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Utilization of municipal sludge in adsorption of cadmium and phenol in Saudi Arabia

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ABSTRACT

Activated carbon (AC) was produced from municipal sewage sludge collected from Al-Khobar wastewater treatment plant in the Eastern Province of Saudi Arabia. The best produced AC sample that was obtained from $ZnCl_2$ activation at an impregnation ratio of 1:1 and activation temperature and time of 700°C and 60 min, respectively, was tested for its capability in the removal of Cd^{2+} and phenol from a synthetic wastewater. Adsorption experiments were conducted in single solute systems for both contaminants, where effects of operational parameters such as pH, initial concentration, adsorbent dosage, and contact time were investigated. The experimental results revealed that removal efficiencies of 28 and 56%were achieved for Cd^{2+} and phenol, respectively, at optimum conditions of pH value of 5.5, AC dosage of 0.15 g per 50 ml and contact time of 120 and 720 min for Cd^{2+} and phenol, respectively. Isotherm modelling of the experimental data showed that Cd^{2+} adsorption can be well described by the Freundlich isotherm, while phenol adsorption was well described by the Langmuir isotherm. The mechanism of adsorption of both contaminants was ascribed to chemisorption, which was based on the adsorption data that fitted well to the pseudo-second order model.

Keywords: Adsorption; Activated carbon; Phenol; Cadmium; Isotherms; Kinetics

1. Introduction

Wastewater treatment facilities across Saudi Arabia (KSA) have been or are being expanded, which directly translates in increased volumes of municipal sludge being produced. The only treatment option available for the produced sludge is thickening and dewatering on solar drying beds or mechanical belt filter presses. In the Eastern Province of Saudi Arabia, produced sludge is not being characterized and is mainly disposed of by land spreading technique at dumping sites outside the cities of Dammam, Qatif and Al-Khobar. The produced municipal sludge is also being utilized by farmers as a fertilizer source, which evidently could result in crops that are contaminated with viruses, toxic organics, and heavy metals [1]. Production of municipal sewage sludge is a continuous process that requires flexible and secure range of outlets for its disposal to be economic and environmentally acceptable [2]. The published literature showed that there are several alternatives for utilizing sewage sludge on land such as its use as a forest fertilizer, a soil conditioner for the restoration of disturbed soils, a soil-forming material for reclaiming derelict land and for producing soil for use on green areas in urban environments [3,4]. Apart from ocean dumping, which is now illegal, all sludge disposal alternatives are land-based, while incineration is another principal alternative of sludge disposal [5]. In addition to disposal, utilization of municipal sewage sludge is a more attractive option that needs to be considered in any integrated sludge management. Municipal sewage sludge was reported to be utilized as a source for biofuel production [6,7], fertilizer for agricultural use [8,9] and as an additive in concrete mixes [10,11]. However, and up to the knowledge of the authors, there is no single work that has been carried out on the utilization of municipal sludge in Saudi Arabia, particularly in the production of activated carbon (AC). Sludge production in Saudi Arabia

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estimated to be around 451,780 tons of dry matter annually [12], which is expected to increase in coming years. As a result, the need for finding efficient, feasible and beneficial alternatives for safe disposal or utilization of the produced amounts of municipal sludge in Saudi Arabia would be highly appreciated by decision makers. Production of activated carbon (AC) from municipal sludge involves two main steps, namely, carbonization and activation that can be implemented simultaneously or individually.

The removal of Cd^{2+} and phenol by adsorption using activated carbon (AC) and other forms of adsorbents have been well studied and documented by numerous researchers in the past [13–17], which revealed that adsorption was found to be an effective process for the removal of these contaminants from aqueous solutions. Some reviewed literature that have focused on single solute adsorption of Cd^{2+} and phenol using sludge-based AC or AC produced from other sources are briefly summarized in the following paragraphs. Bousba and Hassan [18] reported a significant adsorption capacity of 26.16 mg/g that was achieved for phenol at optimum experimental conditions of initial phenol concentration of 40–200 mg/l, adsorbent dosage of 5 g/l, contact time of 180 min and temperature of 20°C using AC produced from sewage sludge that was activated using H_2SO_4. Moreover, the study reported that phenol adsorption was highly depended on its initial concentration and its speciation, which is a function of the solution pH (pH<pKa). Phenol removal from aqueous phase investigated by Zhu et al. [19] revealed a maximum adsorption capacity of 94.9 mg/g was achieved for phenol at a pH value of 5.0, contact time of 120 min and initial concentration of 100 mg/l using AC produced from solidified landfill sewage sludge through $ZnCl_2$ activation. The study concluded that phenol removal by the produced AC was mainly influenced by adsorbent dosage and contact time, while initial solution and pH had no effect on the removal of phenol. Bian et al. [20] studied the adsorption of Cd^{2+} from aqueous-phase using AC modified with oxygen functional groups. The results of the study revealed that a maximum removal efficiency of 88% was achieved for Cd^{2+} over a broad range of pH values of 4.5–6.5. Moreover, the effect of pH on Cd^{2+} adsorption showed that increases in pH values above the initial value of 4.5 resulted in an increase in Cd^{2+} removal efficiency, however, when pH values were increased to values above 6.5, the removal efficiency was found to change insignificantly. The study concluded that the introduced oxygen functional groups on the AC surface contributed significantly to Cd^{2+} adsorption and a maximum adsorption capacity of 25.13 mg/g was reported at the optimum experimental conditions. Ali [13] performed a comparative investigation of Cd^{2+} adsorption using granular activated carbon (GAC), dead biomass and phosphate rock. The results of the investigation indicated that optimum conditions were achieved at pH value of 5, initial concentration of 100 mg/l, adsorbent dosage of 3 mg and contact time of 270 min. Moreover, a maximum adsorption capacity of 17.757 mg/g was achieved for the GAC, based on Langmuir isotherm model.

Based on the above discussion, the main objective of the current investigation is to use activated carbon (AC) produced from municipal sludge that was collected from Al-Khobar wastewater treatment plant in adsorption of cadmium (Cd^{2+}) and phenol. The only treatment that was given to the utilized sludge was thickening and dewatering on sand drying beds or using mechanical belt filter presses. Table 1 shows a comparison between physiochemical characteristics of different sludge samples used for AC production including that of the current investigation [21–30]. Activated carbon (AC) was produced using three activation agents, namely, $ZnCl_2$, KOH and H_3PO_4, however, adsorption isotherms were conducted using AC samples that produced optimum results of yield and Methylene Blue (MB) removal efficiency. Effect of operational parameters such as initial solution pH, time, adsorbent dose and contaminant concentration on the performance of the adsorption process were investigated. The selection of Cd^{2+} and phenol was based on their presence as common pollutants in most industrial wastewater effluents. It is worth to emphasize that the current investigation is the first of its kind in Saudi Arabia.

2. Materials and methods

Dewatered municipal sludge was collected from belt-filter press units of Al-Khobar wastewater treatment plant. The collected sludge was oven dried at 105°C overnight, washed to remove visible dirt and, subsequently, re-dried again. Dried sludge samples were comminuted, sieved through a 2-mm mesh and stored in covered plastic containers. The general physicochemical characteristics of sludge being produced from Al-Khobar wastewater treatment plants can be cited in Al-Malack et al. [31]. Chemical reagents used throughout the study were of analytical grade, which included cadmium nitrate (BDH laboratories supplies), phenol crystal (Sigma-Aldrich), methylene blue (Fischer), potassium hydroxide pellets (Fischer), phosphoric acid (Fischer), zinc chloride (Fischer), nitric acid (Fischer) and sodium hydroxide (Fischer). Moreover, deionized water used was prepared using CORNING Mega Pure™ System.

2.1. Production of AC

In the impregnation step for both $ZnCl_2$ and H_3PO_4 activation, 10 g of the comminuted dried sludge were mixed and stirred with 15 ml solution of the chemical reagents. For KOH impregnation, 10 g of the sludge were dry mixed with varying weights of crushed KOH pellets until a homogenous mixture was attained. The impregnation process for $ZnCl_2$ and H_3PO_4 was performed at room temperature and continued for more than one hour to achieve full penetration, subsequently, the obtained slurry was oven dried at 105°C for 4 h to remove excess moisture. Impregnated samples were packed into 30-cm stainless steel tubes of 50-mm diameter having two narrow ports of 8-mm diameter (for expelling gases). The packed tubes were placed in a muffle furnace and heated to desired temperatures of 600, 700 and 800°C, where heating was performed at 10°C/min. Samples were taken out of the furnace at time intervals of 60, 90, and 120 min, cooled and subjected to repeated cycles of washing with distilled water to remove residues of activation chemicals. The final product was oven dried at 105°C for 24 h, crushed and sieved to a particle size of less than 0.3 mm.

Table 1
Comparison of physiochemical characteristics of different sludge used for AC production

Country	Proximate analysis (wt. %)				Ultimate analysis (wt.%)					Activated Carbon		References
	Moisture	Ash	Fixed Carbon	Volatile Content	C	H	N	S	O	Activation Agent	BET Surface Area of AC (m^2/g)	
Thailand	9.35 ± 0.44	24.40 ± 0.63	5.57 ± 0.16	60.50 ± 0.89	68.69 ± 2.99			0.30 ± 0.04	29.05 ± 3.34	KOH		[21]
China					37.48	5.83	6.69	1.857	21.44	$Fe_2(SO_4)_3$	126.86	[22]
China	79.65	48.1	10.37	41.53	28.4	3.54	2.68	1.17	16.11	$ZnCl_2$	225.09	[23]
Algeria		51.08	3.06	45.86	26.28	2.74	3.49	0.57	66.92	H_3PO_4	296	[24]
Brazil					21.2± 0.08		3.83±0.05	1.88±0.03		KOH & $ZnCl_2$	186; 192	[25]
France		22.0	30.7	49.4	39.4	5.6	6.4	0.9		Steam	144-226	[26]
Spain		31.2			31.4	4.8	4.4	1.0	21.5	NaOH &KOH	1224; 1686	[27]
Spain		22.0	6.88	45.97	57.7	8.5	9.3	0.5	24.0	H_2SO_4	253	[28]
Spain	6.3	44.2		55.8	28.6	4.5	4.9	1.1		CO_2	178.9	[29]
Malaysia	80.41	30.83	14.47	54.70	33.79	5.35	5.74	0.93	54.18			[30]
Saudi Arabia	49	26		34	38.24	5.17	5.80	1.33		$ZnCl_2$	319.5	Current study

2.2. Adsorption experiments

Adsorption capability of best produced AC samples in removing Cd^{2+} and phenol, in single solute systems,was investigated by conducting adsorption isotherms at different conditions of operational factors, namely, initial solution pH, contact time, concentration of contaminant (Cd^{2+} and phenol) and adsorbent dose. A stock solution of 1000 mg/l of Cd^{2+} was prepared from its cadmium nitrate salts ($Cd(NO_3)_2 \cdot 4H_2O$) and was preserve using 0.5 M nitric acid (HNO_3). Similarly, 1000 mg/l stock solution of phenol was prepared using the phenol crystal. Other various concentrations of Cd^{2+} and phenol were prepared from their respective stock solutions by dilution. Batch adsorption experiments were conducted by adding different amounts of the produced AC to 50 ml solutions containing different concentrations of Cd^{2+} or phenol in 125 ml Erlenmeyer flask. The mixtures were agitated using a mechanical shaker at 200 rpm and room temperature. Effects of pH on adsorption of Cd^{2+} and phenol were investigated using 100 mg/l of Cd^{2+} or phenol, AC dose of 0.15 g, contact time of 2 h and different pH values (3–7). Solution pH values were adjusted using 0.1 N NaOH and 0.1 N HNO_3. Effects of contact time on adsorption performance were studied at 100 mg/l of Cd^{2+} or phenol, AC dose of 0.15 g, optimum pH value and contact times of 1, 5, 10, 15, 30, 60, 120, 240, 480, 720, and 1440 min. Effects of adsorbent dose on adsorption were investigated at 100 mg/l of Cd^{2+} or phenol, optimum pH value, optimum contact time and different AC doses (25–300 mg). Investigation of the effect of Cd^{2+} or phenol concentrations on the adsorption performance was conducted at optimum pH value, optimum contact time, optimum AC dose and at different concentrations of Cd^{2+} or phenol, as shown in Table 2.

2.3. Analytical techniques

All adsorption isotherms, including blank samples, were conducted in duplicates. Measurements of pH were conducted using the standard pH electrode-meter (Accumet XL15 pH meter). At the end of each isotherm investigation, samples were filtered using filter papers (Whatman Grade no 41) and analyzed for their Cd^{2+} or phenol content. Analysis of Cd^{2+}was performed using Atomic Absorption Spectroscopy, AAS (PerkinElmer, 700) using the direct air-acetylene flame method. Phenol analysis was conducted using UV-vis Spectrophotometer (Shimadzu, Japan) at a wavelength of 264 nm.

Table 2
Adsorption parameters investigated

Constituents	Concentration (mg/l)	Adsorbent Dosage (mg per 50 ml)	pH	Time (minutes)
Cd^{2+}	25–300	25–300	3–7	0–1440
Phenol				

3. Results and discussion

3.1. Characterization of the produced AC Samples

Porosity and surface area characteristics of the produced AC such as its surface functional groups, surface area, pores structures and elemental compositions are major factors that determine its adsorptive capability for pollutants. These factors together with some preliminary adsorption experiments conducted for Cd^{2+} and phenol removal were employed as the main criteria for selecting the best produced AC sample. Results of some of the selected AC samples that were characterized in terms of surface functional groups using Fourier Transform Infrared Spectroscopy (FTIR) analysis (functional groups), elemental composition (CHNS-O), Brunauer-Emmett-Teller (BET) surface area, and X-Ray Diffraction (XRD) analysis for the mineralogical compositions have been presented and explained in detailed elsewhere [32].

Based on the selection criteria it was observed that the best AC sample was produced using $ZnCl_2$, as the activation agent, at an activation temperature of 700°C, impregnation ratio of 1:1 and activation time of 60 min.

3.2. Adsorption experiments

3.2.1. Effect of initial solution pH

The influence of pH on adsorption is important as it determines the ionization of adsorbates in aqueous phases as well as the surface charge of adsorbents being employed. Interaction of adsorbate with adsorbent, which ultimately determine the efficiency of adsorption are pH dependent. Consequently, the effects of initial solution pH on single-solute adsorption of Cd^{2+} and phenol were investigated at different pH values (3, 4, 5, 6, and 7). Batch adsorption isotherms were conducted using 50 ml solution of 100 mg/l of Cd^{2+}or phenol, AC dose of 0.15 g and contact time of 2 h. The point of zero charge pH (pzc) of the AC used in adsorption studies was also determined according to the pH-drift technique, and the results are provided in Fig. 1. The pHpzc was found to be approximately 5.2; which signifies that at

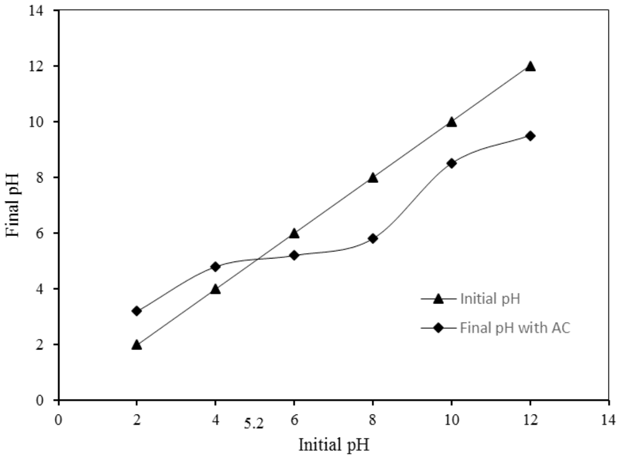

Fig. 1. pHpzc determination for the sludge based AC using pH-drift method.

pH values below 5.2, the net surface charge on the AC will be positive, while at pH values above pH(pzc), the surface charge will be negative.

Figs. 2 and 3 show the effect of initial solution pH on adsorption of the contaminants, together with the effect of pH adjustment on the concentrations of contaminants (blank samples). The figures clearly show that the increase in pH values for both Cd^{2+} and phenol solutions resulted in increasing removal efficiencies. For Cd^{2+}, Fig. 2 shows an initial removal efficiency of 16 and 40% at pH values of 3 and 7, respectively, which can be primarily attributed to the existence of an electrostatic force of attraction between the produced AC surface and Cd^{2+} ions in the solution. Results of the FTIR analysis conducted confirmed the presence of oxygen-based functional groups such as O-H and C-O on the AC surface [32]. In addition, the AC pHpzc value of 5.2 indicate that the predominant functional groups between pH 5.5 and 7 are negatively charged. Therefore, it can be deduced that Cd^{2+} removal from the solution by the produced AC must have been due to its electrostatic interaction with the above-mentioned negatively-charged functional groups. Moreover, the low Cd^{2+} removal efficiency that was noticed at lower pH values could be related to competition of Cd^{2+} and hydrogen ion (H^+) for adsorption sites on the produced AC surface [33]. The figure clearly shows that as pH values were increased, removal efficiencies were found to increase, which resulted from decreases in H^+ ions in the solution that, in turn, resulted in freeing more spaces for Cd^{2+} ions to bind onto the produced AC surface [34].Results on effects of pH variation on Cd^{2+} concentration (blank samples) presented in Fig. 2 show significant Cd^{2+} removal at pH values between 6 and 7 that could be related to the combined effects of adsorption and precipitation occurring at these pH values. Similar observations were reported by Al-Malack-and Basaleh [35] for Cd^{2+} adsorption onto AC produced from municipal organic solid waste. Consequently, an optimum pH value of 5.5 was selected and used throughout the investigation to ensure that Cd^{2+} removal is mainly due to adsorption rather than the combined effect. Phenol adsorption that is depicted in Fig. 3, shows that removal efficiencies increased slightly from 47 to 50% when pH values were increased from 3 to 5 and, afterwards, no change was noticed for pH values of 6 and 7 (50%). Similar adsorption behavior was reported by Pirzadeh and Ghoreyshi [36] in their research work on phenol removal using AC produced from paper mill sludge. It can be observed from the result of pH effect on phenol concentration of blank samples that is shown in Fig. 3, that selected pH values had no effect on phenol concentration. This is possibly due to phenol high pKa value of 9.95, which implies that it will appear in undissociated form in the selected pH range, therefore, phenol adsorption by the produced AC is not based on the electrostatic force of attraction. Several research works have attributed phenol adsorption on AC to its chemical interaction with AC surface functional groups (O-H and C=O) via electron-donor acceptor reaction mechanism, where AC functional groups act as an electron donor, while phenol being the electron acceptor [37,38]. Due to high removal efficiencies noticed at pH values between 5 and 7, a pH value of 5.5 was also selected as optimum for phenol.

3.2.2. Effect of contact time

The effect of contact time on the removal efficiency of Cd^{2+} and phenol in single solute systems was investigated using the produced AC. Batch adsorption isotherms were conducted using 50-ml solutions of 100 mg/l of Cd^{2+} or phenol, AC dosage of 0.15 g, pH of 5.5 (optimum) and at different contact times varying between 1 and 1440 min. Results presented in Fig. 4 for both pollutants show that Cd^{2+} adsorption was rapid at the initial stages of the investigation, where removal efficiency of 27%was achieved within the first 60 min of contact time. An insignificant increase in removal efficiency of up to 28%was noticed after 120 min. The same removal efficiency of 28% was recorded at the prolonged period, which clearly indicates that equilibrium condition was established after 120 min of contact time. However, an equilibrium time of 180 min was adopted for all adsorption isotherms to ensure that equilibrium condi-

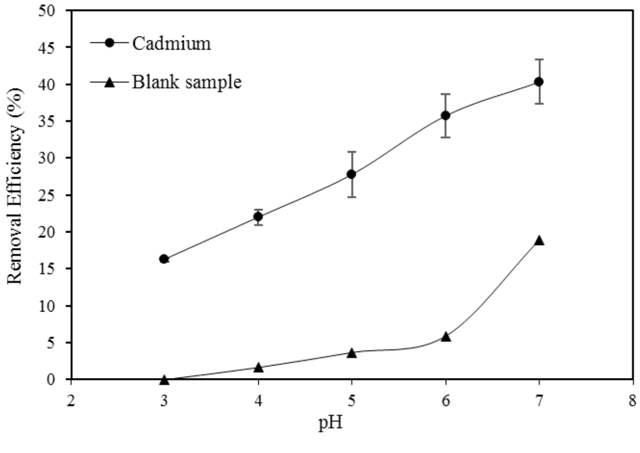

Fig. 2. Effect of initial pH on single solute adsorption of Cd^{2+} (Blank sample indicate removal due to precipitation alone).

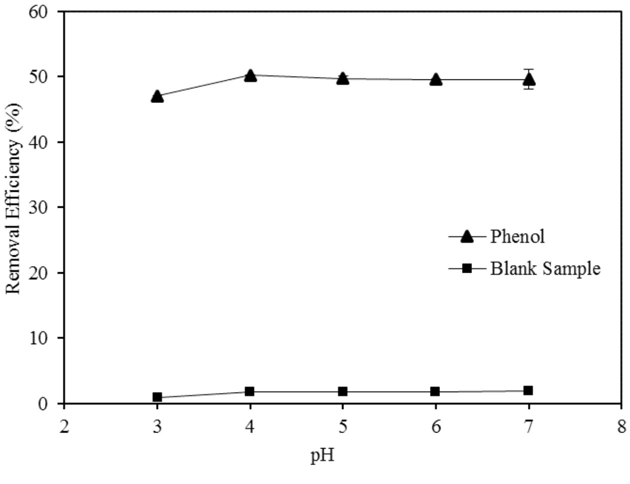

Fig. 3. Effect of initial pH on single solute adsorption of phenol (Blank sample indicate removal without AC).

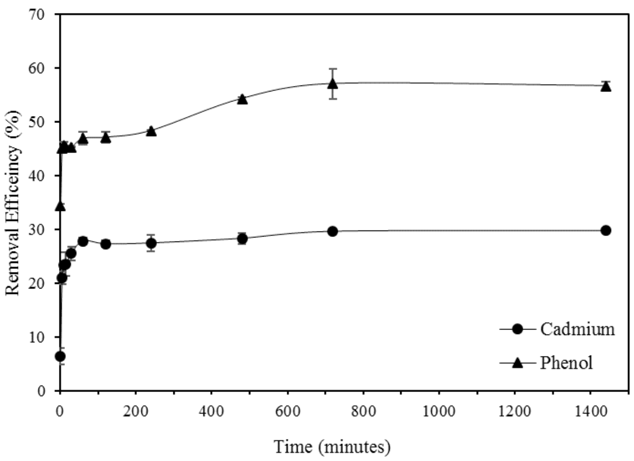

Fig. 4. Effect of contact time on single solute adsorption of Cd^{2+} and phenol.

tions would be established. With respect to phenol, similar fast adsorption rate was noticed at the initial stages of the investigation, after which removal efficiency became almost constant. Based on the results, equilibrium condition was found to be established after 720 min of contact time with constant removal efficiency of 56%. The fast removal rate that was noticed for both pollutants at initial stages of investigations can be attributed to the availability of numerous active vacant sites on the produced AC surface and to the effect of the high-concentration gradient between bulk solutions and the produced AC surface at the beginning of the investigation [39]. However, the gradual increase noticed in later stages might have been due to surface sites that were getting filled, thus resulting in less uptake of the pollutants [40].

3.2.3. Effect of adsorbent dosage

Effect of AC dosage on the removal efficiency and adsorption capacity of Cd^{2+} and phenol, in single solute systems, were investigated, where equilibrium batch adsorption isotherms were performed by adding different amounts of AC (25, 50, 100, 200, 300, 400 and 500 mg) to 50-ml volume of 100 mg/l of Cd^{2+} or phenol solutions and pH value of 5.5. Contact times that were implemented were 180 and 720 min for Cd^{2+} and phenol, respectively. Results presented in Figs. 5 and 6 depict removal efficiencies and adsorption capacities of both contaminants at different AC dosages. Fig. 5 shows that there was an increase in removal efficiency of both contaminants as AC dosage was increased. Significant increase in removal efficiencies from 3 to 59% and from 7 to 78% can be observed for Cd^{2+} and phenol, respectively, as AC dosage was increased from 25 to 300 mg. This can be attributed to the fact that with more AC in solution, there will be an increase in total surface area and surface functional groups available for uptake of contaminants. On the contrary, adsorption capacities of both contaminants were found to decrease with the increase in AC dosages, as shown in Fig. 5. Decreases in Cd^{2+} and phenol adsorption capacities from 16.90 to 8.07 mg/g and from 20.04 to 12.05 mg/g, respectively, were observed, which can be attributed to the effect of unsaturation of adsorption sites that could occur at higher AC dosages for fixed concentrations of Cd^{2+} and phenol, while complete or nearly complete saturation may occur at lower dosages for the same concentration of contaminants. This effect was explained by Gutiérrez-Segura et al. [41] to have resulted from Cd^{2+} dilution at the solid phase at higher AC to solution ratios. Similar findings were also reported by Gutiérrez-Segura et al. [41] and Zhu et al. [19] for Cd^{2+} and phenol adsorption on AC derived from sewage sludge and landfill sewage sludge, respectively.

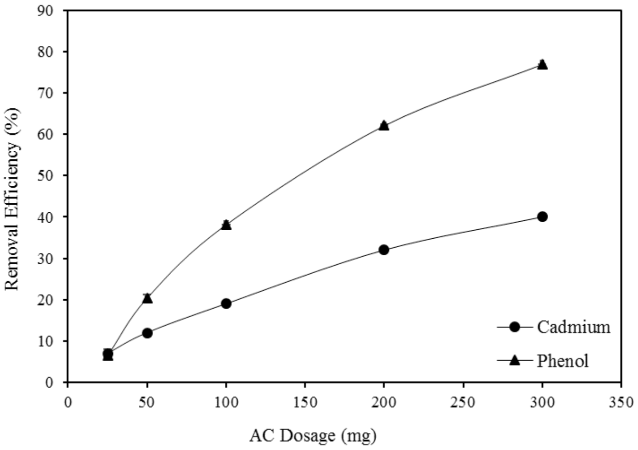

Fig. 5. Effect of AC dosage on the removal efficiency of Cd^{2+} and phenol.

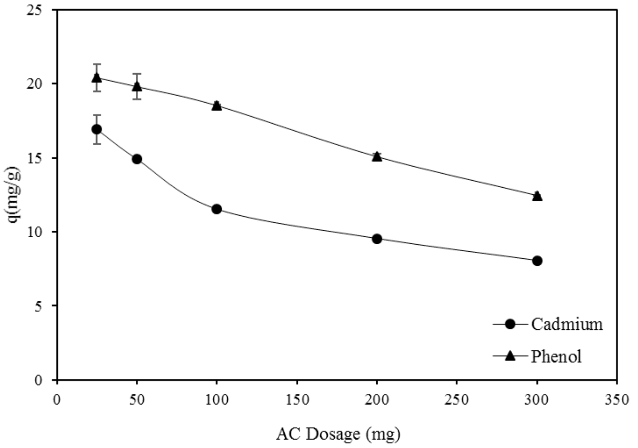

Fig. 6. Effect of AC dosage on adsorption capacity of Cd^{2+} and phenol.

3.2.4. Effect of initial cconcentration

To investigate the effect of initial concentration on removal efficiencies and adsorption capacities of Cd^{2+} and phenol, in single solute systems, batch adsorption experiments were carried out. The isotherms were performed at different concentrations of both contaminants (25–300 mg/l) using AC dosage of 0.15 g, pH value of 5.5 and contact times of 180 and 720 min for Cd^{2+} and phenol, respectively. Fig. 7 represents removal efficiencies and adsorption capacities of Cd^{2+} and phenol at different initial concentrations. The figure shows a decrease in $Cd^{2+}$and phenol removal efficiencies from 57 to 18% and from 59 to 28%, respectively, as initial concentrations were increased from 25 to 300 mg/l, which can be explained based on AC surface energy sites. As described by Ali [13], for a fixed amount of AC and at low initial concentration of pollutants, adsorption normally occurs at high energy sites of the AC. However, as pollutant concentration was increased, pollutant-adsorbent ratios are increased, which can result in higher energy sites being saturated and, therefore, adsorption would shift to lower energy sites, which will result in decreasing removal efficiencies. On the other hand, the figure shows that adsorption capacities of Cd^{2+} and phenol increased with increase in initial concentrations, where Cd^{2+} and phenol adsorption capacities increased from 6.38 to 18.70 mg/g, and from 4.95 to 29.52 mg/g, respectively, as initial concentrations were increased from 25 to 300 mg/l. A possible explanation of this phenomenon might be due to the increased interactions between pollutants at higher concentration with the produced AC surface, which may occur due to high concentration gradients between the solid phase of the produced AC and the bulk liquid phase of Cd^{2+} and phenol. Hence, this provided the driving force in overcoming the mass transfer resistance, which subsequently resulted in the high adsorption capacities that were noticed [42].

3.3. Equilibrium adsorption isotherms

The obtained data on effects of initial concentration of Cd^{2+} and phenol were modeled using two adsorption isotherm models, namely, Langmuir and Freundlich as presented in Eqs. (1) and (2), respectively. Model's parameters presented in Table 3 were calculated from slopes and y-intercepts of linear plots that are shown in Fig. 7.

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (1)$$

$$\frac{1}{q_e} = \frac{1}{q_m K_{ads}}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \qquad (2)$$

where C_e is the equilibrium aqueous concentration of the adsorbate (mass/volume), q_e is the adsorption capacity (mass adsorbate /mass adsorbent), K and n are the Freundlich constants related to sorption capacity and sorption affinity of the adsorbent and q_m is the maximum adsorption capacity for adsorbates. The figure clearly shows that Cd^{2+} adsorption by the produced AC fitted well to Freundlich isotherm with a correlation coefficient (R^2) of 0.92, which was higher than that obtained for Langmuir isotherm (0.79). Based on that, it was deduced that Cd^{2+} adsorption occurs in multilayer over the heterogeneous surface of the produced AC and sites with high affinity for Cd^{2+} ions were occupied first [43]. The high *n*-value (adsorption intensity) of 2.76 >1 obtained from Freundlich isotherm confirmed the heterogeneous nature of the produced AC surface and the favorable nature of the adsorption process [44]. With respect to

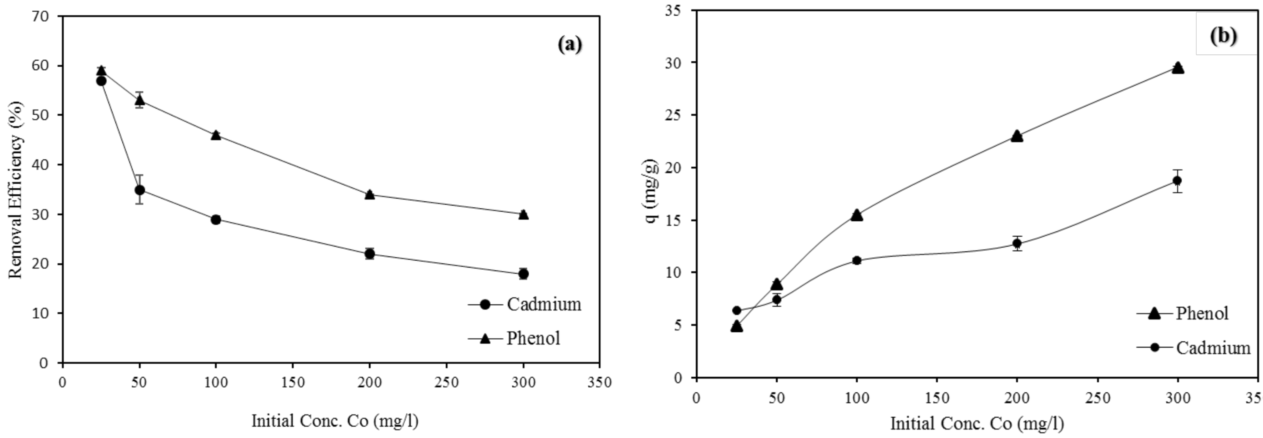

Fig. 7. Effect of initial concentration on (a) removal efficiency and (b) adsorption capacity of Cd^{2+} and phenol.

Table 3
Freundlich and Langmuir parameters of Cd^{2+} and phenol single solute adsorption onto the AC

Components	Freundlich Parameters			Langmuir Parameters		
	n	k_F mg $g^{-1}(Lmg^{-1})^{1/n}$	R^2	q_m (mg/g)	K_L (L/mg)	R^2
Cd^{2+}	2.76	2.21	0.9231	14.20	0.051	0.7877
Phenol	1.72	1.38	0.9907	33.11	0.017	0.9960

phenol, both isotherms were found to well fit the obtained adsorption data, where Langmuir isotherm showed better fit based on its higher R^2 value (0.996). Therefore, it can be concluded that phenol adsorption occurs in monolayer over the entire active surface sites of the produced AC. Maximum adsorption capacity (q_m) of 33.11 mg/g was obtained for Langmuir isotherm, while n value of 1.72 was obtained for Freundlich isotherm that supports the favorable nature of phenol adsorption onto the produced AC.

3.4. Adsorption kinetics

Adsorption kinetics describe the rate at which adsorption process approaches equilibrium conditions. They provide useful insight in determining the main mechanism involved in adsorption process, which could be physisorption or chemisorption. Moreover, kinetic parameters provide valuable information that is useful for adsorption process design and modeling [26]. Therefore, mechanisms of Cd^{2+} and phenol adsorption onto the produced AC were investigated by fitting experimental data to both pseudo-first order and pseudo-second order kinetics models as presented in Eqs. (3) and (4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{4}$$

where q_e is the theoretical equilibrium adsorption capacity (mg/g) derived from the model's plot, q_t is the adsorption capacity (mg/g) at any time (t) derived from the experimental data, k_1 is the pseudo-first order rate constant (min^{-1}) that is calculated from the y-intercept of the plot of $\ln(q_e - q_t)$ versus t (time) and k_2 is the pseudo-second order rate constant (g/mg min) that can be determined from the slope and y-intercept of the plot of t/q_t versus $1/q_e$.

Fig. 9 shows the pseudo-first and second order kinetic plots for both Cd^{2+} and phenol adsorption, while Table 4 provides the kinetic parameters that were computed from both plots. Results of Cd^{2+} adsorption fitted the pseudo-second order model (R^2 = 0.999) better than the pseudo-first order model (R^2 = 0.856), which implies that Cd^{2+} experimental data can be adequately described by the second order model. Moreover, computed Cd^{2+} adsorption capacity (theoretical q_e) of 9.49 mg/g from the pseudo-second order model agreed with the experimental adsorption capacity of 9.48 mg/g.

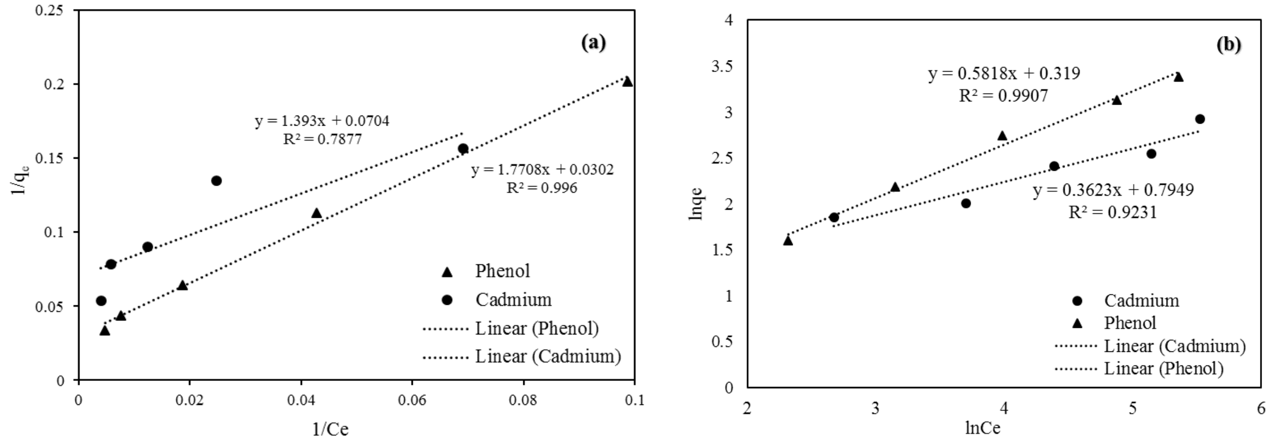

Fig. 8. Isotherms plot for Cd^{2+} and phenol adsorption onto the AC: (a) Langmuir isotherm (b) Freundlich isotherm.

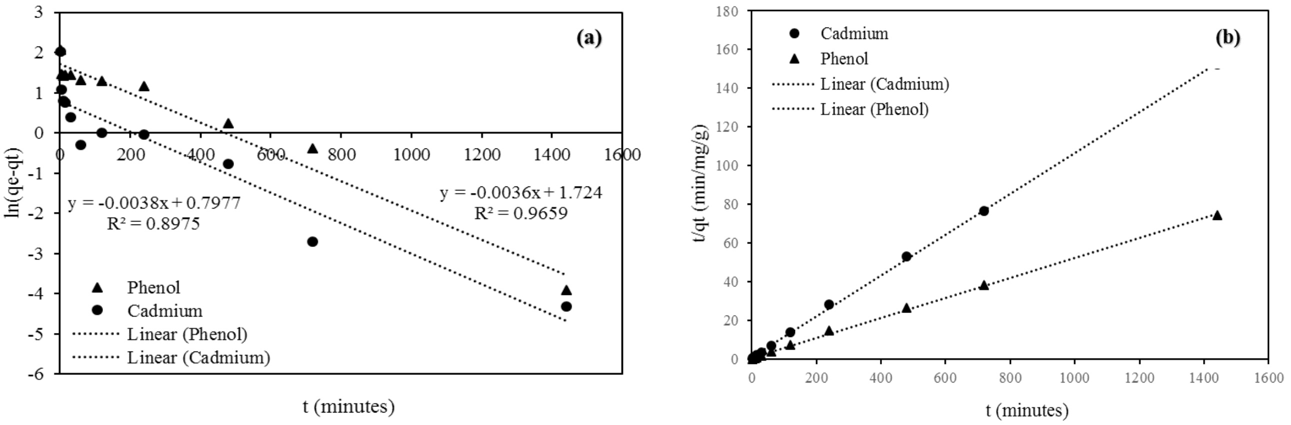

Fig. 9. Effect of initial concentration on (a) removal efficiency and (b) adsorption capacity of Cd^{2+} and phenol. (a) Pseudo-first order and (b) Pseudo- second order kinetic plots for Cd^{2+} and phenol adsorption onto the AC.

Table 4
Kinetic parameters for single solute adsorption of Cd^{2+} and phenol onto the produced AC

Component	Pseudo-first order model				Pseudo-second order model			
	k_1 (min^{-1})	q_e (mg/g)	R^2	Exp. q_e (mg/g)	k_2 (L/g min)	q_e (mg/g)	R^2	Exp. q_e (mg/g)
Cd^{2+}	0.0041	2.22	0.8564	9.48	0.012	9.49	0.9996	9.48
Phenol	0.0036	5.61	0.9659	19.40	0.004	19.34	0.9987	19.40

In the case of phenol, it was observed that the experimental data were well fitted to both kinetic models with R^2 values of 0.9659 and 0.9987, respectively. However, theoretical q_e of 5.61 mg/g computed from pseudo-first order plot deviate greatly from the experimental q_e of 19.40 mg/g, therefore, it was concluded that pseudo-first order model failed to describe the experimental data. On the other hand, the pseudo-second order model produced a theoretical q_e of 19.34 mg/g, which well agreed with the experimental q_e. Therefore, it was concluded that adsorption of both contaminants can be described by the pseudo-second order model, where the adsorption mechanism can be attributed to chemisorption that involves electron sharing or ion exchange between Cd^{2+} or phenol with the AC surface functional groups [43]. It worth mentioning that similar observations were reported by Ma et al. [45] and Bian et al. [20] on adsorption kinetics study of phenol and Cd^{2+}, respectively, using AC.

Surface properties examinations such as FTIR, XRD and SEM-EDS analyses that were carried out for both the original AC and the contaminants-loaded AC samples served to provide details about the adsorption mechanisms of the contaminants onto the AC surface [32]. The results showed that the main mechanism of Cd^{2+} adsorption resulted from its interaction with negatively charged functional groups on the AC surface as evidenced from the FTIR spectra differences between the original AC sample and the Cd^{2+} loaded AC. Moreover, phenol adsorption was attributed to electron donor acceptor complexes reaction mechanism as reported in the published literature [37,38].

4. Conclusions

Based on the outcomes of the various adsorption experiments conducted, it can be concluded that AC produced from the municipal sewage sludge can serve as a potential low-cost material for the removal of contaminants (organic and inorganic) from wastewater. Municipal sewage sludge utilization for AC production in the Kingdom of Saudi Arabia can minimize, if not eliminate, some of the adverse impacts of its current disposal means, which mostly serves as landfill. In addition, the following sets of conclusions could be drawn from this study:

- Adsorption of cadmium (Cd^{2+}) using the produced AC was found to be highly pH- dependent at the employed pH range (3–7) when compared to phenol adsorption.
- Phenol removal was highly favoured by the produced AC, where significant removal efficiencies were observed at relatively shorter contact times.
- Phenol adsorption by the produced AC occurred in monolayer, while Cd^{2+} adsorption occurred in multilayer, which was clearly depicted by the isotherm studies.
- The mechanism of adsorption of both contaminants by the produced AC was dominated by chemisorption, which was depicted by the kinetic modelling of the experimental data.

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