Simultaneous removal of nitrobenzene, 1,3-dinitrobenzene and 2, 4-dichloronitrobenzene from water samples using anthracite as a potential adsorbent

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ABSTRACT

Micro-sized anthracite particles (ANTCs) were used as natural adsorbent for efficient removal of nitrobenzene (NB), 1,3-dinitrobenzene (DNB) and 2,4-dichloronitrobenzene (DCNB) from polluted water samples. Results indicated that the adsorption of NB, DNB and DCNB was rapid and reached a steady state after 3 min. Effects of solution pH, amount of adsorbent, contact time, ionic strength and reusability on the adsorption capability of the ANTC were investigated. Experimental results showed that the removal efficiency is independent of pH and ionic strength of the test solution. The adsorption isotherms were well described by the Langmuir model and kinetics of removal processes were obeyed the pseudo-second-order mechanism. The absorbed amounts of NB, DNB and DCNB were determined by high performance liquid chromatographic (HPLC) measurements before and after the removal process. The loading capacity of ANTC for adsorption of NB, DNB and DCNB was determined to be 0.577, 0.672 and 0.853 mg/g, respectively. This study showed the potential ability of ANTC as an efficient natural adsorbent for removal of NB, DNB and DCNB from industrial wastewater samples.

Introduction

Wastewater treatment is used to remove pollutants and toxic compounds from water samples and also making it fit for reuse or discharge back to the environment. Acceptable overall water quality maintenance needs a proper treatment mechanism and also, concentration monitoring of such hazardous compounds in water samples is challenging.

Nitrobenzene (NB) and its derivatives are a group of compounds that can present high risks to ecological and human health even at low concentrations. Nitrobenzene is a carcinogenic pollutant and is also a member of persistent organic pollutants (POPs) which are compounds of great concern due to their characteristics of toxicity, persistency and bioaccumulation within ecosystems [1–5]. Nitrobenzene (NB) is an important organic compound and has been widely adopted in the manufacture of intermediates in chemical synthesis industries for producing raw materials, such as aniline, quinoline, azobenzene and trinitrotoluene. These chemicals are used to make explosive materials, rubber, pesticides, agricultural chemicals, and solvents for coating materials and dyes. Many studies have reported that NB is ubiquitous in the environment and is present many animals and humans [6,7]. Main contamination sources of surface and wastewaters by NB are oil spills, industrial and municipal discharges, and air input [8]. A large proportion of NB which is generally discharged into wastewater treatment plants is difficult to remove by conventional treatment processes and causes more pollution in the surrounding aquatic environment [9,10]. The high eco-toxic and ubiquitous character of NB and its derivatives are potential threats to the ecosystem and human health. NB is regarded as “pollutant of main concern” by environmental protection agencies (EPA) in many countries [11] and has been classified as one of the 129 priority pollutants by the USEPA [12,13]. Some aromatic compounds such as NB remain in the environment for relatively long time. The half-life of NB in the atmosphere is approximately 4 months [14]. The above-mentioned hazard characteristics of NB and its derivatives are a challenging problem to devote more attention on determining and monitoring these hazardous compounds in aqueous environments.

Several diverse methods were applied for the removal of nitrobenzenes from environmental samples. These methods can be divided into three main categories: physical, chemical and biological treatments [2,9,11–23]. The most frequently used removal method is physical adsorption procedure that is generally considered to be the most effective, low-cost and more convenient for the removal of organic pollutants [13,14,21–23]. However, hazardous chemicals like nitrobenzene, with high water solubility, are especially difficult to remove from wastewater [14].
Anthracite (ANTC) is a hard and compact type of mineral coal that has a high luster and also high carbon content. It has fewest impurities and bituminous coal than lignite. ANTC is the most metamorphosed type of coal with a carbon content of between 92.1% and 98% and low percentage of volatile matter. ANTC has a relative density of 1.3–1.4 g cm$^{-3}$ and luster that is often semimetallic with a mildly brown reflection. ANTC abundantly appear in areas of considerable earth-movements such as the flanks of great mountain ranges.

Recently, increasing attention has been paid to using ANTCs as a feedstock for activated carbon, due to their inherent chemical properties, fine structure and relatively low price that make them excellent raw materials for the production of activated carbon with highly developed micro-porosity. The porous structure (surface area and pore size distribution) and surface chemistry control the adsorption properties of the activated carbon in traditional applications such as water filtration and air purification [24]. However, few articles are published about adsorptive properties of ANTC to remove toxic substances [25,26].

In this investigation ANTC was used as a nontoxic and highly efficient natural adsorbent for simultaneous removal of nitrobenzene (NB), 1,3-dinitrobenzene (DNB) and 2,4-dichloronitrobenzene (DCNB) (Fig. 1) from polluted and spiked water samples without any pretreatment or activation process.

### Materials and methods

#### Chemicals and reagents

All chemicals and reagents were of analytical grade. Acetone (99.5%, w/w), acetonitrile (HPLC grade), water (HPLC grade), nitrobenzene (NB), 1,3-dinitrobenzene (DNB) and 2,4-dichloronitrobenzene (DCNB) were purchased from Merck (Darmstadt, Germany) and used without any further purification. Anthracite particles (average particle size 5 μm) were obtained from Kimia Teb (Ahvaz, Iran). Stock solutions (100 mg/L) for NB, DNB and DCNB were prepared by dissolving 0.1 g of each compound in water–acetonitrile (70:30) solution mixture and were diluted to the mark in a 1000 mL volumetric flask. Other concentrations were prepared by the successive dilutions of these stock solutions with water.

#### Apparatus

Chromatographic measurements were carried out using a Knauer HPLC system (Germany) consisting of a K-1001 pump and a k-2501 UV detector. A pH-meter (827 pH lab, Metrohm, Herisau, Switzerland) was also used. Infrared spectra were obtained using a Fourier Transform-Infrared Spectrometer (FT-IR spectrum 100, Perkin Elmer, Australia) to identify the functional groups and chemical bonding of the ANTC and DCNB@ANTC. Scanning electron microscopic (SEM) analysis was made using Hitachi S-4500 SEM (Japan) at 20 kV to measure particle size and shape. Structural analysis of the ANTC was made using an X-ray diffractometer (XRD, Bruker D8 Discover, Germany).

#### Chromatographic analysis procedure

A Nucleodur (100-5 C18, 250 mm × 4 mm) column, acetonitrile–water mobile phase at the ratio of 70:30 (isocratic) and a 20 μL injection loop were used. The temperature of the column oven was kept constant at 25 °C, while mobile phase flow rate was fixed at 1.0 mL/min. Under these conditions, chromatographic retention times for DNB, NB and DCNB peaks were observed at 4.1, 4.6 and 7.2 min, respectively. The detection wavelength for NB, DNB and DCNB was set at 254 nm.

Calibration curves for three target compounds in the solution mixture were obtained in the concentration range of 4.00–0.10 μg/L. The calibration curve equations relate NB, DNB and DCNB peak areas to their concentrations and were used for all further calculations.

#### Removal procedure

A batch procedure was applied for the removal process. Adsorption of NB, DNB and DCNB on ANTC micro-particles was carried out in a solution at 25 °C. In general, 0.400 g of ANTC particles was added to a 25 mL solution mixture of NB, DNB and DCNB (each 2.0 mg/L) without pH adjustment and stirred for 5 min at 200 rpm. ANTC particles were simply separated by passing the sample solution through an ordinary filter paper. The pH of the test solutions did not change during the removal experiments and remained nearly constant at about 6. The removal efficiencies of NB, DNB and DCNB were evaluated by obtaining the areas of the corresponding chromatograms of analytes in the sample solution before and after the separation process using the following equation:

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

where $C_i$ and $C_f$ are initial (before removal) and final (after removal) concentrations of NB, DNB and DCNB in the test solution.

#### Results and discussion

Primary tests showed that natural anthracite (black coal), ANTC, can efficiently adsorb NB, DNB and DCNB without any pretreatment. Due to its high potential for removal of these hazardous pollutants, low cost and local availability, ANTC may be introduced as an efficient and capable adsorbent for removal of such toxic compounds. Fig. 2 shows the HPLC chromatograms of NB, DNB and DCNB.
DCNB before (solid line) and after (dashed line) the removal process.

Characterization of the anthracite adsorbent

The XRD pattern (Fig. 3) with broad reflections in the range of 20–30 °C shows amorphous structure of anthracite. Graphitic structures developed in the anthracite sample (2θ of 26.5, 44.7). XRD profiles show the dominance of disorganized amorphous carbon in the samples.

FT-IR studies used to identify ANTC functional groups and also chemical bonding of those compounds attaching to it. FT-IR spectra (Fig. 4) show characteristic peaks of ANTC, DCNB and DCNB@ANTC. The spectrum of ANTC shows indications of various surface functional groups. The peaks at 1000–1100 cm⁻¹ are assigned to C–O and C–O–C stretching’s and others at 1650–1450 cm⁻¹ are assigned to aromatics C=C stretching. The stretching of C=O at 1640 cm⁻¹ in the anthracite spectra shows the presence of carbonyl groups. Conjugated or disubstituted unsaturated carbon bonds are developed in the samples as suggested by the peaks at 2400–2300 cm⁻¹ [27]. FT-IR spectrum of DCNB indicates the characteristic N=O peaks at 1538 and 1347 cm⁻¹. The pattern of the out-of-plane C–H bending bands in the region of 900–675 cm⁻¹ and the =C–H stretch at 3100–3000 cm⁻¹ are characteristics of this aromatic compound. The peak at 746 cm⁻¹ shows C–Cl stretching of DCNB. The spectrum of DCNB@ANTC shows the characteristic peaks of both ANTC and DCNB are visible which confirms the adsorption of DCNB on ANTC as adsorbent.

Scanning electron microscopy (SEM) was used to observe the surface physical morphology and determine the size of ANTC and DCNB@ANTC particles. Fig. 5A and B shows the structure of ANTC before and after adsorption process.

The physisorption of aromatics on the surface of carbon based adsorbents takes place mainly through dispersive interactions between aromatic molecules and the carbon basal planes. One of the most important adsorption mechanisms involves the interaction between the delocalized π electron of the carbon surface and the free electrons of the rings of aromatic molecule. These dispersive interactions are basically in the form of van der Waals interactions. The heterogeneous oxygen groups attract and localize the electrons of the basal planes, hence, forming partially positive ‘islands’ in the basal planes. On the other hand the functional group attached to the aromatic adsorbate can activate or deactivate the benzene ring to which it is attached. Activating groups act as
electron donors, which create a partially negative benzene ring by
pushing the electrons toward the ring. Deactivating groups attract
the electrons and produce a partially positive ring. Since the
benzene ring has a larger size compared to the functional group,
the interaction of the benzene ring with the surface basal planes is
more effective in the adsorption mechanism [28,29].

Effect of pH

The effect of sample solution pH on the removal efficiency of
NB, DNB, and DCNB was examined. The pH of test solutions (25 mL,
0.250 mg/L of each analyte) was changed in the range of 2–10 using
HCl or NaOH solutions (0.1 M) and then 0.400 g of ANTC was added
to the solution. Results show (Fig. 6) that the removal efficiency
was practically constant in a wide pH range. As the pH of the
original solutions was about 6.0, in further experiments no buffer
was used to adjust the pH of the solution.

Effect of the amount of ANTC on removal efficiency

The amount of ANTC used for the removal of NB, DNB, and DCNB
from contaminated water samples was optimized. As shown
(Fig. 7) the removal efficiency was almost constant for ANTC
amounts more than 0.200 g. In order to remove trace amounts of
NB, DNB, and DCNB efficiently, 0.400 g of ANTC was selected as
optimum amount of adsorbent in the removal process. This
amount shows more than 98% removal efficiency for a 25 mL
solution mixture containing NB, DNB, and DCNB (1.0 mg/L of each).
It must be mentioned that different tests proved that 0.400 g of
ANTC can be used for higher concentrations (up to 10 mg/L) and
can remove more than 95% of all three components from the
solution mixture.

Effect of contact time

Different contact times from 1 to 10 min were investigated for
removal process. Results are shown in Fig. 8. It was found that
contact time of 3 min at stirring speed of 200 rpm was enough for
the effective removal of NB, DNB, and DCNB from 100 mL sample
solutions (2.0 mg/L of each). It must be mentioned that for solution
volumes more than 100 mL longer contact times are needed for
complete removal of NB, DNB, and DCNB with a fixed amount of
ANTC.

Effect of electrolyte concentration

The effect of electrolyte concentration was investigated on the
removal efficiencies of NB, DNB, and DCNB (0.250 mg/L for each
component) from contaminated water by anthracite adsorbent.
Results showed that the concentration of electrolyte had no
effective influence on the removal efficiencies of these organic
pollutants in the concentration range of 0.01–0.10 M of KNO₃. It
seems that the adsorption of NB, DNB, and DCNB by ANTC is
basically a process of strong physical adsorption and various
concentrations of KNO₃ showed no effective influence on removal
efficiency. However, at higher concentrations (>0.1 M) of KNO₃, the
removal rate decreased slightly due to the saturation of active
adsorbent sites by co-existing ions.

Effect of interfering ions

The effects of co-existing ions such as Na⁺, Cl⁻, Al³⁺, CO₂⁻, SO₄²⁻,
SCN⁻, NO₃⁻, HCO₃⁻, Mg²⁺, Mn²⁺, H₂PO₄⁻, C₂O₄²⁻, CH₃COO⁻, and citrate and aromatic compounds including
phenol, benzene, naphthalene, phenanthrene, and anthracene
were investigated using optimum experimental conditions. To
this end the separation and removal of NB, DNB, and DCNB
(0.120 mg/L for each component) from the solution mixture was
performed in the presence of co-existing ions and some
aromatic compounds. The maximum acceptable error was
±5%. Results showed that these species did not interfere with
the removal process even at high concentration ratios (tolerable
concentration ratio >2000 for inorganic ions and phenol, tolerable
concentration ratio >1800 for benzene and tolerable concentra-
tion ratio >40 for naphthalene, phenanthrene, and anthracene)
with respect to NB, DNB, and DCNB.
Adsorption isotherm

The capacity of ANTC used for the removal of NB, DNB and DCNB was examined by measuring the initial and final concentrations of three components in the test solution (pH 6.25 °C and contact time of 30 min) in a batch process. Different test solutions containing NB, DNB and DCNB in the concentration range of 0.10–10 mg/L were examined with a fixed amount of ANTC (0.400 g). Both the Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results showed that the Langmuir model fitted better \((R^2_{NB} = 0.9932, R^2_{DNB} = 0.9914, R^2_{DCNB} = 0.9244)\) than Freundlich model \((R^2_{NB} = 0.9601, R^2_{DNB} = 0.9468, R^2_{DCNB} = 0.8257)\), demonstrating that the adsorption of NB, DNB and DCNB onto ANTC can be considered to be a monolayer adsorption process. This may be due to the formation of a monolayer strong physical adsorption of NB, DNB and DCNB and active sites of ANTC which covers the surface to the formation of a monolayer. This maybe due to the formation of a monolayer strong physical adsorption of NB, DNB and DCNB and active sites of ANTC which covers the surface of adsorbent and no more molecules can be adsorbed on the first layer. The Langmuir isotherm equation was used to describe the relationship between the amount of adsorbed component and its equilibrium concentration in solutions.

\[
\frac{C_e}{q} = \frac{1}{R^2_m} + \frac{C_e}{q_m}
\]

where \(C_e\) (mg/L) is the equilibrium concentration of one of the NB, DNB and DCNB in the solution, \(q\) (mg of adsorbate per g of adsorbent) is the equilibrium adsorption amount of NB, DNB and DCNB, \(q_m\) is the maximum adsorption amount of adsorbate per gram of adsorbent (mg/g) and \(K\) is the Langmuir adsorption equilibrium constant in liter per mg of adsorbate (L/mg).

The linear relationship between \(C_e/q\) and \(C_e\) shows the applicability of the Langmuir model:

NB: \(y = 1.7332x + 0.2349\) \((R^2_{NB} = 0.9932)\)

DNB: \(y = 1.4883x + 0.1285\) \((R^2_{DNB} = 0.9914)\)

DCNB: \(y = 1.1719x + 0.0324\) \((R^2_{DCNB} = 0.9244)\)

The experiments resulted in \(K = 7.38, 11.58\) and \(36.17\) (as Langmuir adsorption equilibrium constant, L/mg) and \(q_m = 0.577, 0.672\) and 0.853 mg/g (as the maximum adsorption amounts of analyte per gram of adsorbent), for NB, DNB and DCNB, respectively (Fig. 9).

Kinetic studies

Different kinetic models were applied to the obtained data from a batch process to evaluate the mechanism of sorption and potential rate determining steps. Rate constants for surface adsorption of NB, DNB and DCNB on ANTC were also determined using the pseudo-first-order rate expression of the Lagergren model and the pseudo-second-order kinetic rate expression of Ho [30]. The integrated form of the Lagergren equation is given by:

\[
\log(q_m - q_e) = \log q_m - \left(\frac{k_1}{2.303}\right)t
\]

where \(q_m\) and \(q_e\) are sorption capacity at equilibrium and at time \(t\), respectively (mg/g). \(k_1\) is the rate constant of pseudo-first-order adsorption. A plot of \(\log(q_m - q_e)\) versus \(t\) should give a linear relationship; \(k_1\) and \(q_m\) can be calculated from the slope and intercept of the plot, respectively.

The pseudo second order kinetic model is represented by the following linear equation:

\[
\frac{t}{q_e} = \frac{1}{k_2 \cdot q_m^2} + \frac{t}{q_m}
\]

where \(q_m, q_e\) and \(t\) have the same meaning as explained above and \(k_2\) is the overall rate constant of pseudo second order sorption (g/mg min). If pseudo-second order kinetics is applicable, the plot of \(t/q_e\) against \(t\) should give a linear relationship; \(q_m\) and \(k_2\) can be determined from the slope and intercept of the plot. An initial sorption rate can be obtained from the pseudo second order linear plots as \(q_e/t\) approaches zero. Kinetic study results are summarized in Table 1. Lagergren plots of \(\log(q_e - q)\) versus \('t'\) were linear showing the applicability of the equation to the adsorption process. In all cases the calculated regressions of determinations for pseudo-second order model were more than 0.99 whiles the regression values were smaller in the case of first order model. Based on the obtained results pseudo-second order model is preferred as the kinetic model.

Reusability

The reusing ability of the adsorbent in several successive adsorption processes was tested. The obtained results (Fig. 10) showed that the anthracite micro particles can be reused for three times without a considerable loss in their adsorption efficiency. The removal efficiency of ANTC is higher than 95% for NB, DNB and

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Results obtained from a kinetic study on the removal process.</th>
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<tbody>
<tr>
<td>Kinetic model</td>
<td>Fitted parameters</td>
</tr>
<tr>
<td>Pseudo first order (NB)</td>
<td>(k_1 = 0.26), (k_2 = 0.7830)</td>
</tr>
<tr>
<td>Pseudo first order (NB)</td>
<td>(k_1 = 0.27), (k_2 = 0.7951)</td>
</tr>
<tr>
<td>Pseudo second order (NB)</td>
<td>(k_1 = 2.278), (k_2 = 0.9987)</td>
</tr>
<tr>
<td>Pseudo second order (NB)</td>
<td>(k_1 = 2.3510), (k_2 = 0.9965)</td>
</tr>
<tr>
<td>Pseudo first order (DNB)</td>
<td>(k_1 = 0.13), (k_2 = 0.8570)</td>
</tr>
<tr>
<td>Pseudo first order (DNB)</td>
<td>(k_1 = 0.14), (k_2 = 0.8634)</td>
</tr>
<tr>
<td>Pseudo second order (DNB)</td>
<td>(k_1 = 3.44), (k_2 = 0.9999)</td>
</tr>
<tr>
<td>Pseudo second order (DNB)</td>
<td>(k_1 = 3.52), (k_2 = 0.8984)</td>
</tr>
<tr>
<td>Pseudo first order (DCNB)</td>
<td>(k_1 = 0.11), (k_2 = 0.6172)</td>
</tr>
<tr>
<td>Pseudo first order (DCNB)</td>
<td>(k_1 = 0.12), (k_2 = 0.6534)</td>
</tr>
<tr>
<td>Pseudo second order (DCNB)</td>
<td>(k_1 = 15.87), (k_2 = 0.9998)</td>
</tr>
</tbody>
</table>
DCNB in three successive using of used adsorbent. The results show high potential adsorption capacity of ANTC for the removal of such hazardous materials from water samples.

**The effect of solution volume on NB, DNB and DCNB removal**

The maximum applicable sample solution volume was determined by increasing the dilution of the, DNB and DCNB sample solutions, while keeping the total weight fixed at 150 µg for sum of, DNB and DCNB. Different feed volumes between 5 and 200 mL were tested. The obtained results showed that the removal of target analytes was quantitative up to 100 mL of sample volume (removal ≥90%). In more diluted solutions up to 200 mL the removal of DNB and DCNB was more than 90%, but the removal of NB decreased due to its high solubility in water (1900 mg/L) [14].

**Loading capacity**

The loading capacity of adsorbent was determined under optimized conditions (pH = 6, 25 °C, stirring speed = 200 rpm) by batch method. The adsorbent (0.100 g of ANTC) was added to a 25 mL solution containing 4 mg/L of each of NB, DNB and DCNB and was stirred at 200 rpm for 30 min. The removal percentage and adsorbed amount of NB, DNB and DCNB were determined by HPLC measurement of the sample solution before and after the removing process. The loading capacity (0.577, 0.672 and 0.853 mg/g for NB, DNB and DCNB, respectively) of ANTC adsorbent was determined to be 2.10 mg/g for the analytes mixture.

**Analysis of industrial water samples**

To determine the ability of the proposed method for the removal of NB, DNB and DCNB in a real sample, wastewater of Bandare-Imam petrochemical aromatic unit (Mahshahr, South-west of Iran) was tested and spiked. The real samples were filtered for removal of suspended particles. A 10 mL portion of wastewater and 5 mL of 5 µg/L of NB, DNB and DCNB solution was transferred into a 25 mL volumetric flask and diluted to the mark with distilled water. The solution (final spiked concentrations of 1.00 mg/L of each analyte) was transferred to a beaker containing 0.400 g of ANTC and stirred for 3 min at 200 rpm. HPLC analysis showed that the wastewater is contaminated by about 12 mg/L of NB. Excellent removal efficiencies (Table 2) indicated that the matrix of wastewater sample did not interfere with the proposed removal process.


