

Adsorption of some toxic heavy metals from aqueous solutions by activated petroleum coke

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ABSTRACT: Emission of heavy metals in ground and surface waters can pose serious environmental problems affecting both human and wild life. For treatment and decontamination of polluted water, several chemical and physical techniques are available of which adsorption is one of the most efficient and widely used. In this paper the adsorption of some heavy metal ions from aqueous solutions by activated petroleum coke was investigated. Several adsorption parameters were considered including the diameter of the metallic ions, coke dosage, initial concentration of the metallic ions in solution, contact time, pH of solution and temperature. The adsorption mechanism was best described using the second order model. It was concluded that activated petcoke may be efficiently used for the removal of heavy metals from aqueous solutions.

KEYWORDS: Heavy metals, adsorption, activated petcoke, water treatment.

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I. INTRODUCTION

Pollution of water resources is an unwelcome byproduct of modern industry, and the days when one could safely drink from a flowing stream or river are long gone. Water, being a good solvent, is easily polluted and water pollutants may include a wide variety of materials including suspended particles, fungi, algae, oil products, immiscible liquids and heavy metals. Pollution of water resources by toxic heavy metals in particular may be a serious environmental problem that can have grave consequences on both human and wild life. It is estimated that the concentration of lead in water resources has doubled since the Industrial Revolution. According to the statistics of the World Health Organisation (WHO), lead poisoning led to the death of some 143,000 people in 2013 with further 600,000 lead-related afflictions among children in particular.

The term "Heavy metals" may have been first used by the German chemist Leopold Gmelin in 1817 when he divided the chemical elements into heavy metals, light metals and non-metals. The definition of heavy metals, however, may vary depending on the particular field of study. As a practical definition, heavy metals may be defined as metals with a density greater than 5 g/cm³. Toxic heavy metals, on the other hand, are heavy metals with known toxic effects such as lead, cadmium, arsenic, copper and other elements included in the lists of high-priority pollutants as published by such organisations as the U.S. Environmental Protection Agency and the World Health Organisation. The toxic effects of some of these heavy metals such as lead and copper have been known for a long time.

Treatment of polluted and industrial wastewater has become a major concern of governments and research institutions. Several water treatment techniques have been utilized including sweetening, precipitation, sedimentation, coagulation and flocculation, reverse osmosis, ion exchange and adsorption [1-5]. Of such diverse processes and techniques, adsorption remains one of the most important and widely-used. This is mainly due to its simplicity, efficiency and economic viability. In addition, pollutants which are not biodegradable such as heavy metals may be adsorbed and removed from waste and polluted waters.

Adsorption, as is generally known, may be either chemical or physical. In physical adsorption, the adsorbate particles are weakly bonded to the surface of the adsorbent by electrostatic and Van der Waals forces which are easily reversible. In chemical adsorption, on the other hand, the adsorbate particles react chemically with the adsorbent and this is not easily reversible. Physical and chemical adsorptions may be further differentiated by the number of adsorbed layers and the heat of adsorption. A single layer of adsorbate particles is generally formed on the surface of the adsorbent in chemical adsorption while physical adsorption may be

multi-layered. The heat of adsorption is generally less than 80 kJ/mol in physical adsorption, which is an exothermic process, and greater than 80 kJ/mol in chemical adsorption.

Among the several possible adsorbents that may be used for the removal of heavy metals from wastewater, activated carbon is preferably used because of its efficiency, availability and its large surface area [6, 7]. Activated carbon may also be produced from many different easily-available materials including coal, chars, agricultural waste products and petroleum coke. Previous work demonstrated the feasibility and advantages of utilizing activated petroleum coke for the removal of several pollutants from water such as organic compounds and petroleum products [8]. Activated petcoke was also used for the treatment of natural gas and removal of acid gases [22]. In this work, activated petroleum coke was successfully used for the treatment and removal of some heavy metals from aqueous solutions.

Petroleum Coke

The coke used in this work is a product of the delayed coking process at the Homs Oil Refinery. Study of the different types of petroleum coke indicates that the porous sponge coke is most suited for activation and production of activated carbon suitable for adsorption purposes [1, 9]. Previous work shows that the adsorption efficiency of sponge coke may be doubled as a result of activation [10].

Sponge coke is a coherent, dull black porous delayed petroleum coke in which the individual spheres are not apparent and the coke has a continuum of structure [11]. Sponge coke is characterized by a low oxygen content (1.7%) compared to other types of coke, where the oxygen content may be as high as 3% [9].

The coke samples were first crushed so that 95% of the coke passed through a 4-mm sieve. The samples were then weighed and spread on a drying floor to a depth of 8 mm and left to dry until the loss in weight of the total samples was not more than 0.1% per hour. After the determination of the moisture content (As-received basis) the coke samples were pulverised to pass a 250- μ m sieve. Proximate and ultimate analysis tests were carried out on the samples using standard ASTM test methods. Results of the proximate and ultimate analyses of the coke samples are given in Table 1.

Table 1. Analysis of the porous sponge coke

(1) Proximate analysis, air-dried basis

Ash (wt. %)	0.2
Moisture (wt. %)	0.3
Fixed carbon (Wt. %)	0.9
Volatile matter (Wt. %)	12.5
Sulphur (Wt. %)	7.7
Gross calorific value (kJ/kg)	34.8×10^3
Real density (g/cm^3)	1.40

(2) Ultimate analysis, Dry, ash-free basis

Carbon	84.9
Hydrogen	4.6
Nitrogen	1.1
Oxygen	1.7
Sulphur	7.7
Carbon to hydrogen ratio (Wt.)	18.5

Activated petroleum coke

There are two basic methods for coke activation, namely thermal activation using steam [1] and chemical activation. Both methods may be used for activation of petroleum coke and increasing its surface area and porosity. The two methods differ, however, in the size of the pores produced, where chemical activation increases for the most part micropores (with diameters less than 2 nanometers) whereas thermal activation increases larger-size pores. It was suggested by some researchers that this difference may be explained by the gaseous products of chemical activation which tend to increase porosity [12].

For the present work, the physical activation process was used. This process is generally preferred as it does not involve the use of chemicals. Coke activation was carried out by heating the coke sample for six hours in an electric oven in an atmosphere of steam to a high temperature (1200k), with nitrogen as carrier gas. Residence time of six hours is the optimum residence time as indicated in the relevant literature [13]. Temperatures higher than about 1225 K leads to a reduction of the resulting surface area [30]. Activation by steam at elevated temperatures leads to the enlargement of micropores and formation of mesopores [14].

After activation the coke sample was left to cool in the oven in an atmosphere of nitrogen. After removal from the oven, the coke was dried at room temperature, crushed and passed through a 2 cm sieve to

remove the larger coke pieces and the remainder was passed through a 6 mm sieve and the fine powder discarded. The surface area of the activated coke was then measured. It was found to vary between 788-879 m²/g. Activation also lead to some sulphur removal to the amount of 34%.

Aqueous solutions of the metallic ions

Aqueous solutions were prepared for each of the metallic ions selected for this study which are lead, cadmium, copper, nickel and chromium. This was done by dissolving the relevant respective chemicals in distilled water, namely Pb(NO₃)₂, Cd(NO₃)₂·4H₂O, Cu(NO₃)₂·6H₂O, Ni(NO₃)₂·12H₂O and CrN₃O₉·9H₂O. Different concentrations were obtained by diluting with distilled water. A mixed-ion solution was also prepared in order to investigate the mutual effects of the different ions on adsorption and to simulate industrial wastewater in which different ions are to be found. This procedure was chosen in lieu of using actual industrial wastewater because it enables the study of the adsorption of each ion at different concentrations, something which may not be possible with actual industrial wastewater. The pH of the solutions was controlled at the desired value by the dropwise addition of 0.1 M HNO₃ or 0.1 M NaOH.

Adsorption tests

Adsorption tests were carried out in a batch process in which five reactors were used, one reactor for each of the metallic ion solutions, namely lead, cadmium, copper, nickel and chromium. In each reactor, a measured quantity of the activated coke was used. Water was circulated in a closed circuit around the five reactors and through a thermostat in order to regulate the adsorption temperature in the five reactors as shown in Fig. 1. This procedure was chosen because it makes it possible to control the different adsorption parameters.

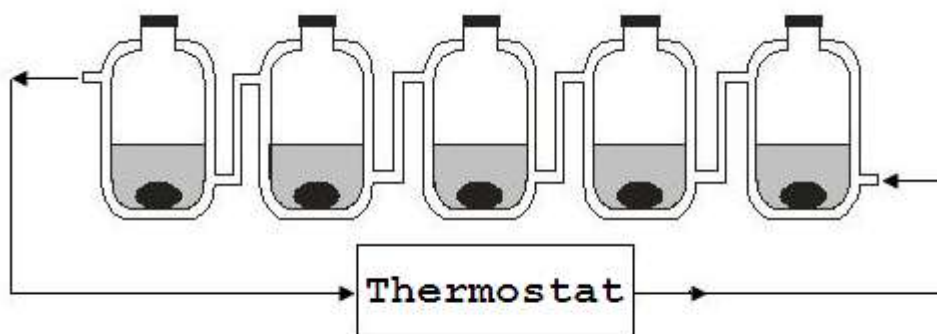


Fig. 1

II. RESULTS AND DISCUSSION

Adsorption of heavy metals from aqueous solutions is expected to be a complex process that is dependent on a number of variables related to the properties of the adsorbent and adsorbates as well as on the adsorption conditions. The adsorbent properties include its porous structure, surface area, the functional groups on its surface and its dosage. The properties of the adsorbates relevant to their adsorption include their solubility and ionic diameter. The adsorption conditions include the temperature of the solution, its pH, contact time and the initial concentration of the metallic ions. Table 1 shows the range of the adsorption variables used in this work.

Table 1. Range of adsorption variables

Variable	Range	Optimum value
pH	1 - 8	6
Contact time	5 - 300 min.	Variable
Initial concentration of the metallic ion	1 - 200 mg/l	
Temperature	0 - 30°C	29°C
Weight of coke for 25 ml of solution		0.5 g

Adsorption efficiency was calculated for each metallic ion using the following equation:

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right)$$

The adsorption capacity of the adsorbent coke (q mg/g) was calculated using the following equation:

$$q = \frac{(C_i - C_e) V}{W}$$

Where:

C_i = Initial concentration of the metallic ion (mg/l).

C_e = Equilibrium concentration (mg/l).

V = Volume of solution (l).

W = Weight of adsorbent (g).

Effect of coke dosage

The coke dosage used was 0.5 g for 25 ml of the aqueous solution (Table 1). The adsorption tests carried out indicate that the adsorption capacity increases with increasing coke dosage up to an optimum value (Fig.2), after which increasing the coke dosage leads to a reduction of the adsorption capacity due to the overconcentration of the adsorbate particles on the available adsorption sites [15, 16]. This result is in general agreement with results reported in the literature for different adsorbents [17, 18].

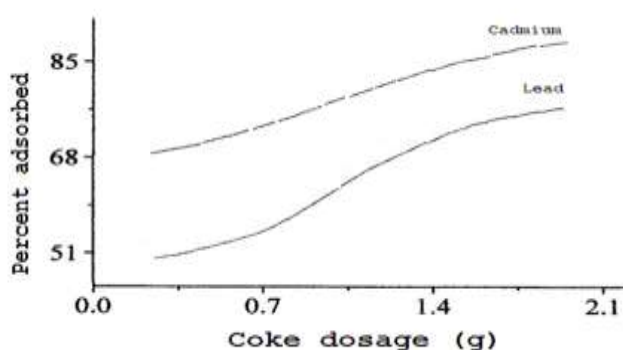


Fig.2. Effect of coke dosage on adsorption capacity

Effect of metallic ion diameter

The adsorption tests conducted showed clearly the effect of the metallic ion diameter on the adsorption capacity, with the smaller diameter ions being easier to adsorb than the larger diameter ions. The efficiency of adsorption of the five elements considered decreased with increased ion diameter in the following order: chromium > nickel > copper > cadmium > lead (Fig. 3 & 4). The ion diameters of the five elements are as follows: Chromium (0.54 Å), copper (0.69 Å), nickel (0.72 Å), cadmium (0.97 Å), lead (1.19 Å).

The ion diameter, however, is not the only factor that affects the adsorption efficiency and this may affect the order of the ions' adsorption. Other factors related to the nature of the metallic ions include the hydration energy [19, 20] and electronegativity [21]. Furthermore, the nature and characteristics of the adsorbent also affect the order of the efficiency of adsorption. For these reasons, the order of the adsorption efficiency does not follow strictly the order of ion diameters. In our tests, the efficiency of adsorption of nickel ions was slightly better than the adsorption efficiency of copper ions although the diameter of the copper ions is slightly smaller than the diameter of the nickel ion. Other researchers found varying orders of metallic ions adsorption depending on the nature of the adsorbent used (Table 2).

Table 2. Order of adsorption efficiency of heavy metals

Order of elements	Adsorbent	Ref.
Nickel > Copper > Cadmium > lead	Petroleum coke	Present work
Copper > lead > Cadmium > nickel	Olive stones	19
Copper > nickel > lead	Carbon cloth	22
Cadmium > copper > nickel	Carbon nanotubes	20
Lead > cadmium > nickel	Peanut husks	23
Lead > copper > cadmium	Bamboo carbon	24
Copper > cadmium	Tannic acid	21

Effect of solution pH

Solution pH is one of the most important factors that affect the adsorption efficiency [19, 25, 26]. This is most probably due to the fact that hydrogen ions would compete with the metallic ions for the active sites on the surface of the adsorbent. Extreme pH values may, however, adversely affect the structure of the adsorbent [27]. Previous work indicates that in most cases there is an optimum pH value in the range of 4.5-6, or 5 on average. In the present work the optimum pH value for the separate ion solutions was in the range 4-6 (Fig.3) and a

similar value was found for the mixed solution (Fig. 4). A similar result was also found in the case of the adsorption of organic compounds from aqueous solutions by activated petroleum coke [8].

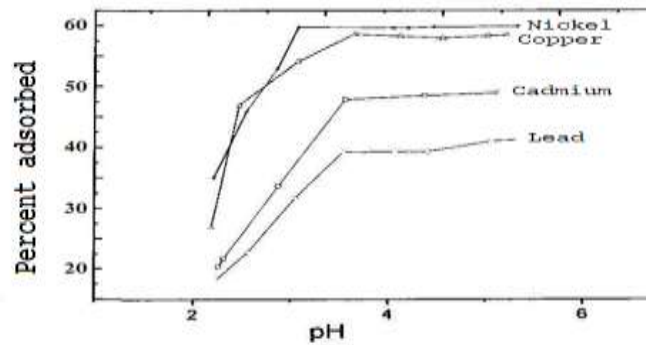


Fig. 3. Effect of solution pH on the adsorption efficiency for separate metallic ion solutions

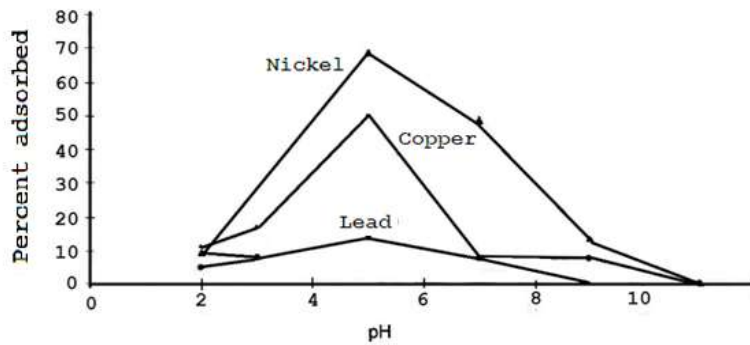


Fig.4. effect of solution pH on the adsorption efficiency for mixed ion solution

Effect of the initial concentration of the metallic ions

The adsorption tests were carried out using a specific coke dosage with 25 ml of the solution of each metallic ion at different initial concentrations of the metallic ions (10-100 mg/L) and at the optimum pH. The adsorption capacity at equilibrium q (mg/g) was calculated using the following equation:

$$q_e = V (C_0 - C_e) / m$$

where:

q_e = Adsorption capacity at equilibrium (mg of the metallic ion/g of adsorbent)

C_0 = Initial concentration of the metallic ion (mg/L).

C_e = Equilibrium concentration of the metallic ion (mg/L).

V = Volume of the metallic ion solution (L).

m = Mass of adsorbent (g).

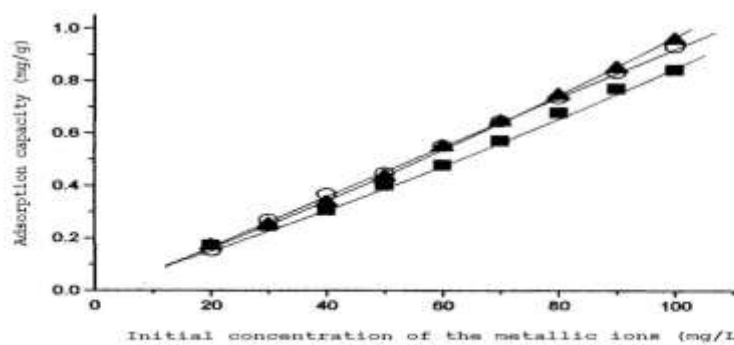


Fig. 5. Effect of the initial concentration of the metallic ions on the adsorption capacity.

The results are shown in Fig. 5, which indicates clearly that increasing the initial concentration of the metallic ions leads to increased adsorption capacity. This is an expected result, as increasing the initial concentration leads to greater availability of the metallic ions at the adsorption sites [27, 28].

Effect of contact time

The test results showed that increasing the contact time up to an optimum value increases the percent adsorbed (Figs 6-7). The optimum contact time was about 140 minutes for cadmium and 40 minutes for the other metallic ions. This difference between cadmium and the other heavy metals is related to the hydration energy which is inversely related to the adsorption capacity; the hydration energy being greater for cadmium than for the other metals [29].

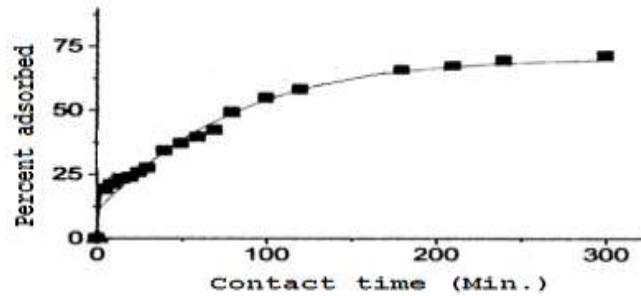


Fig. 6. Effect of contact time on the adsorption of cadmium ions

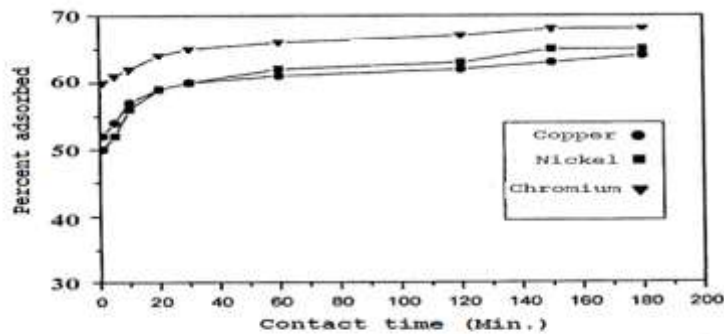


Fig. 7. Effect of contact time on the adsorption of metallic ions

Effect of temperature

Temperature is an important adsorption parameter. In physical adsorption generally, adsorption capacity decreases with increasing temperature. Fig. 8 shows that adsorption percent increase with increasing temperature up to a temperature of 29°C, but raising the temperature after that leads to a decrease of adsorption which indicates clearly an exothermic adsorption process.

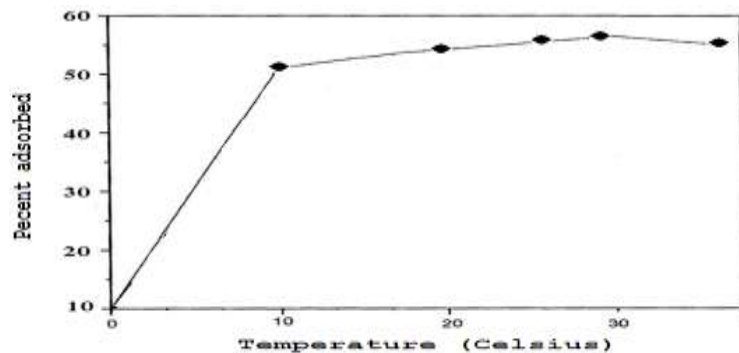


Fig. 8. Effect of temperature on the adsorption of copper ions

Adsorption mechanism

Previous work indicates that the second order model best describes the physical adsorption mechanism. This is represented by the following equation:

$$\frac{d}{dt} q_t = k_2 (q_e - q_t)^2$$

Where:

q_e = Adsorption capacity at equilibrium (mg/g).

q_t = Adsorption capacity at time t (mg/g).

K_2 = Equilibrium constant for second-order adsorption process (g/mg. min).

Integrating between the two border conditions:

$q_t = 0$ at $t = 0$

$q_t = q_t$ at $t = t$

and rearranging we finally get:

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

The results obtained for copper ions are in agreement with results obtained by other researchers [27] (Fig. 9).

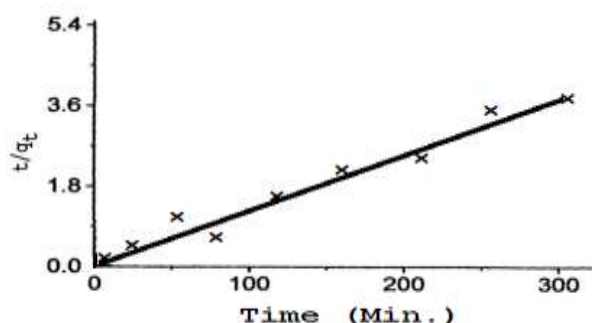


Fig. 9. Adsorption curve

III. CONCLUSION

Activated petcoke may be efficiently used for the removal of heavy metals from aqueous solutions. The coke was activated by a physical activation process. The metallic ions investigated were lead, cadmium, copper, nickel and chromium. The optimal conditions for efficient adsorption of these metallic ions were related to the aqueous solution properties (pH and initial ion concentration), properties of the metallic ions (chiefly ionic diameter) and adsorption conditions (temperature and contact time). The adsorption mechanism was best described using the second order model.

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