Phenol removal from aqueous solution using *Citrullus colocynthis* waste ash

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**A B S T R A C T**

Phenol is a hazardous organic chemical that introduced into the environment by industrial and pharmaceutical discharges. As a versatile option for phenol removal, adsorption would be viable if it accompanying with low cost adsorbents. This article described a natural, very cheap and local available adsorbent for phenol removal. Phenol showed a high affinity to *Citrullus colocynthis* waste ash which mainly composed of SiO₂ (41.6%), Al₂O₃ (17.3%) and MgO (15.9%). Up to 70% of phenol adsorbed in the first 30 min of agitation. The phenol removal was increased by increasing adsorbent dose (0.5–10 g/L) and decreasing pH (2–12) and pollutant concentration (10–100 mg/L). The positive value of ΔH° in thermodynamic data (0.06) revealed that the process is endothermic. The high and positive value of ΔS° (13.01) and negative values of ΔG° (−5.36 to −7.28), showed a high affinity of phenol to the adsorbent and the spontaneous nature of the adsorption. Isotherm modelling revealed that the phenol molecules adsorbed in multilayer with the maximum adsorption capacity of 173.2 mg/g. The rate limiting step in the sorption process was chemisorption, based on the kinetic data.

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1. Data

Phenol recognized as a priority pollutant by US. Environmental Protection Agency [1]. Wastewater treatment is a key factor to prevent water bodies from being contaminated by phenol and its secondary derivatives [2]. Among the physical, chemical and biological techniques, adsorption considered a very effective, environmental friendly and versatile choice for waste streams treatment [3–5]. To have a viable prospective in sorption process, many researchers attempt to explore low cost adsorbents for decontamination of polluted waters [6–10].

On this exploration, we report an adsorbent that prepared from a local available and low cost waste material.

The adsorbent was characterized using X-ray fluorescence (XRF) for elemental analysis and X-ray diffraction (XRD) techniques. The elemental composition of Citrullus colocynthis wastes ash shown in Table 1. As seen, SiO₂ and Al₂O₃ were among the major chemical constituents of the adsorbent. The XRD pattern of the adsorbent also shown in Fig. 1. The IR spectra of C. colocynthis wastes ash in Infrared spectroscopy which is an analytical tool that provides information on the chemical structure of material presented in Fig. 2.

### Table 1
The XRF analysis of the Citrullus colocynthis wastes ash.

| Element | SiO₂  | Al₂O₃ | MgO   | Fe₂O₃  | CaO  | MnO |
|---------|-------|-------|-------|--------|------|-----|
| Percent | 41.6  | 17.3  | 15.9  | 11.9   | 1.6  | 0.4 |
2. Adsorbent preparation, materials and solutions, experimental design, measurements

To prepare the adsorbent, the *C. colocynthis* fruit wastes washed with deionized water and then dried in oven at 80 °C. The dried materials then heated in furnace at 550 °C for 4 h in the presence of oxygen to produce ash. Next, ash strained using a 20 mesh sieve and kept in a dry environment for following use.

All the experiments were performed in batch sorption mode on aqueous phenol solutions. After adjusting the variable parameters for each run, the solution filtered and then analyzed for residual phenol. The phenol concentration was determined by spectrophotometer in 500 nm according to the standard methods for the examination of water and wastewater [12]. The removal efficiency then calculated using the following equation:

\[
\text{Removal(\%)} = \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]

In which \(C_0\) and \(C_f\) are the initial and final concentration of phenol.
3. The effect of adsorbent dose

Adsorbent dose is an important parameter in the sorption process which determine the available sites for adsorbate attachment to the surface. In this work, the removal efficiency determined by adjusting the adsorbent dose in the range of 0.5–10 g/L. As shown in Fig. 3, the phenol removal increased considerably by adsorbent dose and considerable increase in removal observed when the adsorbent dose adjusted beyond 3 g/L.

4. The effect of initial phenol concentration

The phenol removal efficiency as a function of initial phenol concentration is shown in Fig. 4. As shown, the adsorption decreased by phenol concentration.

5. The effect of solution pH

The effect of solution pH in the range of 2–12 on phenol adsorption is shown in Fig. 5. As seen, the removal decreased from about 78% to 58% when pH decreased from 2 to 12.

![Fig. 3. Phenol removal as a function of adsorbent dose (phenol: 50 mg/L, time: 60 min).](image)

![Fig. 4. Phenol removal as a function of initial concentration (adsorbent: 3 g/L, time: 60 min).](image)
6. Thermodynamic modeling

The effect of solution temperature on adsorption was determined by performing the experiments in temperatures ranged from 20 to 50 °C. Three most important thermodynamic parameters are $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ which are standard enthalpy, standard entropy and standard free energy, respectively. The following equations were used to calculate these parameters [13]:

$$\Delta G^\circ = -RT \ln K_L$$  \hspace{1cm} (2)

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$ \hspace{1cm} (3)

In the Eqs. (2) and (3), $K_L$, $R$ and $T$ are the Langmuir constant (L/mg), the universal gas constant (8.314 J/mol K) and the absolute temperature of the solution (K). The increasing the adsorption efficiency by temperature as shown in Fig. 5 as well as the positive sign of $\Delta H^\circ$ in Table 2, indicates that the process is endothermic in nature.

The high and positive value of $\Delta S^\circ$ in thermodynamic experiments showed a high affinity of phenol to the adsorbent and the increasing randomness during the sorption process. Negative sign of $\Delta G^\circ$ also revealed that the adsorption is spontaneous (Figs. 6–8).

7. Kinetic modeling

Kinetic modeling is an important part of a sorption process that investigate the sorption rate in time. This parameter is important in the economy of the process because it determine the volume of real sorption reactors. The data fitted with three most used models that presented in Table 3. The higher conformity coefficient ($R^2$) for Pseudo-second-order kinetic model in this experiments (Table 4), indicate that the rate of sorption process controlled by chemisorption.
Fig. 6. Phenol removal as a function of temperature (phenol: 50 ppm, adsorbent: 3 g/L, time: 60 min).

Fig. 7. Fitting the experimental data with the (a) Pseudo-first-order, (b) Pseudo-second-order and (c) Intraparticle diffusion kinetic model.
Fig. 8. Fitting the experimental data with (a) Langmuir, (b) Freundlich, (c) Dubinin–Radushkevich and (d) Temkin models.
8. Equilibrium modeling

In general, the higher the capacity of adsorbent toward a specific contaminant, the lower cost for the regeneration of the sorption media. Isotherm equations model the sorption data when the adsorption reached equilibrium. The isotherm equations used in the modeling of phenol removal are summarized in Table 5. The correlation coefficient of 0.99 for Freundlich model indicates that the adsorption occurred in multilayer. The highest monolayer capacity of adsorbent in this experiments was 173.2 mg/g.

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Transparency document. Supplementary material

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