CHAPTER 3

Adsorption mechanism of phenol, p-chlorophenol and p-nitrophenol on magnetite surface: molecular dynamics investigations

3.1 Introduction

Adsorption is an attractive and widely used pollutant removal technology due to its high ability, favorable rate, insensitivity to toxic substances, and low cost [Soto et al. (2011)]. The recent focus has been on magnetic iron oxides as an adsorbent for removing different pollutants from wastewater on an industrial scale due to their low cost, chemical stability, and easy separation by applying an external magnetic field [Xu et al. (2012)]. In particular, magnetite (Fe_3O_4) based adsorbents have [Ambashta & Sillanpää (2010), Munoz et al. (2015), He et al. (2015)] been used for the removal of many non-biodegradable organic pollutants such as trinitrotoluene [Matta et al. (2007)], pentachlorophenol [Xue et al. (2009)], phenol [Hanna et al. (2010)], etc.

There are experimental reports demonstrating the adsorption of phenol, *p*-chlorophenol (PCP), or *p*-nitrophenol (PNP) on magnetite nanoparticles [Tural et al. (2016), Yoon et al. (2016), Bastami & Entezari (2012), Sasaki & Tanaka (2011)]. Thus, Mihoc et al. (2014) and Tural et al. (2016) reported magnetite nanopowder to be a suitable adsorbent for the removal of phenol and PCP from aqueous solutions. These authors analyzed the adsorption data of phenol, 2-chlorophenol, and 4-chlorophenol onto magnetite nanoparticles by Langmuir and Freundlich isotherms using the linear regression analysis. But there is still little understanding of the mechanism being followed because the equilibrium data of many experimental studies fits more than one adsorption isotherm. For instance, Yoon et al. (2016) reported that phenol adsorption on magnetite nanoparticles fits both Langmuir and Freundlich isotherms.

Given the paucity of adsorption research from this perspective, this chapter investigates the adsorption mechanism of phenol, PCP, and PNP on magnetite surface by MD simulations in an aqueous medium. The present investigation addresses the question:

how these organic molecules interact with the magnetite (111) surface in the presence of water molecules? The adsorption of different ratios of phenol-water, PCP-water, and PNP-water molecules onto magnetite (111) surface is investigated in this chapter. Density profile data are used to predict the adsorption isotherms followed in each case. Interactions between the magnetite surface and these organic molecules are studied using radial distribution function data. Correlations are drawn between the mechanism followed and adsorption isotherm data fitting. The adsorption efficiencies of these pollutant molecules on the magnetite surface in the presence of water are also estimated.

3.2 Methodology

3.2.1 Simulation models

The adsorption investigations are conducted on the (111) Fe_3O_4 surface because of its stability relative to other magnetite crystal planes. [Yue et al. (2011), Shimizu et al. (2010), Zaki et al. (2018)]. Parallelepiped simulation cells with dimensions of 34.61 Å × 34.61 Å × 40.32 Å were constructed for this purpose (Figure 3.1). Magnetite (111) surface slab of dimension 34.61 Å × 34.61 Å × 8.39 Å was placed in the middle of the simulation cell such that the slab was normal to the z-axis of the simulation box. Equal numbers of solute and water molecules (at fixed density ~1.1 g/cc) were inserted into the space empty on both sides of the magnetite (111) slab using a variation of the Recoil Growth Algorithm by the amorphous builder provided in MAPS 4.1.1 software. The initial density of the solute and the water molecules placed in this way was kept fixed at an appropriate value for all cases considered in the present chapter. Different systems of varying concentrations of Phenol, PCP and PNP in water were studied. For each solute (Phenol, PCP, PNP) six simulation

systems with 10, 20, 30, 40, 50, 60 solute molecules in 1000 molecules of solvent water were built.

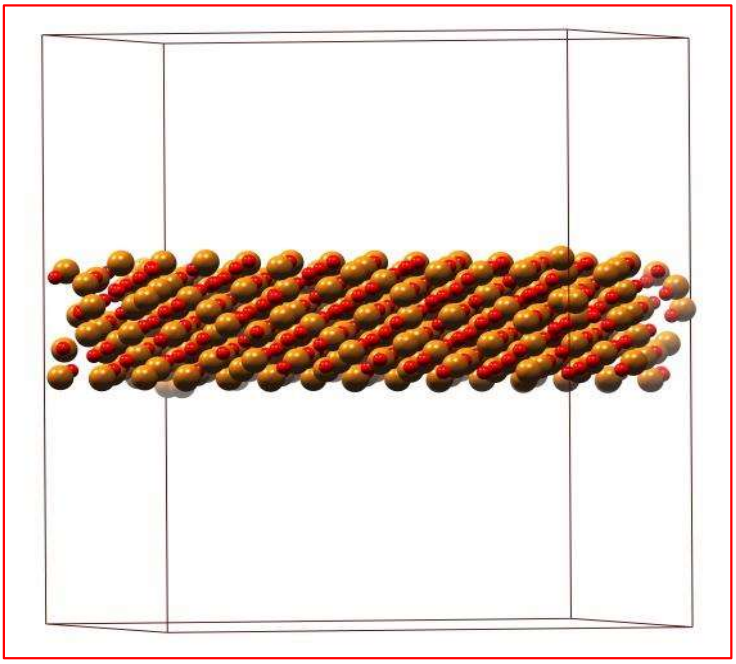

Figure 3.1 Simulation Cell

3.2.2 Simulation method

These model systems were subjected to MD simulations using LAMMPS software [Plimpton (1995)]. Periodic boundary conditions were employed for all three dimensions of the simulated box. Coulomb interactions were simulated with the particle mesh approach using a cut-off distance of 12 Å. Interactions were simulated by the SciPCFF force field [Sun et al. (1994)]. The function below gives the Van der Waal part of the SciPCFF force field.

$$\mathbf{E}_{vdW} = \in_0 \left[\mathbf{2} \left(\frac{r_0}{r_{ij}}\right)^{\mathbf{9}} - \left(\frac{r_0}{r_{ij}}\right)^{\mathbf{6}} \right] \qquad (3.1)$$

In the above function $\in_0$ is the well depth, $\boldsymbol{r_0}$ is Van der Waals radii, and $\boldsymbol{r_{ij}}$ is the distance between atom types i and j. The 9-6 LJ (Lennard Jones) interaction parameters for

two atoms were taken from the SciPCFF database [Sun et al. (1994)]. The details of these interaction parameters are given in Table 3.1. Lorentz–Berthelot combination rules were used for mixed non-bonded interactions between magnetite, solute, and water atoms.

Table 3.1 LJ 9-6 Potential Parameters used in MD simulations.

Atom type	ϵ_0 **(kcal/mol)**	r_0 **(Å)**
Cl (chlorine attached to carbon atom)	0.51	3.42
cp (carbon attached to a benzene ring)	0.119	3.426
N (nitrogen attached to carbon atom)	0.081	3.28
O12(nitrogen attached to oxygen atom)	0.081	2.97
o* (oxygen attached to hydrogen atom of a water molecule)	0.132	3.168
Fex (iron atom in magnetite)	0.83	3.56
ox (oxygen atom in magnetite)	0.132	3.168
h (hydrogen attached to a carbon atom)	0.038	2.51
OH (oxygen attached to a carbon atom)	0.162	3.172
HO (hydrogen attached to an oxygen atom)	0.0135	0.949

Each system was subjected to MD simulation in the NVT ensemble for the simulation time of 5 nanoseconds using a time step of 1 femtosecond. In all simulations, the temperature was kept fixed at T=298.15 K. The atoms constituting the magnetite (111) surface were kept fixed throughout the simulation. Results presented here use data obtained during the last one nanosecond of the trajectories.

3.3. Results and Discussion

3.3.1 Density Profile

Figure 3.2a gives plots of the density profiles of Phenol molecules with an increase in distance (along the z-axis) from the magnetite surface. Different plots in this figure show density profiles for increasing concentrations of phenol in the system. It can be seen that for concentrations up to 30 phenol molecules, only a single peak adjacent to the (111) magnetite surface is formed (Figure 3.2a). For 60 phenol molecules, the height of the first peak increases and a second peak adjacent to the first peak is also formed. The density profile trend for PCP adsorption onto (111) [magnetite surface is shown in Figure 3.2b. Here the first peak keeps getting enriched with the PCP concentration, although the plot for 60 PCP molecules does show broadening. In the case of PNP, along with the major first density profile peak, a small and sharp second peak is also visible for the 60 PNP molecule plot (Figure 3.2c).

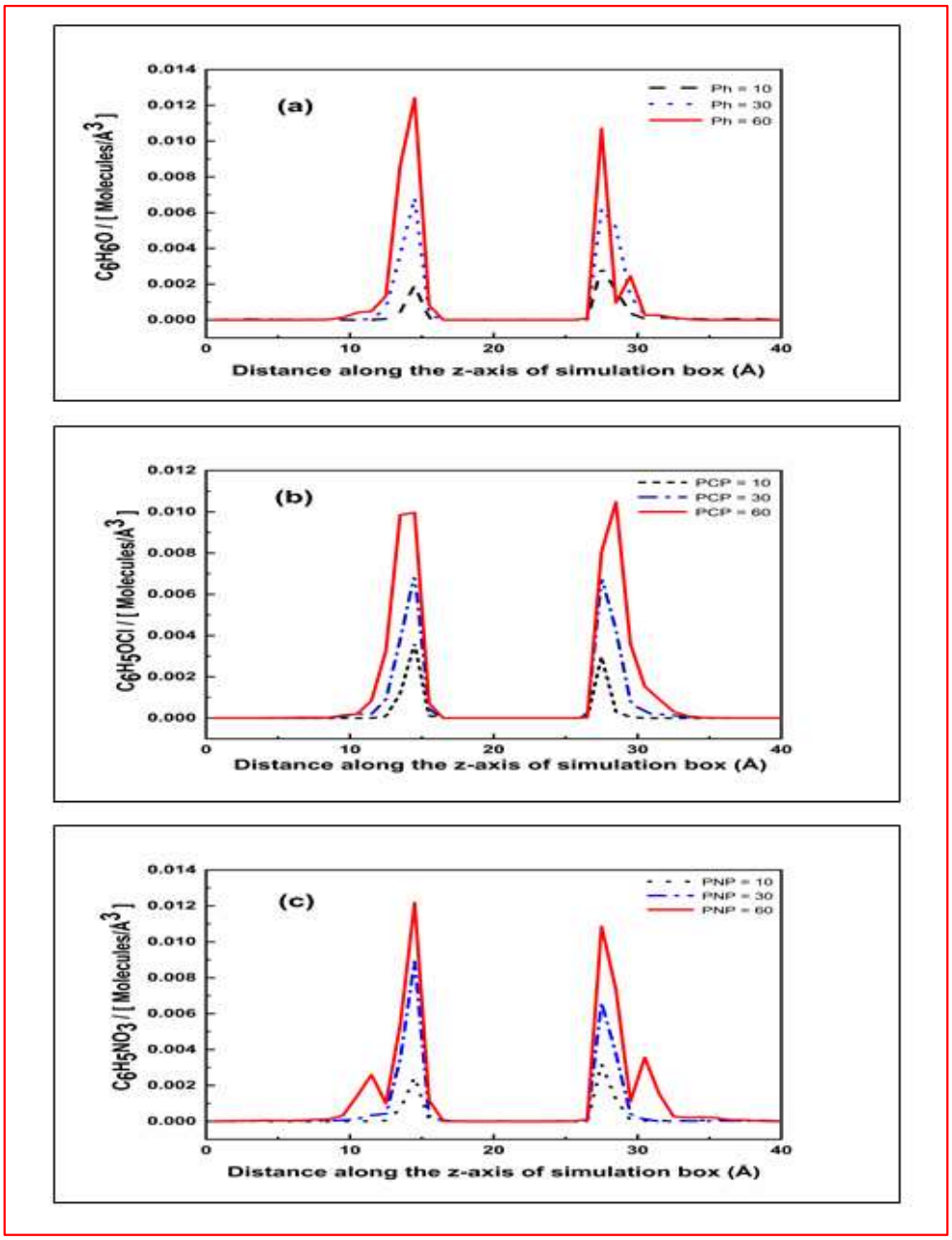

Figure 3.2 Density profile plots for a) phenol, b) PCP and c) PNP adsorption on magnetite slab. [Phenol is denoted by Ph in figure (a)]

3.3.2 Adsorption Isotherms

Adsorption isotherms quantify the nature of equilibrium adsorbate molecular distribution on the adsorbent surface by defining the empirical relation followed between the

concentrations of a solute on the surface of an adsorbent to its concentration in the liquid with which it is in contact. The number of unbound solute molecules is a good approximation of the equilibrium concentration of free molecules [Kyrychenko et al. (2017)]. Following reference [Kyrychenko et al. (2017)], the number of molecules adsorbed (for each initial solute concentration) is calculated by taking the first peak minimum in the corresponding density profile as the cut-off distance. Obtained adsorption results were fitted to the non-linear forms of both Freundlich and Langmuir adsorption isotherm model functions. However, data obtained could only be fitted to the Freundlich adsorption model. Equation 2 gives the Freundlich adsorption model [Kyrychenko et al. (2017)].

$$\mathbf{N}_{\mathbf{ads}} = \mathbf{K} * (\mathbf{N}_{\mathbf{free}})^{\mathbf{n}} \quad (3.2)$$

Where, $\mathbf{N}_{\mathbf{ads}}$ = number of molecules adsorbed to the magnetite surface ($\mathbf{N}_{\mathrm{bound}}$)

$\mathbf{N}_{\mathbf{free}}$ = Number of free molecules

K = Isotherm constant

n = Heterogeneity factor

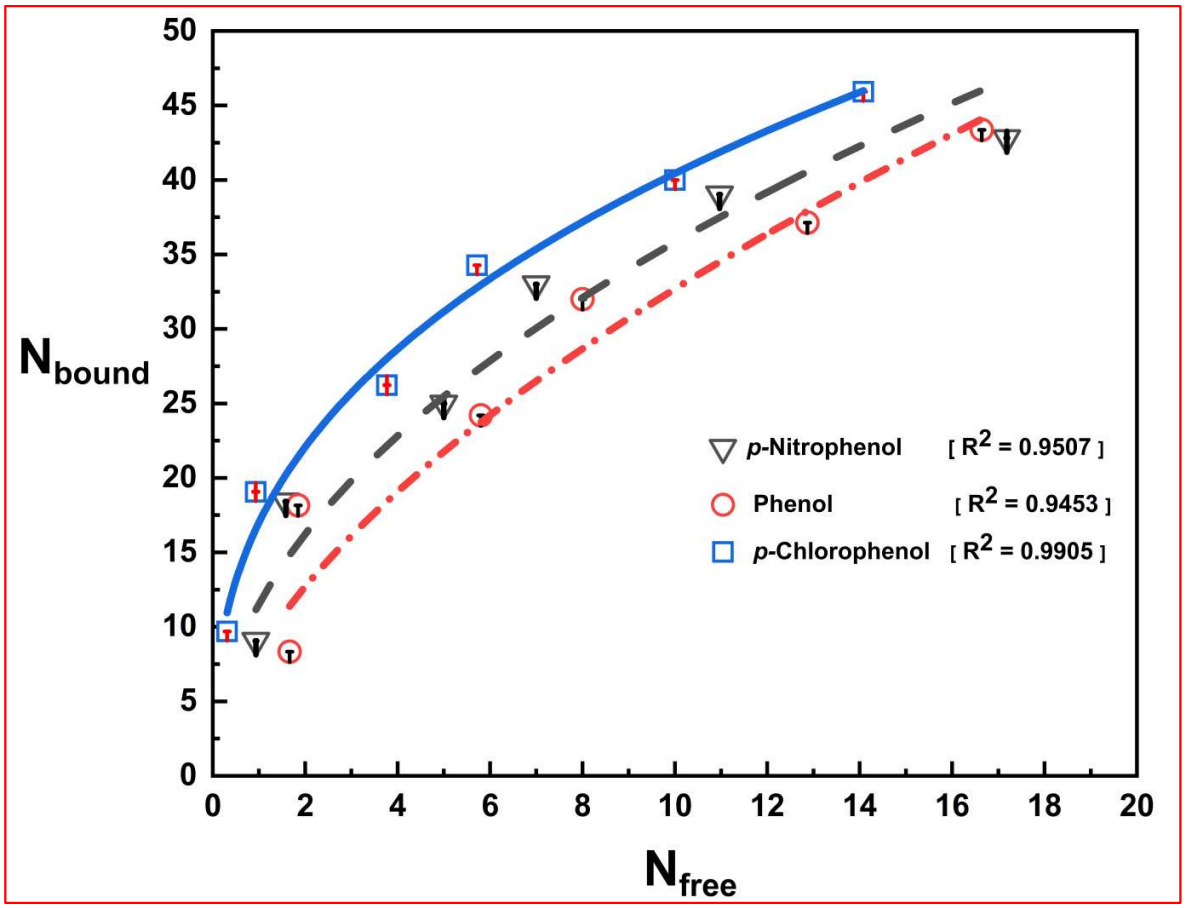

Figure 3.3 Non-linear curves with data points and error bars for all the Freundlich isotherms for Phenol, PCP, and PNP.

Adsorption isotherms of Phenol, PCP, and PNP on magnetite are shown in Figure 3.3. Isotherm results are given in Table 3.2. Freundlich equilibrium adsorption constant values follow the order $K_{PCP} > K_{PNP} > K_{Phenol}$. Hence, PCP is best adsorbed by the magnetite surface in the presence of water. Adsorption energies (E_{ads}) calculated from the computations also validate this conclusion. E_{ads} is the difference between the potential energy (averaged over production run configurations) of the interacting system ($E_{adsorbate+slab+water}$) and the sum of reference model systems. The reference potential energy consists of two parts. One part is the potential energy of a system consisting of solvent and adsorbate molecules ($E_{water+adsorbate}$)

[Heinz (2010)]. The number of solvent and adsorbate molecules in this system is the same as that taken in the interacting system. The reference model simulation is also run for the same amount of time as the interacting model (5 nanoseconds). The second part of the reference energy is that of the system of the bare slab (E_{slab}). The following expression is used to calculate the energy of adsorption.

$$\mathbf{E_{ads} = (E_{slab+water+adsorbate}) - (E_{slab} + (E_{water+adsorbate}))} \quad (3.3)$$

Note that, this adsorption energy is reported in the Table 3.2, 30 adsorbate molecules system was taken only for calculation.

Table 3.2 Computed adsorption isotherm parameter (*n* and K) and energy values.

Compound	n	Adsorption constant (K)	Adsorption energy (Kcal)
***p*-Chlorophenol**	0.375	17.01	-28
***p*-Nitrophenol**	0.491	11.54	-27
Phenol	0.587	8.45	-23

The calculated adsorption energies for the investigated systems are also given in Table 3.2. Adsorption energies are found to follow the order $E_{PCP} < E_{PNP} < E_{Phenol}$. This order is in agreement with the adsorption constant result discussed earlier. From these results, it is concluded that magnetite is best for removing PCP by adsorption from an aqueous solution. These results are in agreement with the experimental results reported by Mihoc et al. (2014) that magnetite is a better adsorbent of PCP as compared to Ph. It is

important to mention that till date no comparable experimental results are available for PNP. Therefore, the calculated order is a prediction.

3.3.3 Radial Distribution Function (RDF) analysis

The molecular interactions underlying the adsorption process are assessed through the RDF of different atoms of adsorbate molecules for Fe and O atoms of magnetite slab. RDF gives the probability of occurrence of atoms of functional groups on the solute molecules in the first layer and (O and Fe) atoms making up the magnetite surface with the distance between them. Calculated RDF's are time averages over the last one nanosecond. Figure 3.4(a) shows the RDF plots of Phenol adsorption on magnetite. Only the first maximum is considered for analysis since it is representative of the first layer of adsorbate molecules formed adjacent to the adsorbent surface. The g(r) plot features at larger distances include interactions due to magnetite atoms not at the surface of the adsorbent. The first peak of the r(Fe(M)-OH(Ph)) interaction is located at ~3.5Å, and the corresponding g(r) value is ~0.8. These results suggest that Fe(M)-OH(Ph) interaction is stronger than that of O(M)-HO(Ph). This inference is supported by Figure 3.4(b), which depicts a snapshot of the Phenol/magnetite system obtained at the end of the 5 nanoseconds MD run. Therefore, the RDF curve analysis tells us that the adsorbent interacts more with the OH side of the phenol molecule. Consequently, phenol molecules appear to orient themselves mostly in an inclined fashion with respect to the adsorbent surface.

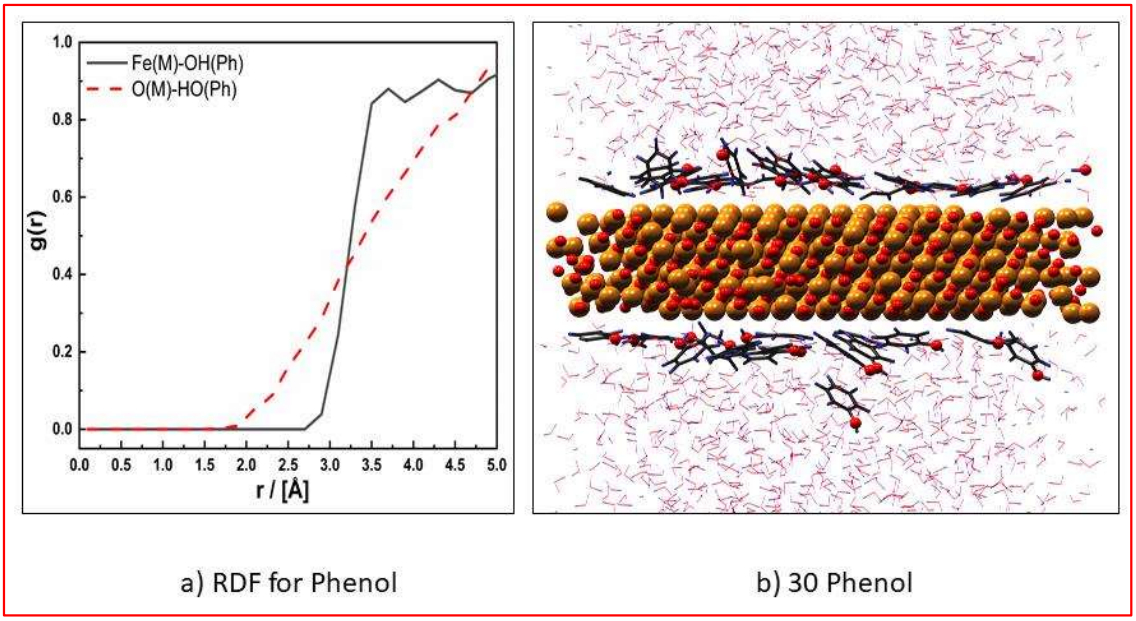

Figure 3.4 (a) The radial distribution function g(r) of various atoms of phenol with magnetite atoms at distance r. [Fe(M): Iron of magnetite, O(M): Oxygen of magnetite, OH(Ph): Oxygen attached to the carbon of phenol, r: represents the distance of approach in Å] and (b) Snapshot of equilibrium configuration of adsorbed 30-Phenol molecules on the magnetite surface at 5nanoseconds. [Colour represents in the figure as black: carbon, light blue: hydrogen, brown: iron, red: oxygen]

Figure 3.5(a) gives the RDF plots of PCP adsorbed on the magnetite surface. The r(Fe(M)-Cl(PCP) maximum is located at ~3.6Å, and the corresponding g(r) value is ~1.4. Interactions between the oxygen of magnetite and other PCP atoms are relatively weaker. Hence, the adsorption is mainly due to the strong interaction between chlorine in PCP and iron of magnetite. Figure 3.5b shows the snapshot of the system obtained at the end of the 5 nanoseconds MD run. In agreement with the RDF observations, one can see that most of the Cl atoms of PCP are oriented towards the adsorbent.

The RDF plots of PNP adsorption on the magnetite surface are shown in Figure 3.6a. First maximums of r(Fe(M)-N(PNP)) and r(Fe(M)-OH(PNP)) occur at ~3.4Å and ~3.6Å of the respectively. Additionally, the corresponding g(r) values are also nearly the same.

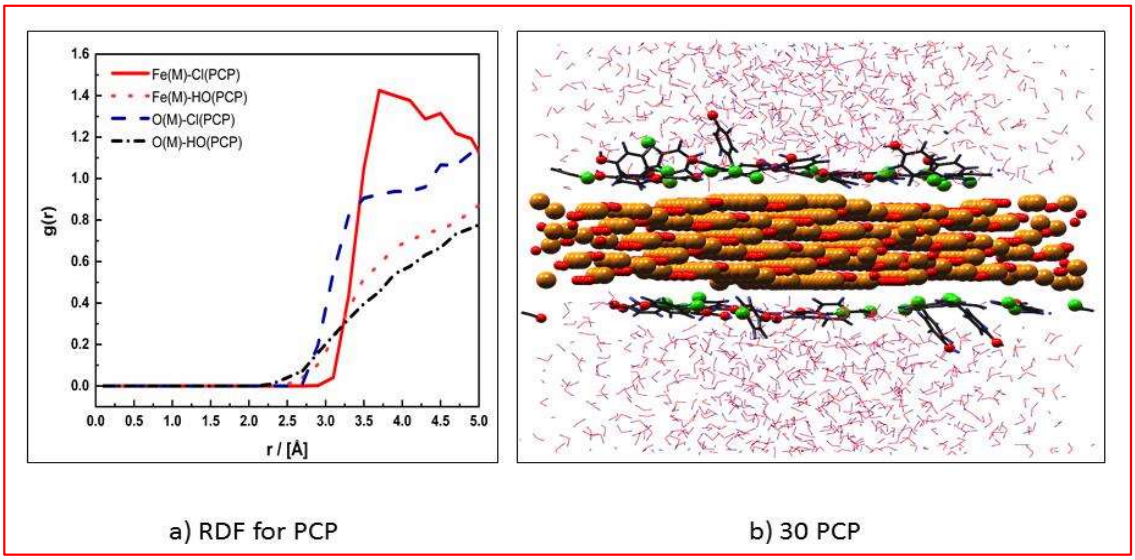

Figure 3.5 (a) The radial distribution function g(r) of different atoms of PCP with magnetite atoms at distance r. [HO(PCP): Hydrogen attached to oxygen with the ring of PCP, Cl(PCP): Chlorine is attached with the carbon of PCP] and (b) Snapshot of equilibrium configuration of 30 PCP molecules adsorbed on the magnetite surface at the end of 5 nanoseconds. [Color represents in the figure as green: chlorine, black: carbon, light blue: hydrogen, brown: iron, red: oxygen]

The -NO_2 and -OH functional groups are in para positions relative to each other. Similar strength of interaction with Fe(M) implies that most of the PNP molecules will be oriented parallel to the magnetite surface. The inference is corroborated by the snapshot summarizing the molecular interaction between PNP and the magnetite surface in Figure 3.6b. It can be seen that the benzene rings of the PNP molecules align themselves nearly parallel to the (111) magnetite surface, ensuring that Fe(M)-N(PNP)) and Fe(M)-OH(PNP) interactions are almost equal.

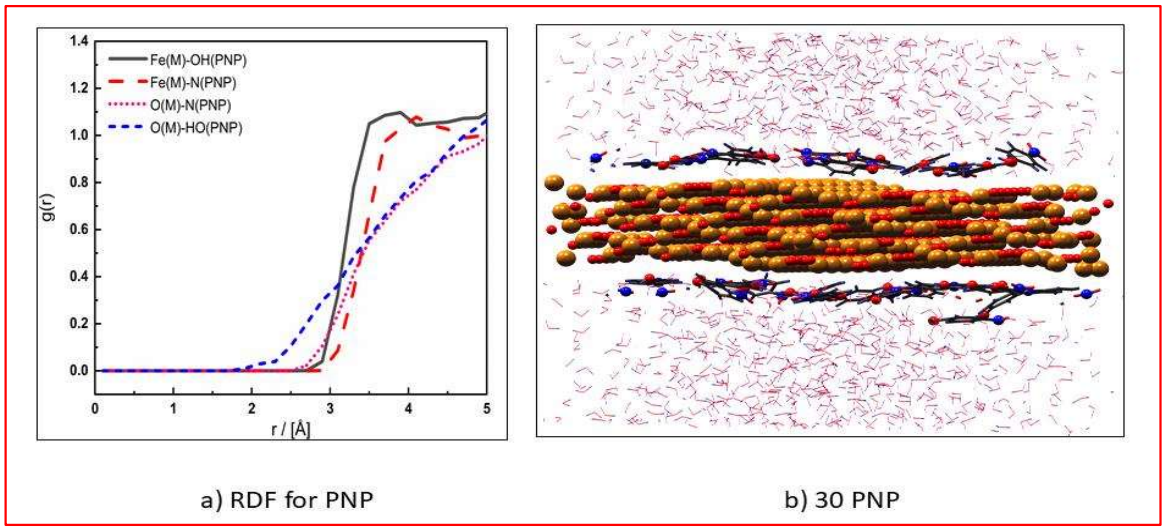

Figure 3.6 (a) The radial distribution function g(r) of different functional group atoms of PNP with (Fe and O) magnetite atoms at distance r. [OH(PNP) : Oxygen attached to the carbon of PNP, HO(PNP): Hydrogen attached to the phenolic oxygen of PNP, N(PNP) : Nitrogen attached to carbon in PNP] and (b) Snapshot of equilibrium configuration of 30 PNP molecules adsorbed on the magnetite surface [Color represents in the structure as black: carbon, light blue: hydrogen, brown: iron, dark blue: nitrogen, red: oxygen]

3.3.4. Discussion on the adsorption mechanism

As mentioned earlier, Mihoc et al. (2014) have demonstrated that magnetite is a better adsorbent of PCP as compared to Phenol. They proposed that the presence of a strong electron-withdrawing chloro-group in PCP reduces the electron density of the aromatic ring, increasing the strength of interaction with the adsorbent. However, this chapter investigation shows that PCP adsorption onto magnetite is driven by the strong Fe--Cl interaction. Then for PNP adsorption on magnetite, it is seen that the RDF's of Fe(M)-N(PNP) and Fe(M)-OH(PNP) are of nearly the same strength, and hence many of the PNP molecules are nearly parallelly oriented to the magnetite surface. In the case of phenol adsorption to magnetite, the Fe interaction with the O atom of the -OH group is the stronger interaction. Moreover, the g(r)'s of the three solutes follow the order Fe(M)-Cl(PCP) > Fe(M)-N(PNP) > Fe(M)-OH(Ph). The g(r) order mentioned is indicative of the solute-magnetite interaction strength

since the order of adsorption energies clearly shows that PCP is most strongly adsorbed, and PNP is the next in the order. The order of equilibrium constants is also in agreement with the energies. Hence, we conclude that the overall strength of adsorption depends on two competing factors. Firstly, the hydrophilic nature of the solute molecule. More hydrophilic the solute, the lesser the chances of its interaction with magnetite. The second factor is the strength of the interaction between the solute molecules and magnetite surface atoms. The overall adsorption strength is the resultant of these two competing factors [Ding et al. (2016), Madannejad et al. (2018), Wu et al. (2019), Zhang et al. (2019)].

3.4. Conclusions

MD simulations have been applied to elucidate the mechanism of adsorption of phenol, *p*-chlorophenol, and *p*-nitrophenol (from their aqueous solutions) on (111) magnetite surface. Simulations were done at different concentrations of each type of solute molecule. Data from density profiles of solute molecules were found to fit the Freundlich isotherm model best. Values of adsorption equilibrium constant for different solutes followed the order $K_{PCP} > K_{PNP} > K_{Phenol}$. Comparison of adsorption energies also shows that PCP is more strongly adsorbed on magnetite.

On the other hand, the adsorption of Phenol on magnetite is the weakest among the solute molecules considered in the present study. Analysis of the radial distribution function between different types of adsorbent-adsorbate atoms was used to elucidate the mechanism of adsorption. PCP was found to adsorb on magnetite mainly by Fe(M)-Cl (PCP) interaction. Fe atoms of magnetite interact almost equally with N and -OH of PNP. Phenol interacts with magnetite more through Fe(M)-OH(Ph) contacts. The order of the strength of these interactions is analogous to that of adsorption energies and adsorption equilibrium constants.