

Potentially poisonous elements removal from vehicle-wash wastewater and aqueous solutions using composite adsorbents

Muhammad Ilyas^{a,*}, Waqas Ahmad^b, Hizbullah Khan^a, Saeeda Yousaf^a

^aDepartment of Environmental Sciences, University of Peshawar, Peshawar, Khyber Pakhtunkhwa, Pakistan, Tel. +923078064028; emails: sirfilyas@yahoo.com (M. Ilyas), hizbullah@uop.edu.pk (H. Khan), saeeda@uop.edu.pk (S. Yousaf)

^bInstitute of Chemical Sciences, University of Peshawar, Peshawar, Khyber Pakhtunkhwa, Pakistan, email: waqasahmad@uop.edu.pk

Received 15 October 2020; Accepted 21 February 2021

ABSTRACT

In recent years, the contamination of water by potentially poisonous elements (PPEs) has got one of the major issues that undermine ecological systems as well as human health. The current examination is aimed at eliminating PPEs like zinc (Zn^{2+}), chromium (Cr^{6+}), lead (Pb^{2+}), and copper (Cu^{2+}) from aqueous solutions and vehicle-wash wastewater (VWW) utilizing biochar/bentonite/waste polyethylene terephthalate (wPET/C/Bt) and biochar/bentonite/waste polystyrene (wPS/C/Bt) as an adsorbents. The adsorbents were investigated by surface area analyser, scanning electron microscopy, and Fourier-transform infrared spectroscopy. To investigate the adsorption of PPEs by synthesized wPET/C/Bt and wPS/C/Bt, different column and batch adsorption tests were conducted with varying different parameters such as pH, contact time, initial PPEs concentration, temperature and dose of adsorbents. Atomic absorption spectrophotometer was used for determining the PPEs concentration in addition to the adsorption efficiencies of the composites were calculated under ideal conditions. The ideal conditions for the highest adsorption of PPEs of aqueous solution on the wPET/C/Bt and wPS/C/Bt adsorbents were found to be: pH 6 for Pb^{2+} and Cu^{2+} , pH 3 for Cr^{6+} and pH 4 for Zn^{2+} , adsorbent dose of 0.20 g, temperature 60°C, contact time of 90 min, and initial concentration of 30 mg L⁻¹. Results demonstrated that highest removal of Pb^{2+} , Cu^{2+} , Cr^{6+} , and Zn^{2+} from aqueous solution achieved over wPET/C/Bt adsorbent was 89.06%, 86.30%, 90.10% and 92.43%, respectively, whereas that of wPS/C/Bt adsorbent was 84.69%, 79.80%, 77.56% and 82.80%, respectively. The highest removal in column tests was seen at an adsorbent bed height of 20 cm with the optimal flow rate of 3.56 mL min⁻¹. Moreover, PPEs removal by wPET/C/Bt adsorbents was seen in the order of $Zn^{2+} < Pb^{2+} < Cu^{2+} < Cr^{6+}$, whereas that of wPS/C/Bt adsorbent was $Cu^{2+} > Zn^{2+} > Cr^{6+} > Pb^{2+}$. The outcomes were likewise assessed by different kinetic as well as isotherm models. Root mean square error was also calculated for the validation of data. The adsorption process proceeded and fitted with Freundlich as well as Langmuir isotherm models and pseudo-second-order equation. The calculated values of thermodynamic factors, for example, entropy (ΔS°), Gibbs free energy (ΔG°) as well as enthalpy (ΔH°) demonstrate that the process of adsorption is endothermic, spontaneous as well as feasible in nature. Findings from this study suggest that wPET/C/Bt and wPS/C/Bt could be utilized as a promising adsorbent at the same time eliminating a number of PPEs from VWW.

Keywords: Adsorbents; Potentially poisonous elements; Aqueous solution; Vehicle-wash wastewater; Adsorptive removal

* Corresponding author.

1. Introduction

Anything that skirmishes with the rule of creating and destroying matter may lead to deterioration in the environment. The plastic matter goes against this rule which results in significant dangers to the environment [1,2]. The most generally utilized plastics around the world, which present 90% of the entire manufacture of plastics are polycarbonate, low-density polyethylene, polyvinyl chloride, polystyrene, polyamide (nylon), polyethylene terephthalate, polypropylene and high-density polyethylene [3]. As an outcome, the manufacture of plastics has expanded, especially throughout the most recent 60 years; worldwide plastic production has sustained to rise. In any case, the present levels of their use and disposal produce various ecological issues. Roughly 4% of world gas and oil production is used as feedstock for plastics and around 3%–4% is utilized in their assembling to give energy [4].

Plastics possess many properties due to which it is a fundamental part of our lives. The drivers for such development are their low-cost, fabrication and design capabilities, robustness, strength, and low density. Thus, because of such properties, plastics are used in industrial, automotive applications and as packaging materials. Despite its many positive properties, plastics have their disadvantages from the perspective of waste organizations [5]. The plastics business has developed astonishingly since the advancement of various courses for the production of polymers from petrochemical sources. In terms of its lightweight, durability, and low cost compared to other materials, plastic has considerable advantages [3].

The advantages of plastics are especially obvious in public health and medicine. Plastics are adaptable, require less energy for their production than alternative materials, cost-effective – for example, glass or metal, and can be fabricated to have various characteristics. Because of these qualities, polymers are used as a piece of different wellbeing applications, for example, intravenous bags, disposable syringes, joint replacements, sterile packaging for tissue engineering as well as medical instruments, etc. [6]. Over the previous century in human society, most advances have been encouraged by the utilization of plastics. Plastics are made of monomers bound together to form macromolecules. Today, about more than 20 distinctive significant sorts of plastics are being used around the world [7].

One of the most challenges of modern days in the world is the management of waste plastic. Waste plastic is not biodegradable because of its stable chemical structure; therefore, it can stay for longer in the environment constituting a large part of the solid waste. Due to the extensive usage of plastic in our daily life, a large amount of waste plastic is disposed to the environment [1]. Several approaches have been adopted for waste plastic handling which include: conversion into useful materials, microbial degradation, incineration, landfilling, and recycling. All of these methods have their own disadvantages and there are need to explore the most ideal alternative for the administration of waste plastics [1].

Wastewater from different industrial units like glass production, mining operations, paint industries, and hospitals produces potentially poisonous element (PPEs), for

example, Zn^{2+} , Mn , Pb^{2+} , Ni , Cd , Cu^{2+} as well as Cr^{6+} [8]. PPEs can cause a number of ecological issues in view of their bio-amplification, bioaccumulation, long persistence, and toxicity in the food chain, and as a result, these are considered as poisonous elements for human beings, aquatic fauna and flora [9]. PPEs go into the human body via inhalation of air, food ingestion as well as drinking polluted water. PPEs increases blood acidity. Subsequently, the bones release calcium (Ca) into the blood, as a result the blood pH is restored. This marvel causes osteoporosis (brittle bone), which is ordinarily found in aged people and children [10]. Higher concentrations of PPE such as Pb^{2+} , Cu^{2+} , Cr^{6+} and Zn^{2+} , etc. have harmful effects. It can cause diseases such as memory loss, behavioral disorders, diarrhea, anorexia, dermatitis, polycythemia, depression, immune dysfunction, and thyroid abnormalities. PPEs are the most important problem in water because some of them are carcinogenic and can cause stomach and lung cancer, as well as kidney and nerve damage [11]. Excess Cu^{2+} can cause mental illness, among which children are most affected by Pb^{2+} . This can lead to behavioral disorders and memory loss. Pb^{2+} may cause nerve damage, as well as high blood pressure and kidney damage. Excessive Zn^{2+} can also cause anemia. When Pb^{2+} is found to be part of water, it is found to have a negative effect on health, and it is the heaviest and most common metal [12]. The basic health risks caused by Cr^{6+} are developmental and reproductive problems, skin allergies, nasal and lung ulcers, and cancer. It can also cause death due to excessive intake [13]. Removal of PPEs from industrial wastewater is fundamental since they critically harm the environment. The elimination of these PPEs should be possible by different conventional strategies including complexation, flocculation or coagulation, bio-sorption, chemical precipitation, electrochemical treatment, membrane technology, filtration and chemical oxidation/reduction [14]. Although, each innovation has its own restrictions, for example, generation of toxic sludge, incomplete removal, and production of poisonous intermediate chemicals in addition to greater expense because of high energy demand. As of late, different strategies have been developed to use accessible as well as economical organic wastes, for example, sawdust, coconut shell (apricot stone, rice hull, and peanut shell) [15], for the purposive expulsion of PPEs from industrial wastewater or aqueous solutions.

Therefore, in this article, an exertion has been made to eliminate different PPEs including Pb^{2+} , Cr^{6+} , Zn^{2+} , and Cu^{2+} from vehicle-wash wastewater (VWW) as well as aqueous solutions via column and batch experiments using biochar/bentonite/waste polystyrene (wPS/C/Bt) and biochar/bentonite/waste polyethylene terephthalate (wPET/C/Bt) composites as adsorbent. Furthermore, various trial conditions were set to identify their effects and explore the ideal removal performance of composite adsorbents.

2. Materials and methods

2.1. Sample collection and preparation

The VWW samples from both heavy vehicle-wash stations (oil carriages, trailers, buses, and trucks) and light vehicle-wash stations (mini-coaches, pickups, cars, etc.)

were collected and homogenized in pre-cleaned 2.5 L amber glass bottles. The samples were brought to the Laboratory Department of Environmental Sciences, University of Peshawar. The detail of the waste plastic, biochar, and bentonite clay collection and preparation is already given in our previous paper [2].

2.2. Adsorbent preparation and characterization

The wPET/C/Bt and wPS/C/Bt composites were set up by similar methods as given in our past paper [2]. The adsorbents were characterized by scanning electron microscopy (SEM; JSM-5910, JEOL, Japan), Fourier-transform infrared spectroscopy (FTIR; Spectrum Two, S. No: 103385) analysis, and specific surface area analysis (NOVA 2200e, Quantachrome, USA).

2.3. Adsorption experiments

2.3.1. Batch experiments

Adsorption of PPEs over the composite adsorbents was studied in batch mode experiments. In distilled water, a 1,000 mg L⁻¹ (stock solution) of PPEs was prepared by dissolving their respective salts (CuSO₄, Pb(NO₃)₂, K₂Cr₂O₇, and ZnSO₄). All analyses were done by putting various adsorbent doses of the adsorbents into single metal solutions for different contact times (15, 30, 45, 60, and 90 min), whereas pH in the range of 1–7 was maintained. The pH was optimized utilizing 0.1 M HCl/NaOH. At different temperatures (30°C, 40°C, 50°C, 60°C) the mixtures were agitated for various contact times at 200 rpm. At that point, the liquid and adsorbents were isolated by filtration.

2.3.2. Column experiments

The column experiment was used for the removal of PPEs from VWW. A glass column with a height and internal diameter of 40 and 2.8 cm, respectively, was used for this purpose. At the base of the column for preventing outlet blockage and supporting the column, a glass wool was utilized. To control the composites and activated carbon washout with water and equal water dissipation beneath and above the materials, cleaned sand was put. The thermal solution uniform flow was maintained into the column. The column was filled with composite adsorbents up to 5, 10, 15, and 20 cm height. Wastewater with a controlled flow (5 mL min⁻¹) was allowed with various initial concentrations from the top of the column. At various times intervals (15, 30, 45, 60, and 90 min), samples of water were collected and analyzed for PPEs.

2.4. Analyses and calculations

Atomic absorption spectrophotometer (AAnalyst 700, PerkinElmer, USA), was used for filtrate analysis. The adsorption efficiency q_e (mg g⁻¹) was assessed according to the following equation.

$$q_e = \frac{(C_0 - C_i)V}{M} \quad (1)$$

Since, C_i and C_0 are the initial and equilibrium concentrations (mg L⁻¹) of PPEs, respectively; V is the volume of PPEs (L); M is the weight of wPS/C/Bt and wPET/C/Bt composites (g).

The removal percentage (%) of PPEs was evaluated by the next equation:

$$\text{Removal, \%} = \frac{(C_0 - C_i) \times 100}{C_0} \quad (2)$$

To assess the fitness of the isotherm, as well as the kinetic equations to the experimental data, the root mean square error (RMSE) was utilized to determine the isotherm along with kinetic constants. RMSE can be defined as:

$$\text{RMSE} = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{e,\text{exp}} - q_{e,\text{calc}})^2} \quad (3)$$

where N is the number of observations and the subscripts “calc” and “exp” show the calculated and experimental values in the experimental data. The smaller the RMSE value, the better the curve fitting [16].

2.5. Kinetic studies

There are many kinetic-models utilized to assess the monitoring mechanisms of adsorption process like chemical-reaction, diffusion control, and mass-transfer. In the current study, two different kinetic models; namely, Lagergren pseudo-second-order kinetic and pseudo-first-order kinetic were examined. The equations for these models are given in Table 1.

2.6. Adsorption isotherm

The equilibrium adsorption isotherms are always essential to describe the adsorbent–adsorbate interaction and it is necessary for analyzing as well as designing of the adsorption process. There are several isotherm-models utilized to demonstrate the adsorption at equilibrium. In this study, the Langmuir and Freundlich models were examined to demonstrate the adsorption at equilibrium. The Langmuir and Freundlich equations are given in Table 2.

3. Results and discussion

3.1. Characterization of composite adsorbents

The wPET/C/Bt and wPS/C/Bt composites prepared in the laboratory were described by FTIR, SEM in addition to specific surface area analysis and details in our previous paper published in the Desalination and Water Treatment Journal [2]. The SEM images of the composite adsorbent wPS/C/Bt as well as wPET/C/Bt are shown in Figs. 1a and b, respectively. Clearly, the surface morphology of wPS/C/Bt shows the stuffing of bentonite and biochar inside the pores of wPS and finally resulted in uniform microcellular foaming in the composite. Similarly, the wPET/C/Bt SEM micrograph shows that in the holes of wPET, the bentonite and biochar were embedded and

Table 1
Kinetic models used in the study

Model	Equation
Pseudo-first-order [17]	$\ln(q_e - q_t) = \ln q_e - k_1 t$ (4)
	where q_e and q_t are the amounts of adsorbed PPEs (mg g^{-1}) at equilibrium and time t (min), respectively, and k_1 is the rate-constant of pseudo-first-order (min^{-1}).
Pseudo-second-order [18]	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$ (5)
	where k_2 is the rate-constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) and at equilibrium the sorption capacity is presented by q_e .

Table 2
Isotherm models used in the study

Model	Equation
Langmuir [19]	$\frac{C_e}{q_e} = \frac{1}{KQ_{\max}} + \frac{C_e}{Q_{\max}}$ (6)
	where q_e is the quantity of adsorbed PPEs on the composite at equilibrium (mg g^{-1}) and C_e is the equilibrium-concentration of the PPEs (mg L^{-1}).
Freundlich [20]	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$ (7)
	where n and K_f are the adsorption intensity and capability, respectively.

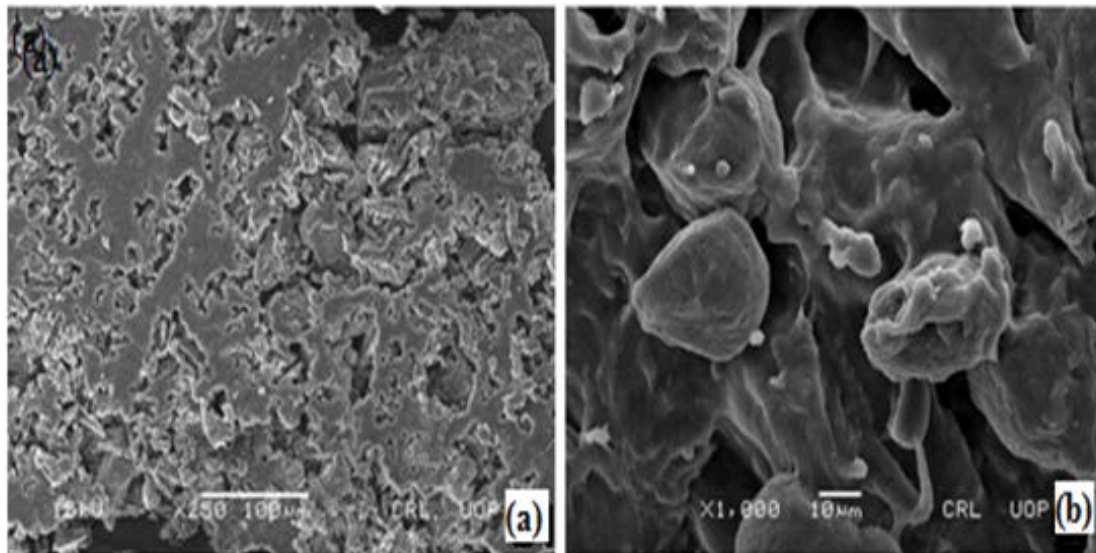


Fig. 1. SEM images of (a) wPS/C/Bt and (b) wPET/C/Bt.

combined tightly. In the surface cracks or pores of wPET, there were many club-shaped crystals, which had a much larger size having 5–6 and 9–10 μm diameter and length, respectively [2].

The wPET/C/Bt and wPS/C/Bt composite FTIR spectrum is shown in Figs. 2e and f, respectively. The new wPET/C/Bt and wPS/C/Bt composite adsorbent had functional groups

of both the waste polymers as well as fillers, and therefore its adsorption efficiency was considered better than that of fillers or waste polymers [2].

The surface properties, that is, pore radius, pore-volume, Brunauer–Emmett–Teller (BET) surface area (S_{BET}), and Barrett–Joyner–Halenda (BJH) surface area (S_{BJH}) of the composite adsorbents were determined using N_2

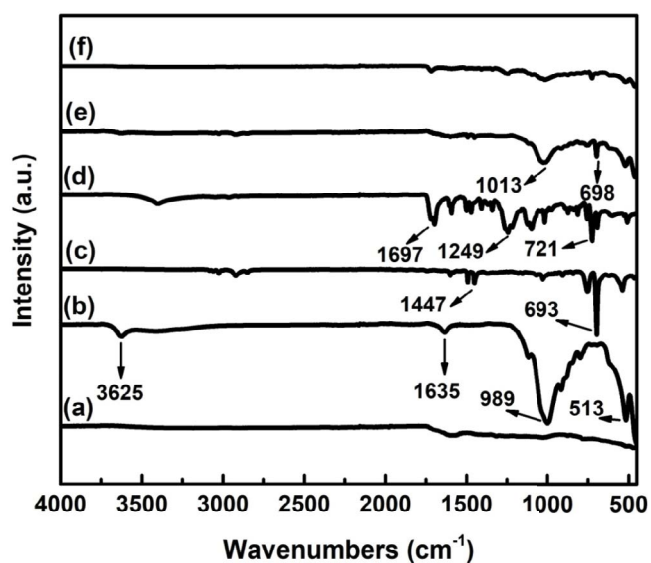


Fig. 2. FTIR spectra of (a) biochar, (b) bentonite, (c) wPS, (d) wPET, (e) wPS/C/Bt, and (f) wPET/C/Bt.

adsorption isotherms at 77.35 K [2]. The results are given in Table 3.

3.2. Effects of the studied parameters on the adsorption capacity

Initial adsorption tests were completed at constant conditions, for example, composite adsorbent to solution ratio of 0.10 g/20 mL, temperature (ambient), stirring speed (100 rpm) and contact time (1 h) to screen the better adsorbent. Further analyses were led under various conditions to examine the ideal parameters for the adsorption process.

3.3. Batch adsorption experiment

3.3.1. Effect of contact time

The contact time is one of the interesting parameters which effects on the adsorption process. Therefore, the removal of PPEs by wPS/C/Bt and wPET/C/Bt composites at different contact times, that is, between 15–90 min., was studied and presented in Figs. 3a and 4a, respectively. The outcomes demonstrated that with expanding contact time there is an increase in the % removal. The reason behind the higher removal with expanding contact time is PPEs availability to adsorb over the surface of adsorbents. After a contact time of 90 min, the majority of active sites present on the adsorbents have been occupied and equilibrium is attained. Thus, 90 min were reported as the optimum contact time for removing PPEs at equilibrium

3.3.2. Effect of temperature

The impact of temperature of the solution on the percentage removal of PPEs from the solution by wPET/C/Bt and wPS/C/Bt is presented in Figs. 3b and 4b, respectively. An expansion in the expulsion of PPEs with temperature increment was acquired. This shows that the process of adsorption is an endothermic one. As the temperature rises, the PPEs procure more vitality to overcome the energy barrier between the composites and PPEs, at the same time, due to the separation of the surface fragments of the composite material, more additional adsorption sites are generated on the surface of the adsorbent [21].

3.3.3. Effect of initial metal ion concentration

The ability of wPET/C/Bt and wPS/C/Bt to remove PPEs from the solution at various initial concentrations was resolved and introduced in Figs. 3c and 4c, respectively. As an expansion in the take-up limit with respect to PPEs with increment in initial concentration was acquired. This sorption trademark showed that surface immersion is a component of the underlying concentration in solution. The reason behind this pattern is that, in solution fewer metal ions at lower concentration are accessible, hence the greatest binding of the PPEs on the wPET/C/Bt and wPS/C/Bt active sites was not accomplished, yet as the concentration expands, the presence of a high concentration gradient generates a stronger driving force which overcomes the resistances to mass transfer, in the process, making maximum use of the active sites resulting in higher adsorption per unit mass of wPET/C/Bt and wPS/C/Bt [22].

3.3.4. Effect of pH

The pH is an interesting parameter, which affects the adsorption process of PPEs through wPET/C/Bt and wPS/C/Bt composites. The pH of a solution may tend to change the extent of dissociation of the adsorbent functional groups, the degree of ionization of the adsorbate, and the surface charge of an adsorbent [23]. The influence of pH in the range of 1–7 on the adsorption of PPEs onto wPET/C/Bt and wPS/C/Bt was studied and presented in Figs. 3d and 4d, respectively. Since when the pH transcends 7 metal hydroxide precipitation may happen, the trials on the impact of pH were done in neutral and acidic single metal solutions. The optimum pH for maximum adsorption of PPEs from aqueous solution on the wPET/C/Bt as well as wPS/C/Bt composites was observed to be: pH 6 for Cu^{2+} and Pb^{2+} , pH 3 for Cr^{6+} , pH 4 for Zn^{2+} .

3.3.5. Effect of adsorbent dose

It is well known that the adsorbent dose has a serious effect on the removal percentage of PPEs from aqueous

Table 3
Surface properties of the composite adsorbents

Adsorbent	BJH surface area ($\text{m}^2 \text{g}^{-1}$)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore radius (\AA)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
wPET/C/Bt	50.68	58.53	27.68	0.06
wPS/C/Bt	55.59	44.95	27.71	0.07

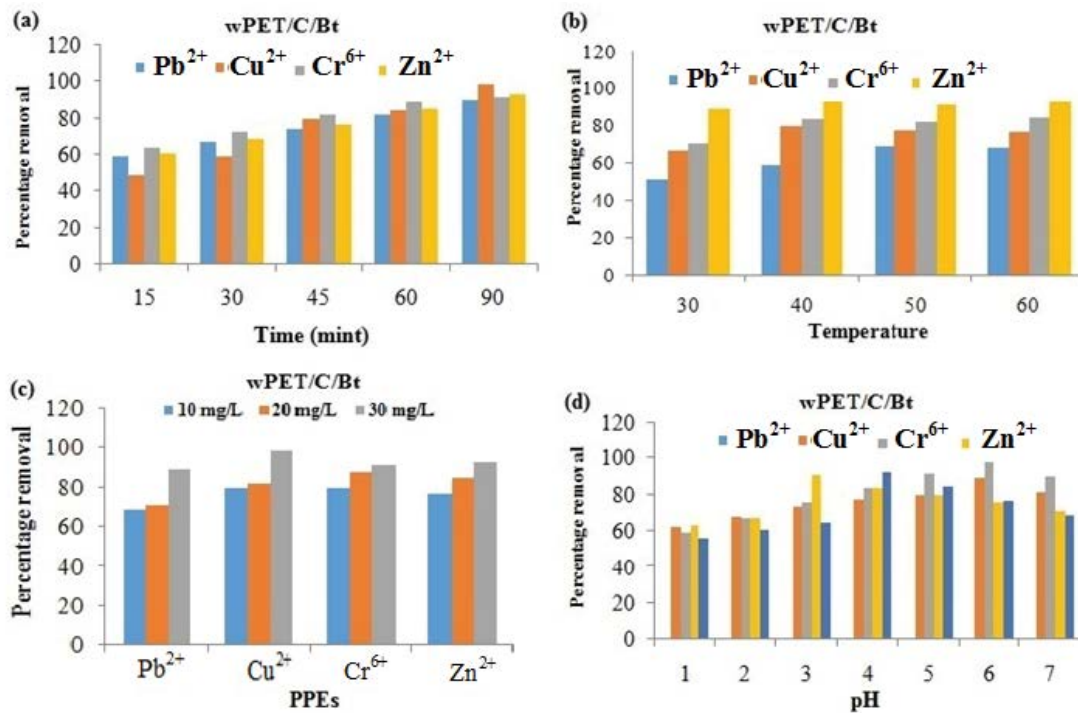


Fig. 3. Removal (%) of PPEs using wPET/C/Bt under different experiment conditions: (a) effect of contact time, (b) temperature, (c) effect of initial concentration, and (d) effect of pH.

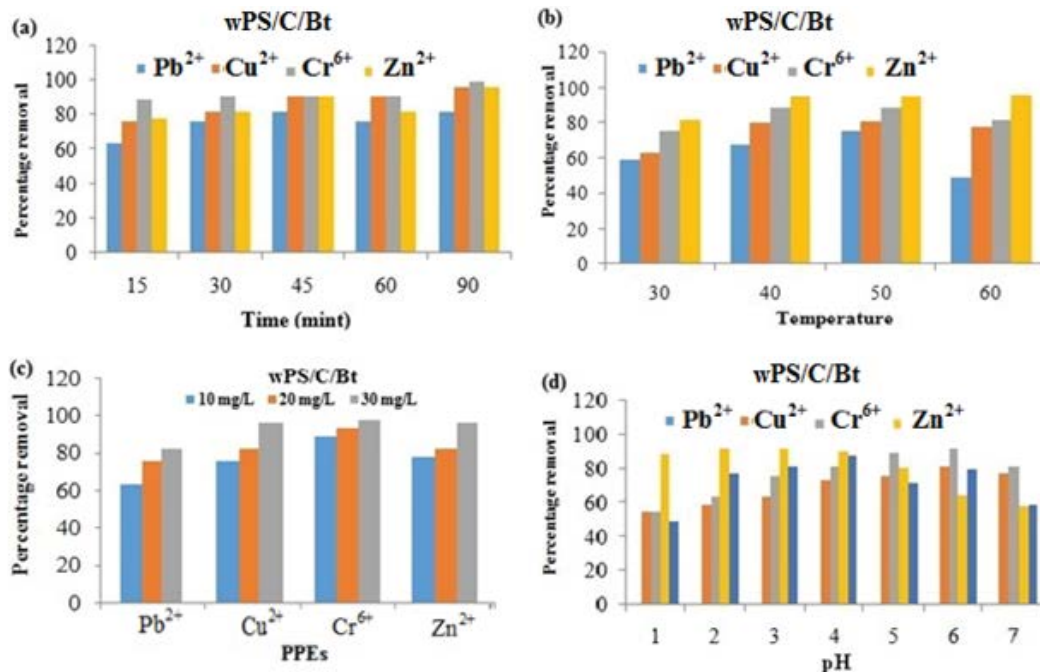


Fig. 4. Removal (%) of PPEs using wPS/C/Bt under different experiment conditions: (a) effect of contact time, (b) temperature, (c) effect of initial concentration, and (d) effect of pH.

solution. In the solution, the amount of adsorbent accessible decides the active binding sites number accessible for PPEs [24]. The effect of adsorbent dose on the adsorption of PPEs from aqueous solution onto wPET/C/Bt and

wPS/C/Bt is presented in Figs. 5a and b, respectively. It is indicated that the removal percentage of PPEs rises quickly as the composite increases from 0.05 to 0.2 g. Generally, these results are associated with the existence of a greater

number of available adsorption sites on adsorbent surfaces with increasing their doses. The maximum percent adsorption of PPEs were accomplished for an adsorbent dose of 20%, and after this stage the adsorption turned out to be constant. The PPEs elimination is not considerably affected by an extra increase in the adsorbent dose more than 0.2 g owing to the chance of aggregation, which restricts the number of active-site surfaces available for adsorption [25]. Similar behavior has been seen in past investigations and emerges from the impact of associations between adsorbent and metal ions. The expanded dose is consistent with the large number of adsorption sites as well as surface area [26]. According to the obtained results in Figs. 5a and b, the dose 0.2 g is selected as the optimum adsorbent dose at which the removal percentage exhibits its highest value.

3.4. Column experiments

3.4.1. Effect of adsorbent bed height

The influence of various adsorbent heights (5.0, 10, and 20 cm) on the removal of PPEs from VWW was studied. The flow rate of the adsorbate was kept constant (5 mL min^{-1}). The results are displayed in Figs. 6a and d. It tends to be seen clearly that the elimination of PPEs is expanded by increasing the height of the column (5–20 cm).

3.4.2. Effect of contact time

Results demonstrated that with increasing contact time, the removing percentages are relatively increased. The details of removal efficiencies at all contact times in VWW are given in Figs. 6b and e. The explanation behind the higher removal after longer contact time is the greater accessibility of active sites and good interaction with the adsorbent.

3.4.3. Effect of flow rate

The effect of various flow rates (3.60 , 5.00 , and 8.56 mL min^{-1}) on the PPEs removal utilizing composite adsorbents was also investigated in the column experiment.

It was observed that the flow rate of 3.56 mL min^{-1} was the most appropriate for PPEs removal from VWW. Results revealed that by expanding the flow rate, the removal of PPEs reduces consistently, as shown in Figs. 6c and f. The decrease of PPEs removal is because of the accessibility of lacking contact time of the adsorbents with PPEs in the wastewater.

3.5. Kinetic study

The adsorption kinetics of PPEs on wPET/C/Bt and wPS/C/Bt composites were investigated by pseudo-first-order and pseudo-second-order reactions to investigate which of them are fitting with the adsorption process; also, to compare the values of calculated and experimental adsorption capacities. It can be seen from Table 4 that the pseudo-first-order model doesn't fit well with the adsorption process since it gives low linear regression correlation coefficient (R^2). The kinetic parameters achieved from the pseudo-first-order and pseudo-second-order kinetic models as well as their corresponding RMSE values are illustrated in Table 4. It is appeared that the adsorption process is well fitted with the pseudo-second-order model during the studied adsorption time since R^2 values are very high and reach 0.999. In view of the pseudo-second-order model [17,27], it tends to be inferred that the adsorption of PPEs onto wPET/C/Bt and wPS/C/Bt is a chemisorption comprising the valence forces via the contribution or exchange of electrons between the adsorbent and adsorbate.

3.6. Isotherm study

This process describes the relation between the total amount of adsorbate in the liquid medium and its amount adsorbed at the interface [28]. In the present study, the equilibrium isotherms were examined by Langmuir and Freundlich-models to investigate the elimination capacity of wPET/C/Bt and wPS/C/Bt composite for PPEs. The Langmuir hypothesis assumes that monolayer coverage of the adsorbate on homogeneous and equivalent sites of the adsorbent are happened during the process.

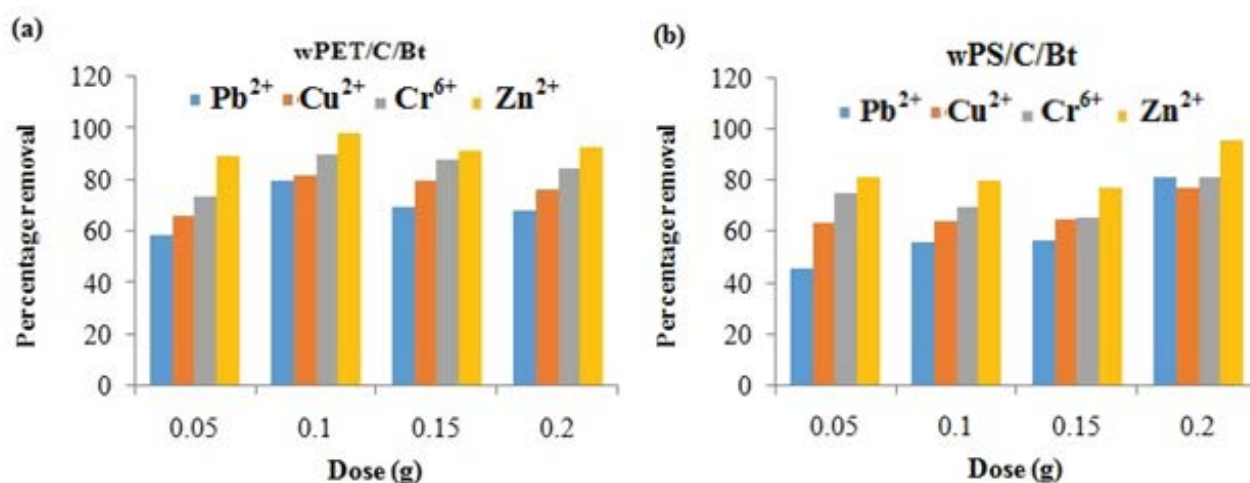


Fig. 5. Effect of adsorbent dose on the % removal of PPEs from aqueous solution over the wPET/C/Bt (a) and wPS/C/Bt (b).

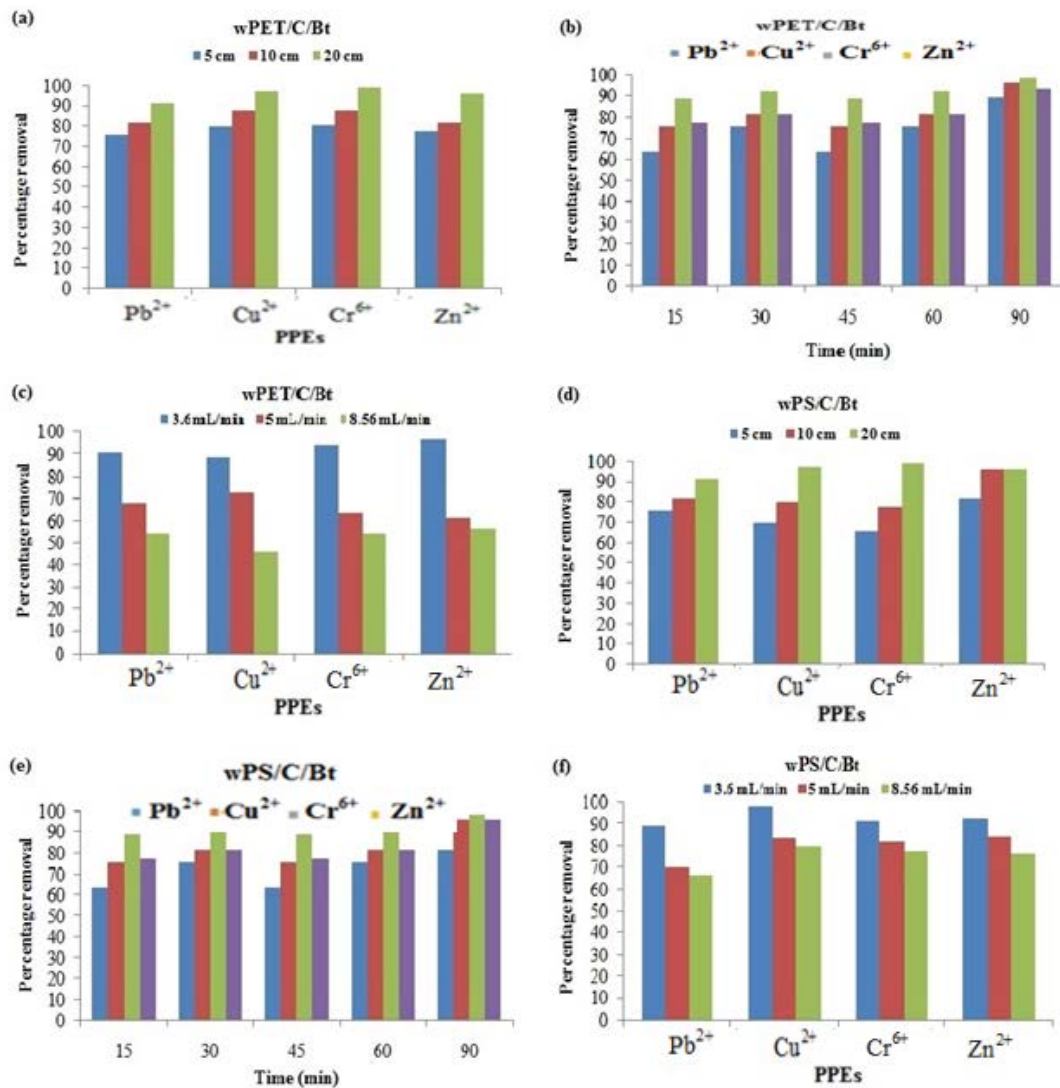


Fig. 6. Removal (%) of PPEs by wPET/C/Bt and wPS/C/Bt in column experiments under the experimental conditions: (a and d) effect of column height, (b and e) effect of contact time, (c and f) effect of flow rate in column experiments.

In Freundlich model, it is assumed that the adsorption occurs on the heterogeneous surfaces and can form mono or multilayers depending on the amount of adsorbate adsorbed at equilibrium. The calculated Freundlich constants (n and K_f) and Langmuir constants (k_1 and q_m) as well as the coefficients of correlation (R^2) for both isotherms and their corresponding RMSE values are detailed in Table 5. The outcomes demonstrated that the adsorption data were better fit to both the Freundlich and Langmuir adsorption isotherms, which were firmly identified with Langmuir model parameters in other studies [29].

3.7. Thermodynamic studies

The spontaneity, thermal effect in addition to feasibility of the adsorption system was determined from the variation of the thermodynamic equilibrium constant, K_D , with temperature. Thermodynamic factors, for example, the entropy change (ΔS°), free energy change (ΔG°)

and enthalpy change (ΔH°) were assessed according the following equation [30,31]:

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

$$\Delta H^\circ = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{k_2}{k_1} \quad (9)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (10)$$

The values of ΔS° , ΔG° as well as ΔH° are shown in Table 6. The positive values of ΔS° and ΔH° show the endothermic nature of PPEs onto wPET/C/Bt and wPS/C/Bt. The negative value of ΔG° confirms the feasibility and spontaneous nature of the adsorption process. An expansion in the ΔG° esteem demonstrates that the level of spontaneity additionally expanded at higher temperature.

Table 4
Pseudo-second-order kinetic parameters for adsorption of PPEs over wPET/C/Bt and wPS/C/Bt

Adsorbents	k_2 (mg g ⁻¹ min ⁻¹)	q_{e2} (mg g ⁻¹)	R^2	RMSE	k_2 (mg g ⁻¹ min ⁻¹)	q_{e2} (mg g ⁻¹)	R^2	RMSE
wPET/C/Bt				wPS/C/Bt				
Aqueous solution								
Pb ²⁺	2.1×10^{-4}	0.097	0.999	0.090	53.428	0.568	0.999	0.560
Cu ²⁺	53.370	0.568	0.998	0.561	10.31	0.097	0.999	0.047
Cr ⁶⁺	0.380	0.488	0.997	0.332	0.004	0.064	0.998	0.082
Zn ²⁺	0.166	0.278	0.999	0.044	0.001	0.061	0.999	0.250
Vehicle-wash wastewater								
Pb ²⁺	2.1×10^{-4}	0.097	0.999	0.492	53.428	0.568	0.999	0.255
Cu ²⁺	53.370	0.568	0.998	0.561	10.31	0.097	0.999	0.047
Cr ⁶⁺	3.085	0.499	0.996	0.070	0.681	0.263	0.997	0.387
Zn ²⁺	0.053	0.047	0.997	0.044	0.317	0.254	0.997	0.250

Table 5
Isotherm model parameters for PPEs adsorption onto wPET/C/Bt and wPS/C/Bt

Adsorbents	q_m (mg g ⁻¹)	k_1	R^2	RMSE	q_m (mg g ⁻¹)	k_1	R^2	RMSE
Langmuir isotherm parameters				Langmuir isotherm parameters				
wPET/C/Bt				wPS/C/Bt				
Aqueous solution								
Pb ²⁺	27.778	0.973	0.999	0.167	0.319	8.928	0.995	0.004
Cu ²⁺	0.009	-0.903	0.996	0.002	-0.903	0.010	0.995	0.953
Cr ⁶⁺	9.174	0.524	0.995	0.611	0.004	0.064	0.992	0.138
Zn ²⁺	25.641	0.481	0.995	0.962	27.778	0.972	0.999	0.986
Vehicle-wash wastewater								
Pb ²⁺	21.739	0.686	0.998	0.471	16.667	0.984	0.986	0.857
Cu ²⁺	47.619	0.292	0.993	0.612	111.112	0.095	0.967	0.861
Cr ⁶⁺	43.478	0.384	0.986	0.572	5.650	0.414	0.993	0.486
Zn ²⁺	8.403	0.364	0.995	0.900	5.208	0.486	0.992	0.204
Adsorbents	N	K_f	R^2	RMSE	N	K_f	R^2	RMSE
Freundlich isotherm parameters				Freundlich isotherm parameters				
wPET/C/Bt				wPS/C/Bt				
Aqueous solution								
Pb ²⁺	2.1×10^{-4}	0.097	0.997	0.622	53.428	0.568	0.996	0.090
Cu ²⁺	1×10^{-4}	-1.098	0.993	0.460	-1×10^{-8}	-0.558	0.999	0.827
Cr ⁶⁺	1.629	4×10^{-4}	0.972	0.933	1.098	1×10^{-4}	0.993	0.247
Zn ²⁺	1.230	0.099	0.990	0.227	0.926	0.237	0.996	0.922
Vehicle-wash wastewater								
Pb ²⁺	0.973	0.012	0.981	0.007	1.107	0.084	0.993	0.087
Cu ²⁺	0.955	0.011	0.995	0.044	0.872	0.003	0.979	0.047
Cr ⁶⁺	0.613	0.0004	0.993	0.155	0.190	0.095	0.994	0.097
Zn ²⁺	0.955	0.011	0.995	0.008	0.971	0.013	0.992	0.009

3.8. Comparison of adsorption potential of different adsorbents

The comparative adsorption efficiency of the different adsorbents reported in the literature and the adsorbents, that is, wPET/C/Bt as well as wPS/C/Bt for PPEs removal is summarized in Table 7.

3.9. Desorption experiment

In the removal processes of PPEs, regeneration/desorption of adsorbents is one of the essential aspects as it controls the economy of water treatment technology [42]. For PPEs recovery and effective regeneration of adsorbents,

Table 6
Thermodynamic parameters for the adsorption of PPEs onto wPS/C/Bt and wPET/C/Bt

Temperature (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)
	Pb ²⁺			Cu ²⁺		
	wPS/C/Bt:1:2:2					
30	-10.891			-4.8693		
40	-19.915			-4.2384		
50	-20.335	31.111	12.097	-3.0255	8.4470	0.0289
60	-20.762			-1.4481		
	wPET/C/Bt:1:2:2					
30	-10.506			-3.2281		
40	-18.636			-3.1760		
50	-19.014	14.433	7.248	-2.1098	2.8592	0.0093
60	-19.397			-0.1443		
	Cr ⁶⁺			Zn ²⁺		
	wPS/C/Bt:1:2:2					
30	-4.6763			-10.495		
40	-4.0430			-20.465		
50	-2.6785	9.6526	0.0329	-20.944	77.062	16.47
60	-1.9799			-21.523		
	wPET/C/Bt:1:2:2					
30	-4.2830			-9.598		
40	-3.6734			11.63		
50	-2.7668	10.010	0.0342	-11.752	6.516	4.059
60	-1.8201			-11.915		

Table 7
Comparison of different adsorbents used for PPEs removal

Adsorbent	Adsorption potential				References
	Pb ²⁺	Cu ²⁺	Cr ²⁺	Zn ²⁺	
wPET/C/Bt:1:2:2, mg g ⁻¹	–	118.65	127	–	[2]
wPS/C/Bt:1:2:2, mg g ⁻¹	–	109.65	107.88	–	[2]
Palygorskite, mg g ⁻¹	–	–	30.70	–	[32]
Crosslink cationic starch, mg g ⁻¹	–	–	97.08	–	[33]
Acid activated palygorskite, mg g ⁻¹	–	32.24	–	–	[34]
Expanded perlite, mg g ⁻¹	–	8.62	–	–	[35]
Activated carbon, mg g ⁻¹	–	24.21	34.70	–	[36]
Polyaniline, mg g ⁻¹	–	92	101	–	[37]
Polyaniline/palygorskite composite, mg g ⁻¹	–	114	198	–	[38]
Petiolar felt-sheath palm, mg g ⁻¹	96.9	89.8	77.5	56.9	[39]
Spherical cellulose adsorbent, mg g ⁻¹	–	30.8	–	–	[40]
Papaya wood, mg g ⁻¹	–	9.65	–	5.72	[41]
Clinoptilolite, mg g ⁻¹	23.03	–	–	13.02	[41]
wPET/C/Bt, mg g ⁻¹	126.2	118.65	127	138	This article
wPS/C/Bt, mg g ⁻¹	115.5	109.65	107.88	111	This article

acids (such as CH₃COOH, HCOOH, HNO₃, H₂SO₄, and HCl), alkalis (such as K₂CO₃, KOH, Na₂CO₃, NaHCO₃ and NaOH), salts (such as C₆H₅Na₃O₇·2H₂O, KNO₃, NH₄NO₃, CaCl₂·2H₂O, (NH₄)₂SO₄, KCl and NaCl), buffer solutions (such as

phosphate and bicarbonate), chelating agents and deionized water were used in various studies [43]. In this study, Deionized water and 0.1 M HCl was used for the desorption experiment. Acid (HCl) gave satisfactory desorption result.

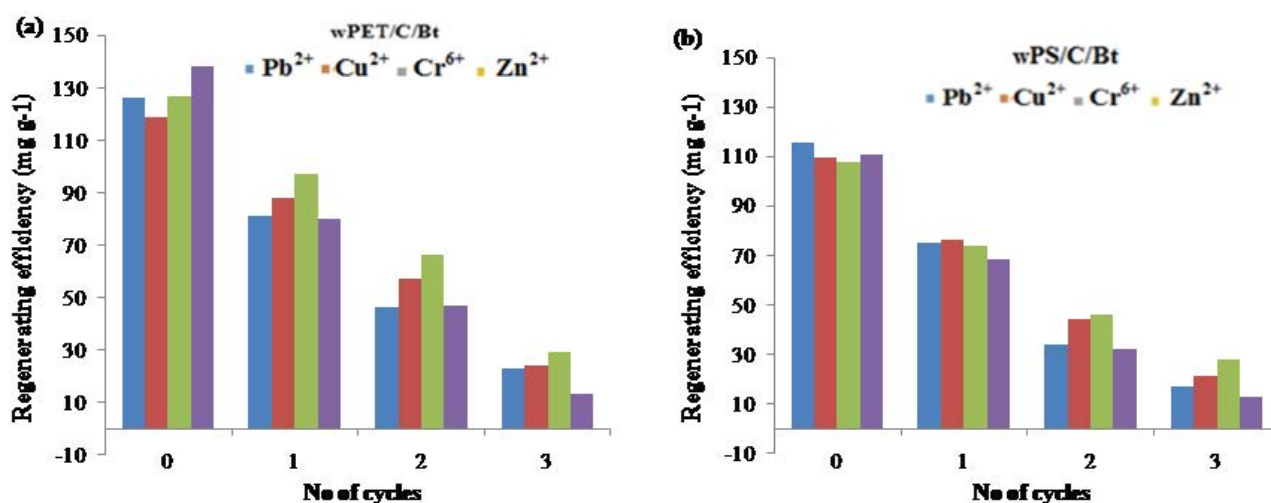


Fig. 7. Regenerating efficiency of (a) wPET/C/Bt and (b) wPS/C/Bt.

Table 8
Summary of the desorbing agent for regeneration of adsorbents

PPEs removed	Desorbing/regenerating agent used	Desorption/regenerating efficiency ($n = \text{no. of cycles}$)	
		wPET/C/Bt	wPS/C/Bt
Pb ²⁺	Deionized water and 0.1 M HCl	22.8 mg g ⁻¹	16.97 mg g ⁻¹
Cu ²⁺	Deionized water and 0.1 M HCl	24.14 mg g ⁻¹	21.45 mg g ⁻¹
Cr ⁶⁺	Deionized water and 0.1 M HCl	29.4 mg g ⁻¹	28.16 mg g ⁻¹
Zn ²⁺	Deionized water and 0.1 M HCl	13.02 mg g ⁻¹	12.51 mg g ⁻¹
		$n = 3$	$n = 3$

The regeneration studies were carried out in batch for three successive cycles using 100 mL of VWW (Figs. 7a and b). The summary of the adsorbents used for adsorption of PPEs, PPEs removed, desorbing or regenerating agents used, and desorption efficiency is given in Table 8. These findings were in agreement with the findings of [39,40,44,45].

4. Conclusions

In the present work, the composites adsorbents wPET/C/Bt and wPS/C/Bt were synthesized by an economical and simple method. The synthesized adsorbents were effectively used for the removal of PPEs from VWW and aqueous solutions. Generally, the wPET/C/Bt exhibited better removal percentages for PPEs than wPS/C/Bt. The adsorption process is totally depended on pH, contact time, initial concentration, and adsorbent dosage. The adsorption process proceeded and fitted with Langmuir and Freundlich isotherms and pseudo-second-order equations. Thermodynamic calculations indicated that the adsorption process is endothermic, spontaneous as well as feasible in nature. Findings from this study suggested that wPET/C/Bt and wPS/C/Bt could be a promising adsorbent for the effective removal of PPEs from VWW and aqueous solutions. The current study proves to be a milestone in reducing the environmental pollution, in terms of minimizing the wastewater and plastic debris lying around

the drains, roads, and streets. This will in turn lead to increase the aesthetic value of the local environment.

Acknowledgment

The authors acknowledge the funding offered by Department of Environmental Sciences, University of Peshawar, Khyber Pakhtunkhwa, Pakistan.

References

- [1] M. Ilyas, W. Ahmad, H. Khan, S. Yousaf, K. Khan, S. Nazir, Plastic waste as a significant threat to environment – a systematic literature review, *Rev. Environ. Health*, 33 (2018) 383–406.
- [2] M. Ilyas, W. Ahmad, H. Khan, I. Ahmad, Application of composite adsorbents prepared from waste PS and PET for removal of Cr and Cu ions from wastewater, *Desal. Water Treat.*, 171 (2019) 144–157.
- [3] A.L. Andrady, M.A. Neal, Applications and societal benefits of plastics, *Philos. Trans. R. Soc. London, Ser. B*, 364 (2009) 1977–1984.
- [4] H. Jefferson, R. Dvorak, E. Kosior, Plastics recycling: challenges and opportunities, *Philos. Trans. R. Soc. London, Ser. B*, 364 (2009) 2115–2126.
- [5] B.G. Mwanza, C. Mbohwa, Drivers to sustainable plastic solid waste recycling: a review, *Procedia Manuf.*, 8 (2017) 649–656.
- [6] E.J. North, R.U. Halden, Plastics and environmental health: the road ahead, *Rev. Environ. Health*, 28 (2013) 1–8.
- [7] R.U. Halden, Plastics and health risks, *Annu. Rev. Public Health*, 31 (2010) 179–194.

- [8] S. Khan, I. Ahmad, M. Tahir Shah, S. Rehman, A. Khaliq, Use of constructed wetland for the removal of heavy metals from industrial wastewater, *J. Environ. Manage.*, 90 (2009) 3451–3457.
- [9] A.F. Tajar, T. Kaghazchi, M. Soleimani, Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells, *J. Hazard. Mater.*, 165 (2009) 1159–1164.
- [10] N. Fiol, I. Villaescusa, M. Martínez, J. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep. Purif. Technol.*, 50 (2006) 132–140.
- [11] M. Said, M. Tahir Shah, S. Khan, Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan, *Microchem. J.*, 98 (2011) 334–343.
- [12] M.A. Kahlowan, A. Majeed, Water-resources situation in Pakistan: challenges and future strategies, *Water resources in the South: present scenario and future prospects*, 20 (2003) 33–45.
- [13] K. Shekhawat, S. Chatterjee, B. Joshi, Chromium toxicity and its health hazards, *Int. J. Adv. Res.*, 3 (2015) 167–172.
- [14] R. Camarillo, A. Pérez, P. Cañizares, A. de Lucas, Removal of heavy metal ions by polymer enhanced ultrafiltration: batch process modeling and thermodynamics of complexation reactions, *Desalination*, 286 (2012) 193–199.
- [15] P. Patnuka, A. Kongsuwan, P. Pavasant, Batch studies of adsorption of copper and lead on activated carbon from *Eucalyptus camaldulensis* dehn. bark, *J. Environ. Sci.*, 20 (2008) 1028–1034.
- [16] S.-C. Tsai, K.-W. Juang, Comparison of linear and non-linear forms of isotherm models for strontium sorption on a sodium bentonite, *J. Radioanal. Nucl. Chem.*, 243 (2000) 741–746.
- [17] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.*, 70 (1998) 115–124.
- [18] S.H. Chen, J. Zhang, C.L. Zhang, Q.Y. Yue, Y. Li, C. Li, Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from *Phragmites australis*, *Desalination*, 252 (2010) 149–156.
- [19] M. Lawrinenko, Anion Exchange Capacity of Biochar, Graduate Theses, Iowa State University, 2014.
- [20] Y. Yao, B. Gao, J. Fang, M. Zhang, H. Chen, Y.M. Zhou, A.E. Creamer, Y.N. Sun, L.Y. Yang, Characterization and environmental applications of clay-biochar composites, *Chem. Eng. J.*, 242 (2014) 136–143.
- [21] K.G. Bhattacharyya, S.S. Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution, *Sep. Purif. Technol.*, 50 (2006) 388–397.
- [22] F.A. Dawodu, K.G. Akpomie, Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution onto a Nigerian kaolinite clay, *J. Mater. Res. Technol.*, 3 (2014) 129–141.
- [23] B.K. Nandi, A. Goswami, M.K. Purkait, Adsorption characteristics of brilliant green dye on kaolin, *J. Hazard. Mater.*, 161 (2009) 387–395.
- [24] M.N. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, *J. Hazard. Mater.*, 143 (2007) 478–485.
- [25] H. Liu, S. Liang, J.H. Gao, H.H. Ngo, W.S. Guo, Z.Z. Guo, J. Wang, Y.R. Li, Enhancement of Cr(VI) removal by modifying activated carbon developed from *Zizania caduciflora* with tartaric acid during phosphoric acid activation, *Chem. Eng. J.*, 246 (2014) 168–174.
- [26] S. Athapaththu, A comprehensive study of Cd(II) removal from aqueous solution via adsorption and solar photocatalysis, *Electron. Thesis Dissertation Repository*, 19 (2013) 1783.
- [27] V. Vadivelan, K. Vasanth Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interface Sci.*, 286 (2005) 90–100.
- [28] S.-N. Joanna, U. Narkiewicz, A.W. Morawski, R.J. Wróbel, B. Michalkiewicz, The increase of the microporosity and CO₂ adsorption capacity of the commercial activated carbon CWZ-22 by KOH treatment, *Microporous Mesoporous Mater.*, (2016) 2–19, doi: 10.5772/63672.
- [29] M.R. Shrestha, I. Varga, J. Bajtai, M. Varga, Design of surface functionalization of waste material originated charcoals by an optimized chemical carbonization for the purpose of heavy metal removal from industrial waste water, *Microchem. J.*, 108 (2013) 224–232.
- [30] W. Konicki, I. Pelech, E. Mijowska, I. Jasińska, Adsorption of anionic dye Direct Red 23 onto magnetic multi-walled carbon nanotubes-Fe₃C nanocomposite: kinetics, equilibrium and thermodynamics, *Chem. Eng. J.*, 210 (2012) 87–95.
- [31] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, *Water Res.*, 37 (2003) 4038–4044.
- [32] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, *Miner. Eng.*, 19 (2006) 463–470.
- [33] S.-M. Xu, J. Wei, S. Feng, J.-D. Wang, X.-S. Li, A study in the adsorption behaviors of Cr(VI) on crosslinked cationic starches, *J. Polym. Res.*, 11 (2004) 211–215.
- [34] H. Chen, Y.G. Zhao, A.Q. Wang, Removal of Cu(II) from aqueous solution by adsorption onto acid-activated palygorskite, *J. Hazard. Mater.*, 149 (2007) 346–354.
- [35] A. Sari, M. Tuzen, D. Citak, M. Soylak, Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution, *J. Hazard. Mater.*, 148 (2007) 387–394.
- [36] M. Kobya, E. Demirbas, E. Senturk, M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, *Bioresour. Technol.*, 96 (2005) 1518–1521.
- [37] Y. Kong, J.X. Wei, Z.L. Wang, T. Sun, C. Yao, Z.D. Chen, Heavy metals removal from solution by polyaniline/palygorskite composite, *J. Appl. Polym. Sci.*, 122 (2011) 2054–2059.
- [38] M. Iqbal, A. Saeed, N. Akhtar, Petiolar felt-sheath of palm: a new adsorbent for the removal of heavy metals from contaminated water, *Bioresour. Technol.*, 81 (2002) 151–153.
- [39] M. Liu, Y. Deng, H. Zhan, X. Zhang, Adsorption and desorption of copper(II) from solutions on new spherical cellulose adsorbent, *J. Appl. Polym. Sci.*, 84 (2002) 478–485.
- [40] A. Saeed, M.W. Akhter, M. Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, *Sep. Purif. Technol.*, 45 (2005) 25–31.
- [41] E. Katsou, S. Malamis, M. Tzanoudaki, K.J. Haralambous, M. Loizidou, Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems, *J. Hazard. Mater.*, 189 (2011) 773–786.
- [42] I. Ali, New generation adsorbents for water treatment, *Chem. Rev.*, 112 (2012) 5073–5091.
- [43] S. Lata, P.K. Singh, S.R. Samadder, Regeneration of adsorbents and recovery of heavy metals: a review, *Int. J. Environ. Sci. Technol.*, 12 (2015) 1461–1478.
- [44] T. Motsi, Remediation of Acid Mine Drainage using Natural Zeolite, School of Chemical Engineering, The University of Birmingham, United Kingdom, 2010.
- [45] T. Motsi, N.A. Rowson, M.J.H. Simmons, Adsorption of heavy metals from acid mine drainage by natural zeolite, *Int. J. Miner. Process.*, 92 (2009) 42–48.