665	11.99	7.11×10^{-2}	0.9995

From the outcomes shown in Table 2, it was established that the explanation for the uptake of phenol from aqueous media can best be demonstrated by Pseudo second order model. This kinetic model recorded R^2 values > 0.89 for all the sorbents. Further, the calculated q_e, (cal) values attained from the plot of the pseudo second order model were near to the experimental quantities removed q_e, (exp) by all the adsorbents studied. Experimental uncertainties are responsible for the difference in the experimental and calculated values. This kinetic model assumes that chemisorption is the rate limiting step consequently, the uptake of phenol from solution by the sorbents applied in this study is bimolecular [37].

It was established that quaternized adsorbents had higher adsorption capacity, qe (cal) values than the raw forms. The adsorption rates were also higher in quaternized forms than in the raw forms which could be attributed to differences in porosity between the two adsorbents as well other factors such as electrostatic attraction differences amongst the adsorbate and the adsorbent [38]. Among the modified adsorbents, quaternized *C. metuliferus Thunb peels* (QTP) recorded the highest value of 1.24 x 10^{-1} g/mg/min while for the raw forms; *C. meturiferus Thunb* peels (RTP) recorded the highest rate at 7.66 x 10^{-2} g/mg/min.

3.4 Adsorption thermodynamics studies

The parameters from thermodynamic studies are imperative in describing adsorption behavior of phenolate ions. Thermodynamic studies of raw and quaternized adsorbents were done and the results presented in the following subsections.

3.4.1 Adsorption thermodynamics studies for phenol

The thermodynamic parameters for uptake of phenol from solution by all the adsorbents applied are displayed in Table 3.

Table 3
Thermodynamic parameters for the removal of phenol from solution

Ads	ΔH°	ΔS°	ΔG° at different temperatures							
			288 K	298 K	308 K	318 K	333 K	348 K	363 K	373 K
RTP	-10.02	14.38	-2.23	-6.09	-5.25	-5.22	-5.22	-4.46	-4.40	-2.09
QTP	-13.52	25.10	-3.62	-6.32	-5.60	-5.33	-5.13	-4.49	-4.42	-1.95
RAP	-12.10	42.28	-3.52	-5.87	-5.28	-4.52	-3.91	-3.51	-2.89	-1.49
QAP	-18.02	18.17	-4.52	-7.15	-6.95	-6.93	-6.88	-6.42	-5.80	-3.27

From Table 3, it was validated that the elimination of phenol from aqueous media is exothermic owing to the negative values of enthalpy change (ΔH). Further, these values lie in the range of -1.30 kJ/mole to -20.23 kJ/mole implying that uptake of phenol from solution is mainly physisorption that is enhanced by

chemical adsorption [23]. In addition, quaternized adsorbents had higher enthalpy change values than the raw forms in the uptake of phenol. Higher ΔH values can be attributed to increased affinity of the adsorbents for phenol [39]. It was also observed that all entropy (ΔS˚) values were positive for all the sorbents, implying that the uptake of phenol had increased disorganization or randomness that occurred at the interface between the aqueous media and the adsorbent in the course of the process of adsorption [40]. This increase in randomness enhances the efficiency of uptake of phenol from contaminated water, in addition to making the system move towards a state of high thermodynamic stability [10]. This is because phenol will be more disordered, thus possessing higher kinetic energy and are more likely to collide with and be adsorbed by the sorbent material [22].

All the examined adsorbents yielded negative values of Gibbs free energy (ΔG˚) exhibiting an automatic and viable process for the uptake of phenol [41, 42]. Moreover, all ΔG˚ values were within the range – 0.83 to -8.45 kJ/mole, an indication that the uptake process is chemical in nature [43]. The results revealed that free energy decreased with temperature increment, an indication that uptake of phenol from solution was more favorable at low temperatures [23].

3.5 Regeneration studies

Renewal of the sorbents was explored by separately weighing batches of 1.0 g of raw and quaternized sorbents into a 200 mL plastic screw cap bottles holding 100 mL at a concentration of 20 mg/L of phenol solution. In this study, efficiencies of 0.5 M HCl to desorb phenol was done and the outcomes are given in Fig. 5.

The results in Fig. 5 shows high regenerability of the adsorbents for phenol uptake by both raw and quaternized adsorbents with QTP giving a percentage recovery of 70.27% within the first cycle. The percentage recovery of RTP, RAP and QAP of 42.4, 45.43 and 55.73% was also achieved within the first cycle respectively. Subsequent cycles resulted to a decrease in percentage recovery of phenols in all the adsorbents [44].

3.6: Reuse of regenerated adsorbents

Similar observations were recorded

The process of reclaiming and reusing the regenerated adsorbents for uptake of phenol was done and the outcomes displayed in Fig. 6.

From Fig. 6, the process of adsorption and desorption was seen to continue up to the five cycles with efficacy of > 50% recorded for all the adsorbents for phenol uptake. It was revealed that the percentage uptake of phenol reduced after the fifth cycle. As a result, the sorbents are durable and have a high rate of efficiency up to the fifth cycle.

3.7 Environmental water samples

Batches of 1.0 g of quaternized adsorbents independently weighed into 200 mL screw cap bottles holding 100 mL of phenol solutions. The solutions were readied using environmental water samples by spiking with 5 mg/L phenol. The optimal conditions for uptake of phenol were maintained and thereafter residual concentration of phenol was analyzed at its respective wavelength that led to maximum absorption. The outcomes are given in Table 4.

Table 4
Levels of phenol in environmental water samples and spiked solutions and percentage recovery of phenol from water

Adsorbent	**phenol found in environmental water sample (mg/L)**	**phenol found in spiked solutions water sample (mg/L)**	**phenol found in solution after sorption (mg/L)**	**% Removal**
QTP	0.17 ± 0.01	2.43 ± 0.07	1.24 ± 0.01	20.23 ± 0.5
QAP	0.17 ± 0.01	2.57 ± 0.03	2.05 ± 0.08	28.94 ± 2.1

From the data given in Table 4, it was revealed that the greatest uptake for phenol from the environmental samples was by QTP and it was lowest by QAP. The uptake percentages are lower than those realized with synthetic water samples and in either case the removal percentages were below 30%. This is attributed to the high solubility of phenol in water that in turn facilitates its increased residence in solution form [14]. It was established that uptake from solutions prepared from environmental water samples was lower than those from the solutions prepared using synthetic water. This is linked to the fact that the environmental samples have other dissolved ions and or substances which could be battling out with the resultant phenolate ions for the accessible sites of adsorption [45, 46]. Even though the removal percentages reported with environmental water samples are lower than those for synthetic water samples, the prepared sorbents can still be utilized for the uptake of phenol from environmental water samples to safe levels.

Conclusion

This study conclusively establishes raw and quaternized peels from *Cucumis metuliferus Thunb*. (RTP/QTP) and *Aframomum melegueta* (RAP/QAP) as highly effective, low-cost biosorbents for remediating phenol from contaminated water in Kenya's Ruiru Sub-County. Agricultural wastes, typically discarded in local markets, were transformed into viable adsorbents, addressing phenolic pollution from industrial effluents and runoff that endangers ecosystems and human health through toxicity, bioaccumulation, and carcinogenicity. Traditional treatments like incineration or membrane filtration prove impractical due to high costs and secondary pollutants; these sorbents provide a sustainable alternative by leveraging natural lignocellulosic matrices.

Quaternization with epichlorohydrin, propylene oxide, and polyDADMAC markedly superior performance, boosting porosity, surface charge, and binding sites for electrostatic and hydrogen-bond interactions with deprotonated phenolics. Optimized batch conditions—pH 4, 30–60 min contact, 0.03–0.05 g/20 mL dose, 5–60 mg/L concentrations, 298 K—yielded peak removals of 95.95% (QAP for phenol) and capacities up to 17.61 mg/g, outperforming raw peels 2-4-fold. Langmuir isotherms ($R^2 > 0.90$) evidenced monolayer chemisorption; pseudo-second-order kinetics ($R^2 > 0.89$, K_2 up to 0.124 g/mg·min^{-1}) confirmed chemisorption rate-limitation. Thermodynamics indicated exothermic (ΔH° -10 to -18 kJ/mol), spontaneous (negative ΔG°), entropy-increasing processes, optimal at lower temperatures.

Regeneration with 0.5 M HCl preserved > 50% efficiency across five cycles, while Ruiru River trials achieved 20–29% removal despite matrix interferences, affirming real-world applicability. These findings pioneer waste-to-resource strategies, advancing circular economy models for wastewater treatment in resource-limited regions. Future efforts should prioritize pilot-scale columns, long-term stability, and multi-pollutant efficacy to facilitate industrial deployment.

Abbreviations

- **PNP**: p-Nitrophenol
- **RTP**: Raw *C. metuliferus Thunb* peels
- **QTP**: Quaternized *C. metuliferus Thunb* peels
- **RAP**: Raw *A. melegueta* peels
- **QAP**: Quaternized *A. melegueta* peels
- **q_e**: Equilibrium adsorption capacity (experimental, mg/g)
- **q_t**: Adsorption capacity at time t (mg/g)
- **q_{max}**: Maximum adsorption capacity (Langmuir, mg/g)
- **b**: Langmuir constant (L/mg)
- **K_f**: Freundlich constant (mg/g)
- **1/n**: Freundlich heterogeneity factor
- **K_1**: Pseudo-first order rate constant (min^{-1})
- **K_2**: Pseudo-second order rate constant (g/mg/min)
- **ΔH°**: Standard enthalpy change (kJ/mol)
- **ΔS°**: Standard entropy change (J/mol·K)
- **ΔG°**: Standard Gibbs free energy change (kJ/mol)
- **R^2**: Coefficient of determination

Declarations

Competing of interest

The authors declare that there are no conflicts of interest.

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All the data associated with this research has been provided herein.

Ethics declarations

Ethical approval

This research did not involve any human or animal subjects or their data.

Consent to participate

This is not applicable.

Consent for publication

This is not applicable.

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Figures

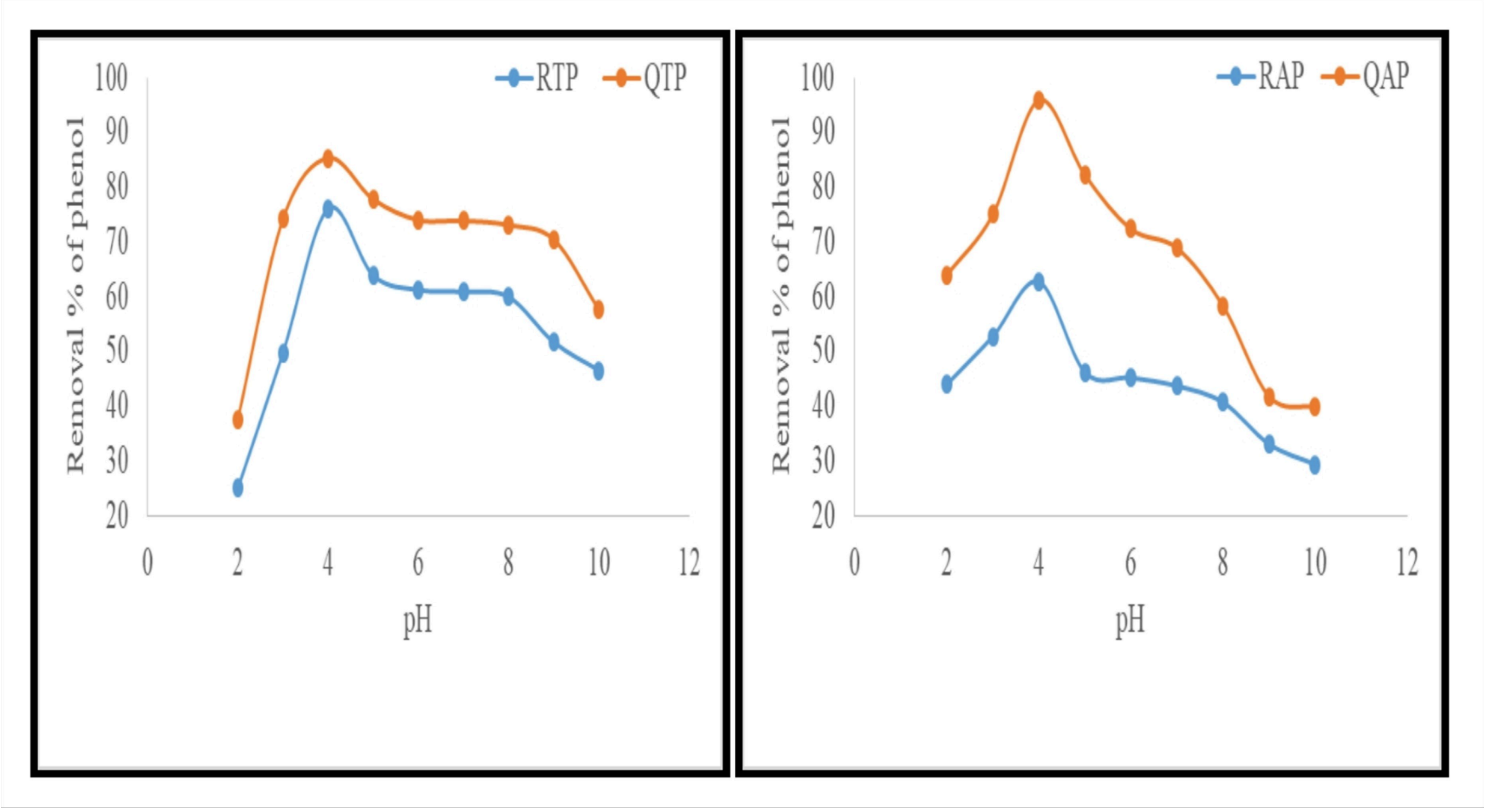


Figure 1

Impact of pH on the adsorption of phenol on raw and quaternized adsorbents

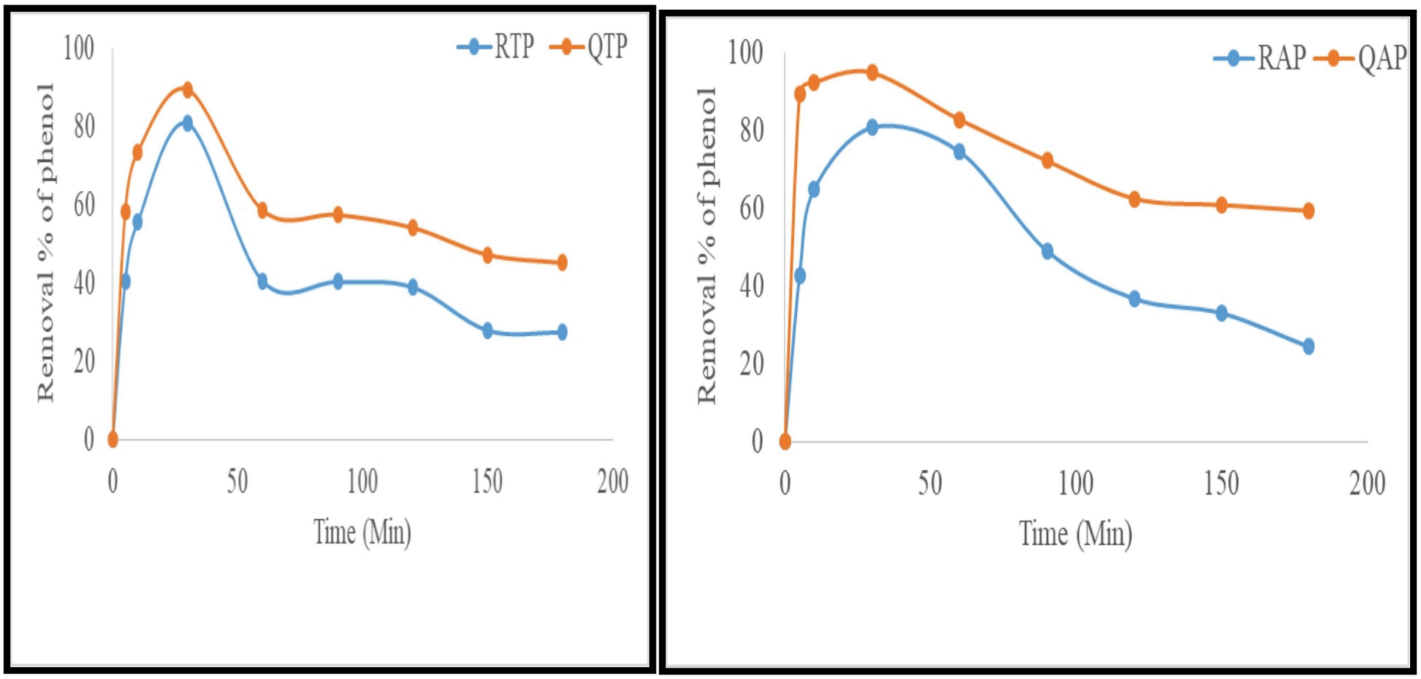


Figure 2

Impact of time of contact on the uptake of phenol using raw and quaternized adsorbents

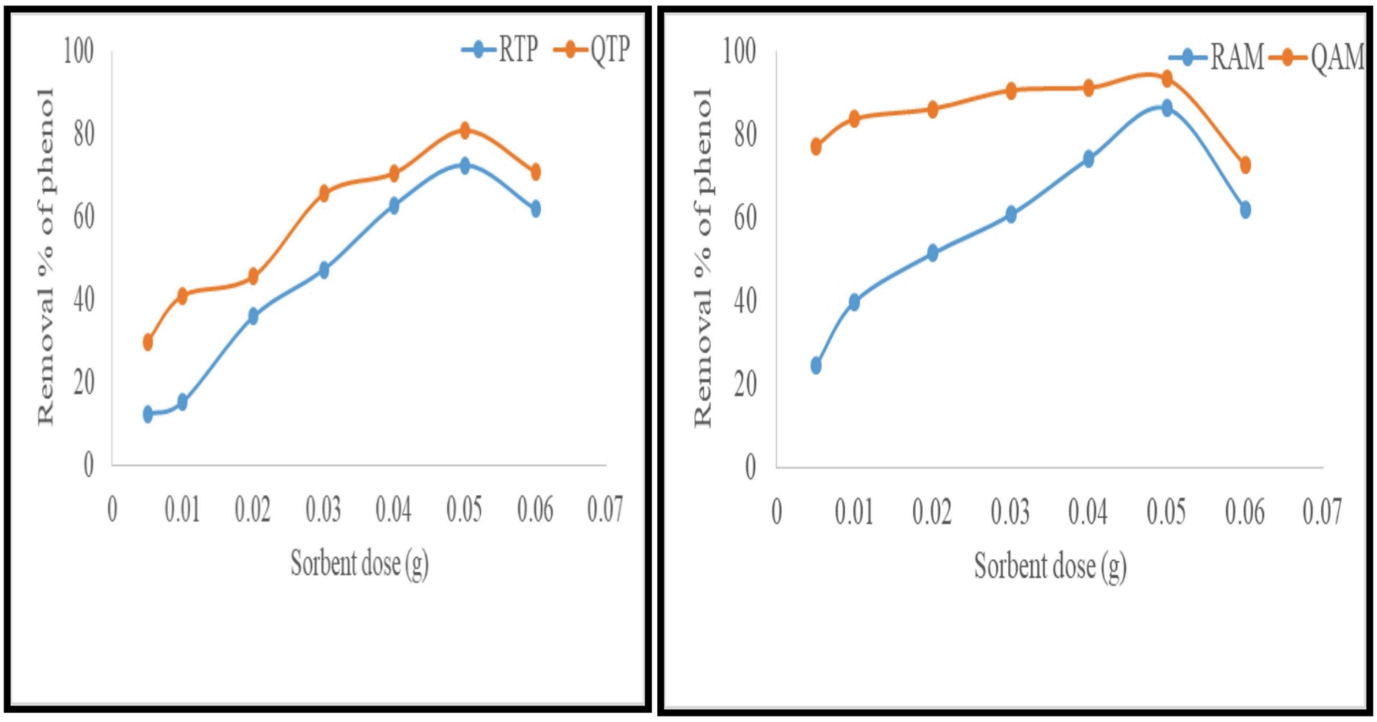


Figure 3

Effect of sorbent dose on the adsorption of phenol by raw and quaternized adsorbents

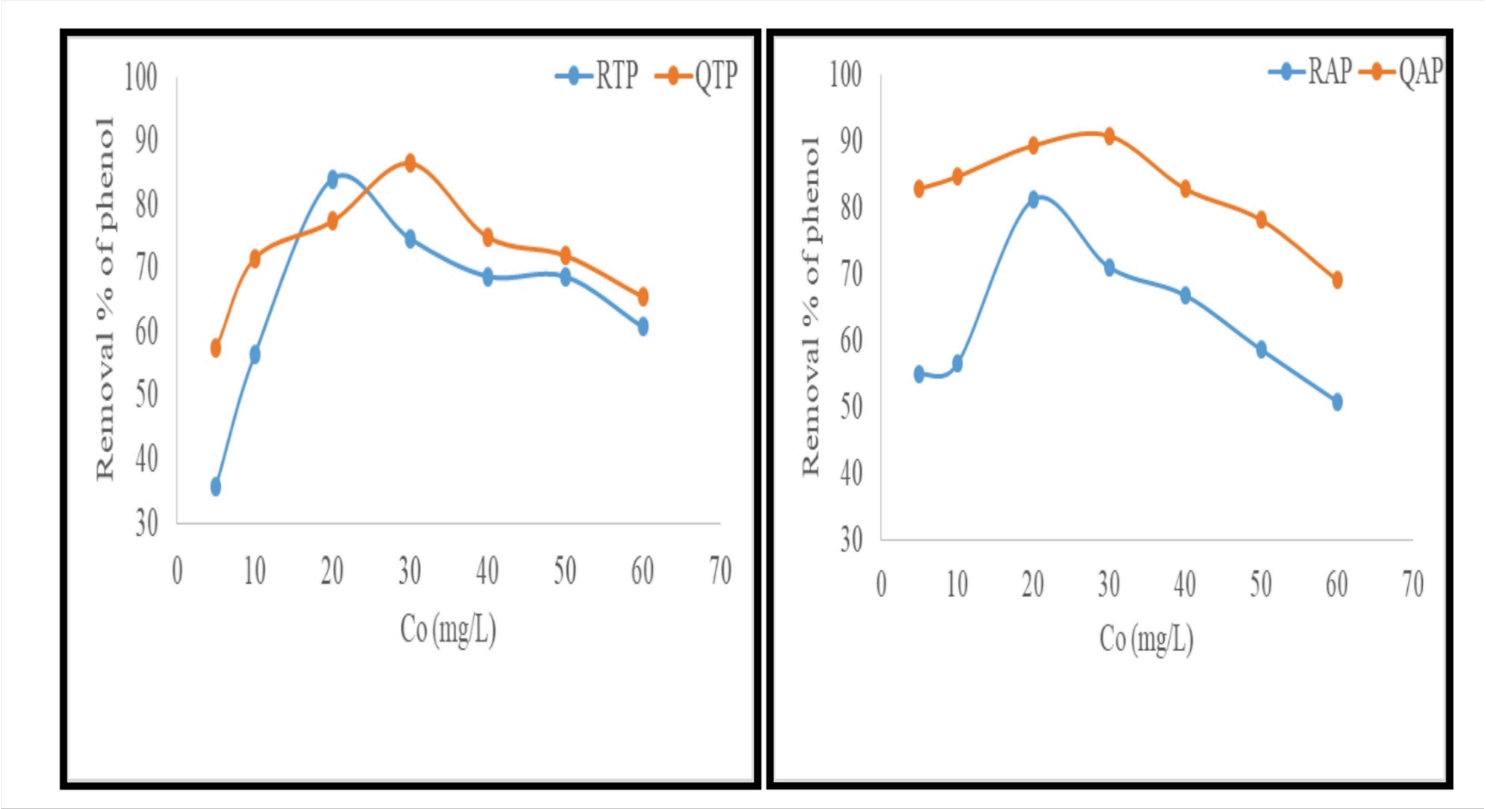


Figure 4

Effect of original phenol concentration on the adsorption of phenol on raw and quaternized adsorbents

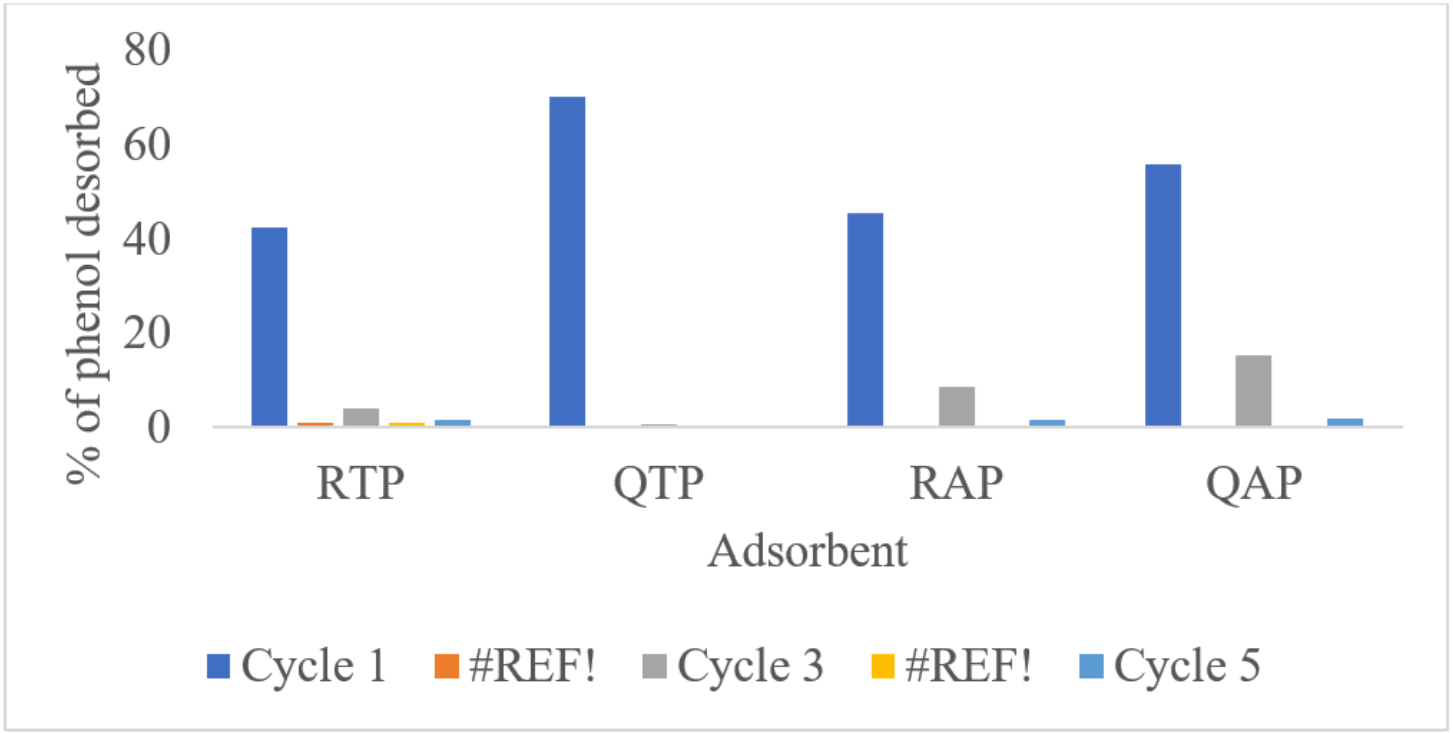


Figure 5

Percentage desorption of phenol ions from adsorbents using 0.5 M HCl

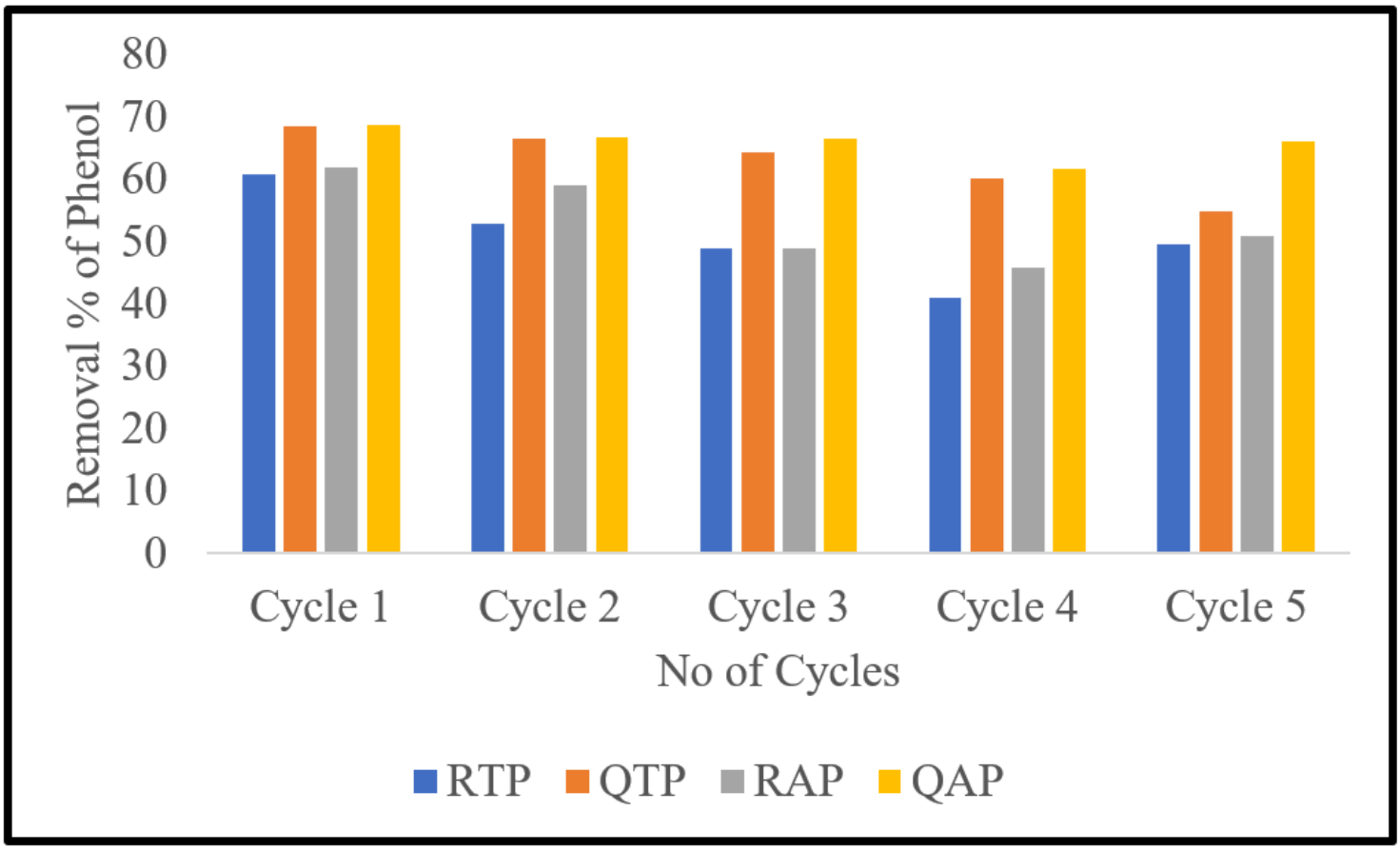


Figure 6

Adsorption desorption cycles for phenol using different adsorbents

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