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Chapter

Adsorption Configurations of 2-Chlorophenols on Colloidal Silica

Lakmal Jayarathna, Nelum Karunathilake, Athula Bandara and Rohan Weerasooriya

Abstract

Chlorophenol (CP) is the organic-chloride compound which widely used as pesticides. Industrialization and modern agriculture release a vast amount of chlorophenol to the environment. Adsorption behavior and retention of chlorophenol in the environment still not cleared. Interaction of 2-chlorophenol (2-CP) with silica surface was investigated with different reaction conditions. The study was conformed that outer-sphere complexation of 2-CP with silica surface and different surface speciation was observed at different pH conditions. Maximum adsorption (1.5×10^{-8} mol m^{-2}) was observed around neutral pH conditions. 2-CP adsorption on silica surface followed the first order kinetics, and it indicates multilayer formation through capillary condensation. FTIR spectral analysis reveals the formation of a bidentate complex on the silica surface with 2-CP.

Keywords: adsorption, chlorophenol, complexation, FTIR, silica

1. Introduction

Industrialization and sophisticated agricultural techniques discharge many chlorinated compounds into the environment as primary organic pollutants [1]. Chlorophenols (CP) is designated as the most toxic organic pollutants in the list of hazardous wastes since these have a strong resistance to physical, chemical, or biological treatments [2, 3]. CPs have been used in agriculture, industry, and public health since 1920s [2]. Uses of malathion introduce 2-chlorophenol (2-CP) to the environment as one of the main toxic organic pollutant [4, 5].

2-CP is toxic, resistant to microbial attack, and accumulates in the food chain even from chlorophenol treated materials [6]. Accidental spillage, misuse, and improper disposal have resulted in ground water pollution [6, 7].

2-CP is lethal to a variety of organisms at the level of 1 mg dm^{-3} [8]. Direct exposure of 2-CP is fatal, and the long term exposure of 2-CP may cause cancers and affect the function of the liver and immune system [3].

Although the production and the use of these are banned in some countries, chlorophenols are found in many parts of the world due to abundant usage and their environmental transportation. Owing to the toxicity and persistence of chlorophenol the controlling its levels and reducing the diffusion in the environment

is necessary. In literature, the standard concentration levels for chlorophenols in industrial effluent and waters is set to 2 and 0.1 $\mu g\ L^{-1}$, respectively [9].

The fate and the diffusion of CPs depend on the neutral and ionic forms (speciation) of them. pH value of the aqueous phase governs the partition of the CP between different environments. Neutral form of CPs exhibit low solubility in water and high sorption capacity in soils, whereas the ionic form of CPs enhances the solubility in water and mobility in aqueous phase [10].

Adsorption is the major technique used for the removal or reduction of chlorinated compounds. Clays have been widely used as adsorbent due to their high specific surface area [10]. There are several reports appeared in the literature on the usage of different clay minerals as an absorbent for the removal of chlorinated pollutants [11]. These studies have proven to be very useful in describing the macroscopic nature of adsorption and adsorption kinetics. *In-situ* spectroscopic measurements further provide information on the adsorbate configurations and possible intermediates involved in some surface mediated reactions [12]. The stability of adsorbate's configuration and intermediates depends on numerous factors such as the structure of the surface and a complex formed, the coordination number of the metal atom in the complex, the thermodynamic equilibrium constant of the reaction, pH of the medium, etc. [13].

Surface properties of the adsorbents play central role in the adsorption process. The porosity of the surface and functional groups present on the surface are the main factors that govern the adsorption process [14, 15]. The efficiency of the clay mineral in the adsorption has been thoroughly investigated by several researchers [16]. Functional groups present in the organic compounds or the charge of the metal ions interest favorably with the specific properties of the mineral to enhance the adsorption. The adsorption process is influenced by many factors such as the chemical form of the adsorbate, solution pH, time of contact, adsorbate concentration, the amount of adsorbent, particle size, presence of competing adsorbates and others [17, 18].

Adsorption is one complex process involves in clay minerals with the association of contaminants. It is a mass transfer process from the aqueous phase to the solid phase accompanied by chemical and physical forces [19]. Physical characteristics of clay minerals are the governing factors in the adsorption process. Silica is reported as popular model adsorbent in the adsorption studies as it is the major constituent of natural clays by restricting the adsorption on one component. Low cost, non-toxicity, and the structural arrangements of them favor the adsorption of toxic contaminants. Silica is used as a model of soil adsorbent due to prevalence in the environment and well-characterized surface properties. The surface area of silica is an essential factor because the extent of the available surface is correlated with the surface reactivity [20].

The objective of this research is to investigate the adsorption behavior and configurations of 2-CP with silica surface using UV-visible and FT-IR spectroscopic methods.

2. Materials and methods

Colloidal silica was obtained from Fluka (Switzerland). All the other chemicals were purchased from Sigma Aldrich. Stock solutions of 2-CP and 20 g dm^{-3} suspension of silica were prepared in deionized water. The suspension was stirred for 12 hours for equilibrating. The ionic strength of the suspensions was varied in the range of 0.0001–0.01 mol dm^{-3} using 0.10 mol dm^{-3} NaNO$_3$ solutions. All experiments were repeated for silicate suspensions with different ionic strength conditions.

An aliquot of silica suspensions was pipetted out to Duran 100 mL sealed type laboratory glass bottle and initial solution pH values were adjusted in the pH range from 2 to 12. Known amount of 2-CP was added to silicate suspensions. Then the system was sealed and was stirred for 1 hour. The final concentration of 2-CP was determined. The effect of the initial concentration of 2-CP and effect of contact time was studied.

The treated solid silica sample was recovered after the centrifugation and used for the FT-IR measurements after subsequent dying for appropriate times to eliminate water from samples. FT-IR measurements were carried out using JASCO FT-IR 410 spectrometer.

3. Results and discussion

3.1 Effect of pH and ionic strength

Variation of the adsorption density with pH is shown in the **Figure 1**. Similar pattern was observed at different ionic strength conditions.

When examining the values of initial and final pH, initial pH was higher than the final pH after adsorption under acidic condition and vice-versa under basic condition. Therefore, it will predict the different types of surface interactions between 2-CP and hydroxyl groups present on silica which are responsible for the changing in solution pH due to the adsorption process [20–22].

Under the acidic conditions, 2-CP interacts with surface silanol groups releasing $-H_2O$ molecule to the medium resulting increase the final pH [20]. Surface interactions between 2-CP and silanol groups in the acidic condition are shown in **Scheme 1**.

The surface interactions between silanols and 2-CP under basic conditions are shown in **Scheme 2**. Decrease of final solution pH is due to the releasing of $-HCl$ molecule to the medium by forming a bi-dentate diphenolate complex. This observation further conformed by spectroscopic studies.
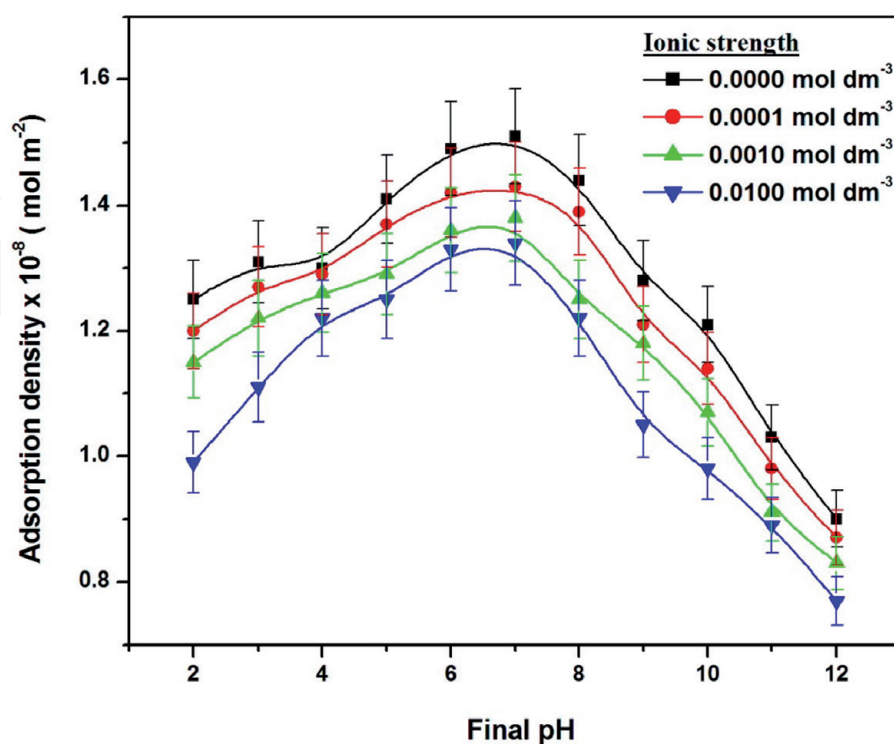
Figure 1.
Adsorption density of 2-CP as a function of initial pH with different background ionic strength conditions with NaNO₃.
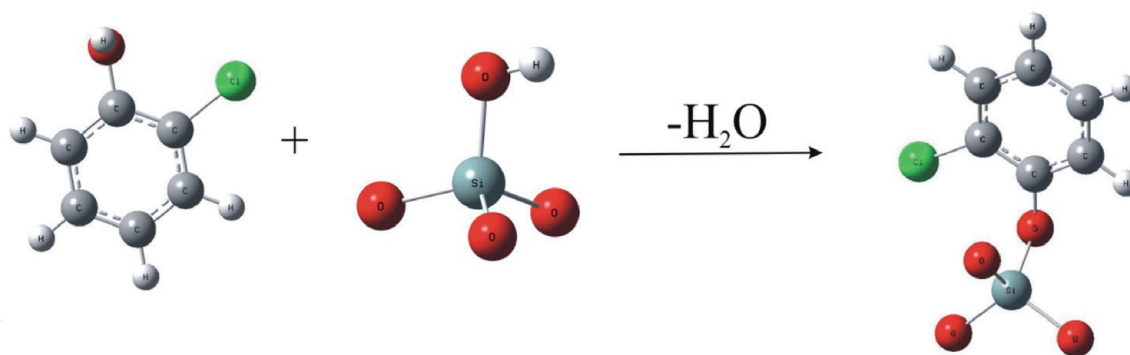
Scheme 1.
Proposed surface complexation of 2-CP with silica surface at acidic conditions.
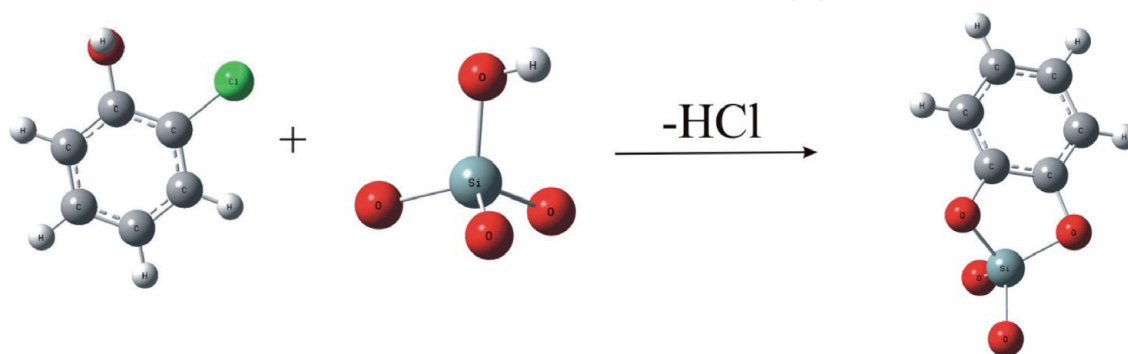
Scheme 2.
Proposed surface complexation of 2-CP with silica surface at basic conditions.

According to **Figure 1**, the adsorption density increased significantly from pH 2 to 7 and then decreased gradually solution pH up to 12. The maximum adsorption capacity was observed around pH 7.

Experimental results revealed that surface charge of the species present in the system at different pH conditions governs the surface interactions between the silica and adsorbate, resulting in variation in adsorption densities [23]. Further, the important parameters such as dissociation constant and the point of zero charges of adsorbent affect the adsorption amount [18]. Point of zero charge (pH_{ZPC}) of silica is 3.5 [24]. Surface charge of silica is positive below the pH_{ZPC} and negative above the pH_{ZPC}. Dissociation constant (pK_a) of 2-CP is 8.10 [25–27].

According to the pK_a value, 2-CP dissociated into negative charge ions over the pH range of 9–12, and it remains as neutral molecule in the pH range of 2–7.8. Further, most of the silanol groups were neutral around pH 6. Dominant silanol groups were positively charged in the pH range of 2–3 and negatively charged in the pH range of 8–12.

The dissociation of 2-CP showed a negative effect on the adsorption mechanism due to the repulsive forces between negatively charged silanol groups and 2-CP ion. Therefore, the adsorption amount was low in the pH range of 10–12. Surface interactions between the less number of undissociated 2-CP and silica molecules showed a significant amount of adsorption even under the extreme acidic and basic conditions. However, the adsorption density was higher in the acidic region than in the alkaline area because the surface interactions were feasible due to the absence of molecules. Favorable surface interactions between neutral 2-CP and silanol groups showed a higher amount of adsorption density around pH 6 [28].

Furthermore, according to **Figure 1**, it shows that adsorption density was inversely proportional to the ionic strength of the medium. Effect of ionic strength on the adsorption process indicated that adsorption on to variable charge mineral surfaces could form outer-sphere complexes via electrostatic interactions [20, 29].

Outer-sphere complexation is sensitive to the changes of ionic strength due to the competition with counter ions in the background electrolytes [30]. Competition between counter ions and adsorbate was more significant at higher ionic strength conditions than at lower ionic strength conditions. These facts prove the formation of outer-sphere complexes upon the adsorption of 2-CP on silica [30].

3.2 FTIR investigation

Adsorption configuration between surface silanols groups and 2-CP at different pH conditions further confirmed by FT-IR spectral studies. **Figure 2(a)** shows the FT-IR spectra of untreated silica along with the adsorbed 2-CP at different solution pH conditions. Spectrum is divided into two parts of 500–1800 cm^{-1}, and 2800–4000 cm^{-1} for simplicity as no bands were observed between 1800 and 2800 cm^{-1}. The spectrum of untreated silica is shown in line (A).

In the spectrum A, the bands for Si-OH bending modes at ~1080–1270 cm^{-1}, Si-OH deformation mode at ~811 cm^{-1} and Si-O stretching mode at ~915 cm^{-1} were observed. In addition to these characteristic bands, a band appeared at ~1637 cm^{-1} could be attributed to the H-O-H bending vibration of physically adsorbed water as the broad band further supports this at ~3475 cm^{-1} [21, 31]. The band at 3743 cm^{-1} is typical for isolated O-H stretching vibration, and it indicates that the presence of isolated OH groups on the surface [32]. It was observed that the adsorption of 2-CP onto silica surface influence the IR spectrum of the untreated silica. For better comparison, IR spectra of silica surface treated with 2-CP at pH 5 and 9 are shown in lines (B) and (C), respectively, in **Figure 2(a)**. These spectra were measured after 3 hour equilibration time of the silica with 2-CP at respective pH. Upon adsorption of 2-CP, new bands appeared at 1280, 1482 and ~3030–3070 cm^{-1} with an observation of complete disappearance of the isolated O-H groups at 3743 cm^{-1} while all the other bands of untreated silica showed significant losses in their intensities. These observations suggest that the 2-CP chemisorbed on the surface [33, 34]. This behavior of chemisorption is further explained in **Figure 2(b)** where the difference
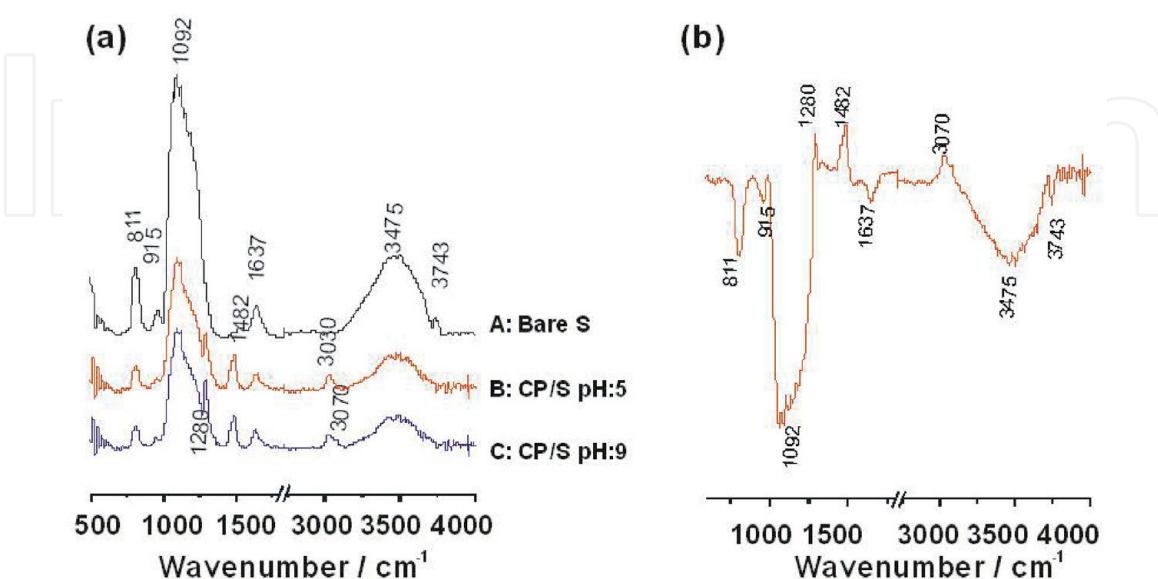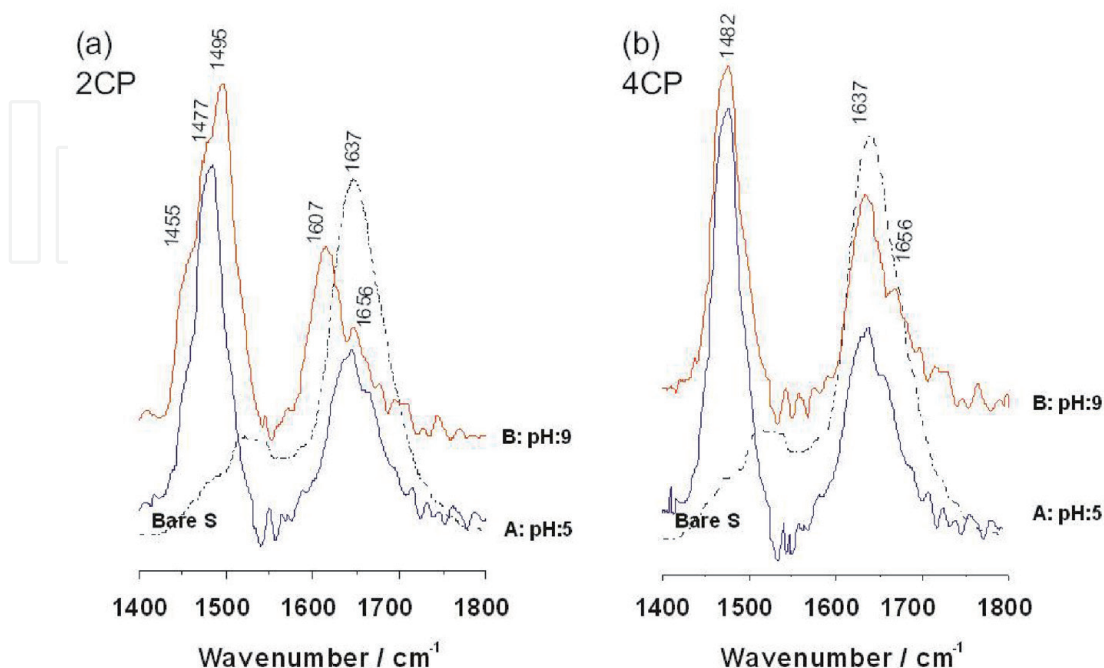

Figure 2.
(a) FTIR spectra of (A) bare silica, (B) silica treated with 2-CP at pH 5 and (C) silica treated with 2-CP at pH 9. The bare silica samples prepare at pH 5 and 9 gave coincident spectra. All the spectra are plotted in the same scale for direct comparison. Scale is broken between 1800 and 2750 cm^{-1} as no bands were observed in the region. (b) Difference spectrum at pH 9. The positive bands are characteristic for 2-CP on the surface while negative bands indicate the loss of surface sites due to chemisorption of 2-CP.

spectrum (2-CP adsorbed—bare silica) is depicted. Negative bands at ~811, 915, 1270, 1637, 3475 and 3743 cm^{-1} suggest the loss of original nature of Si-O(H) moieties upon adsorption of 2-CP while the positive bands appeared at ~1280, 1482 and 3070 cm^{-1} clearly shows the presence of 2-CP on the surface [21]. The disappearance of 3743 cm^{-1} bands indicated that the isolated hydroxyl groups are one of the major adsorption sites for 2-CP. Reduced intensities of other characteristic bands of silica further suggest the interaction of 2-CP with the surface. The new bands appeared at 1280, 1482 and 3050 cm^{-1} are assigned to the C-O stretching, C=C stretching of the benzene ring, and aromatic C-H stretching modes, respectively, of 2-CP [31]. It should note here that the 1280 cm^{-1} band appeared at pH 9 is more intense compared to that observed at pH 5 even though the amount adsorbed (64%) was lesser than that observed at pH 5 (74%) [33, 34].

The IR observations can further explain the variation of solution pH with the adsorption. **Figure 3(a)** shows the results in the 1400–1800 cm^{-1} region for the untreated (bare: dash-dot line) silica, and silica treated with 2-CP at pH 5 (line A) and 9 (line B).

As described earlier, the intensity of the band due to H-O-H bending mode of silica at 1637 cm^{-1} decreased in intensity and shifted to around 1630 cm^{-1} upon adsorption of 2-CP in both cases. When the pH of the medium was 9, the band at 1637 cm^{-1} lost its intensity with the appearance of a new band at 1607 cm^{-1}. Also, a clear change was observed in the band at ~1482 cm^{-1}. A new band appeared at 1495 cm^{-1} with a remaining shoulder at ~1477 cm^{-1} and a second shoulder at ~1452 cm^{-1} was observed. These observations suggest that different type of bonding species are involved in these two pH conditions. The new band appeared at 1495 cm^{-1} along with the shift in the band at 1637–1607 cm^{-1} reveal the formation of catechol type intermediate [35, 36]. The bands at 1495 cm^{-1} can be attributed to the C-C stretch of the above catechol type intermediate and that the appearance of strong band at 1280 cm^{-1} (**Figure 2**, line C) might indicate the presence of more-oriented C-O bonding in the same species of the above. The shift in 1482 cm^{-1} band

Figure 3.
FTIR spectra in 1400–1800 cm^{-1} region (a) 2-CP and (b) 4-CP, bare silica: dashed-dot line, (A) silica treated with 2 and 4 CP at pH 5 and (B) silica treated with 2 and 4 CPs at pH 9. The bare silica samples prepare at pH 5 and 9 gave coincident spectra. All the spectra are plotted in the same scale for direct comparison.

to 1477 cm^{-1} and another shoulder peak at ~455 cm^{-1} indicate the changes in the electronic environment of the benzene ring due to the formation of catechol intermediate in which that can be in bi-dentate or bridging configuration to the silica surface. The experiments done with 4-CP further confirmed the formation of this intermediate and the results are shown in **Figure 3(b)**. The adsorption of 4-CPon silica at different pHs showed quite similar spectra and the bands at 1607 and 1495 cm^{-1} did not appear. Further, the band shift at 1637 cm^{-1} was negligible. 4-CP cannot form catechol type intermediate upon adsorption hence giving no bands around the above frequencies. Study on the adsorption of 2-CP vapor on fused silica at high temperature revealed that the formation of catechol type intermediate species by the bonding of 2-CP via Cl atom and phenolic oxygen and formation of such species are proved by the observation of a band at ~1600 and 1494 cm^{-1} [25, 35, 37].

Though the pH 9 of the medium is higher than pKa of 2-CP (8.52) the above observations clearly show the supportive information for the proposed adsorbed species. When the pH is higher than pKa, anionic species formed may have a high tendency towards interacting with silica by the elimination of H$_2$O and HCl molecules [33]. However, previous studies on the adsorption of 2-CP on fly ash and Ca-montmorillonite showed the reduction in the adsorption capacity when the pH was higher than pKa where the dissociated organic molecules experience the repulsion from the negatively charged surface [38]. In the present study, the amount adsorbed at pH 5 was ~74% while that at pH 9 was 64%. Despite that repulsion and ~10% reduction in the adsorption, the step of the elimination of Cl atom may make some favorable path for the remaining (or dissociated) 2-CP to interact with the Si-O sites [39].

4. Conclusions

Adsorption of 2-CP on silica surface was examined under different pH conditions. The maximum adsorption capacity of 1.5 × 10^{-8} mol m^{-2} on silica surface was observed at pH 7. There are different adsorbed species were predicted in different pH conditions. The interaction between colloidal silica (SiO$_2$) and 2-CP was investigated in an aqueous medium with the emphasis of Fourier Transform infrared (FT-IR) spectroscopy.

Effect of ionic strength on the adsorption was significant as the adsorption capacity was inversely proportional to the ionic strength of the medium. Experimental results confirmed the formation of outer-sphere complexes during the adsorption process. FTIR spectroscopic studies revealed the direct interaction between 2CP and silica via catechol type bidentate complex by eliminating HCl while the experiments with 4CP further confirmed the formation of such an adsorbate configuration. In the future, these observations can also apply to identify degradation pathways of 2-CP in natural soil system in different environmental conditions.

Conflicts of interest

All the authors declare that there are no potential conflicts of interest in any financial or nonfinancial.

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Abbreviations

2-CP   2-chlorophenol

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