Original Article

Adsorption of polymers onto iron oxides: Equilibrium isotherms

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\section*{Abstract}

The interactions of polymers (corn starch, dextrin from maize starch, humic acid sodium salt and sodium carboxymethyl cellulose) with iron oxides (hematite and magnetite) have been investigated by measuring adsorption isotherms and by electrophoresis. According to the electrophoresis measurements at pH 7 both iron oxides present negative surface charge and positive at pH 5. The equilibrium adsorption isotherms were then determined at pH 7 for all the adsorbates except for humic acid which was studied at pH 5, due to its anionic characteristics. The equilibrium data of both iron oxides were studied using Freundlich and Langmuir models and it was found to best fit the Freundlich one. The values for Freundlich constants indicate that the mechanism that contributes most to the adsorption process in all experiments was the hydrogen bonding. However, the coexistence of more than one adsorption mechanism is what best explains the process itself, in addition to explaining the differences found amongst theories over the years.

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\section*{1. Introduction}

In nature, iron occurs bound to more the 1200 different minerals but only from very few it can be economically extracted. Among all these minerals, hematite (α-Fe\textsubscript{2}O\textsubscript{3}) and magnetite (Fe\textsubscript{3}O\textsubscript{4}) are the main iron oxides found in iron ores from which metallic iron can be economically extracted. Prior to the production of metallic iron, separation processes are required. These processes always explore some intrinsic properties of the minerals to generate a contrast between them and have a differentiating ability: shape, specific gravity, magnetic susceptibility and surface reactivity.

Among the techniques currently applied to process iron ores, magnetic separation is the most used one [1], however faced to the challenges that the mineral industry has been experiencing with the emergence of raw materials containing less minerals of interest and exhibiting less contrast between them, this technique has often proved inefficient and/or insufficient. The exploration of low-grade iron ores is very often associated with more complex mineralogical composition [2], requiring finer grinding to achieve the desired
mineral liberation. Flotation process which involves the use of the physical-chemistry properties of the minerals to separate them, appears in this case as a solution to produce high grade concentrates, being able to be applied to very fine particles and complexes silicates gangue systems [3,4]. Its first industrial application debuted in 1954 [5] and since then a lot of research has been conducted in flotation of iron ores [1,2,4,6–19]. The surface chemistry of iron oxides has been investigated over the years aiming to find solutions mostly for environmental issues related to the presence of these chemical species. The ability of iron oxides to adsorb metal ions [20–22], inorganic anions [20] and organic compounds [23–25] were the object of several studies to have a better understanding of the surface and the collector and depressant adsorption behaviour of these minerals. However, an in-depth study of how the main depressants used in this process adsorb on the minerals surface has never been conducted in a systemic way. Several studies presented the adsorption of natural polysaccharides (dextrin, starch) on mineral surfaces through chemical interactions with superficial metal hydroxides. Khosla and Bisiyaw have suggested a starch adsorption mechanism on calcite and hematite surfaces as chemical complex formations [26]. This fact has been supported by studies of starch adsorption on the hematite and Filippov et al. studies on the Fe-bearing amphiboles [27]. Even the chemical interaction was proposed as the main mechanism of polysaccharide adsorption on mineral surfaces the totally different mechanisms were observed by different researchers for the same mineral-polysaccharide system. However, for the flotation system it is crucial to understand how the adsorption of each reagent takes place on the minerals surfaces and what is the adsorption capacity of each one to have more information about the rate of overcoating of the minerals and which adsorption processes are involved.

The aims of this study were to determine extents of adsorption of polymers onto iron oxides, and to investigate the mechanisms involved in each process. The experimental data were treated and modelled according to adsorption theories. Despite the Langmuir adsorption isotherms have been originally developed to describe gas-solid-phase adsorption, it have been widely used for other phase systems as well [25,28–35]. This theory refers to a homogeneous adsorption and the empirical model assumes that the adsorption occurs only in a monolayer having no interactions between the adsorbed molecules. Freundlich adsorption isotherms were also investigated to compare with that Langmuir adsorption isotherms. Freundlich model does not limit the adsorption to the formation of monolayer and it is widely used to describe heterogeneous surfaces, as expected for the case of adsorption of polymers on iron oxides.

2. Materials and methods

2.1. Materials

2.1.1. Iron oxides

Hematite (α-Fe₂O₃) and magnetite (Fe₃O₄) samples are from Brazil and present a high degree of purity. They were prepared in the same way as the silicate samples described by [1], being the fraction below 38 μm used for the adsorption tests and the fraction below 5 μm for the electrophoretic measurements. The identities of the iron oxides were confirmed by XRF (X-ray fluorescence) (Table 1) and by XRD (X-ray diffraction) analyses (Fig. 1).

Table 1 – Chemical analyses of pure mineral samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analyses (% of oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeO</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.43</td>
</tr>
<tr>
<td>Magnetite</td>
<td>29.90</td>
</tr>
</tbody>
</table>

Table 2 – Specific surface area of pure minerals by BET method.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Magnetite</td>
<td>1.4 ± 0.2</td>
</tr>
</tbody>
</table>

The chemical analyses show that FeO and Fe₂O₃ values are very close to the theoretical values for hematite and magnetite, indicating an excellent level of purity of the samples used. The XRD diffractograms (Fig. 1) show only the characteristic peaks of the magnetite and hematite, supporting the results of the XRF analysis.

2.1.2. Reagents

The reagents – corn starch (C₆H₁₀O₅)n, dextrin from maize starch (C₆H₁₀O₅)ₙ, humic acid sodium salt (C₆H₁₃Na₂O₆)(CO₃)ₙ and sodium carboxymethyl cellulose (CMC) (C₆H₁₀Na₃O₆)(CO₃)ₙ, used during the adsorption tests were purchased from Sigma Aldrich, Table 2 presents the average molecular weight informed by the supplier.
Fig. 1 – X-ray diffraction spectrum of hematite (a) and magnetite (b).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn starch</td>
<td>500,000</td>
</tr>
<tr>
<td>Dextrin from maize starch</td>
<td>20,000</td>
</tr>
<tr>
<td>Humic acid sodium salt</td>
<td>500,000</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>700,000</td>
</tr>
</tbody>
</table>

Corn starch preparation was carried out with its gelatinisation by adding NaOH at a 5:1 ratio and deionised water while aqueous solutions of all other reagents were prepared with deionised water. A stock solution at 1000 mg L\(^{-1}\) of each depressant was prepared daily, to avoid degradation of the compounds as discussed by Balajee and Iwasaki [9]. Analytical grade HCl and NaOH were used as pH modifiers for the adsorption tests.

2.2. Specific surface area measurements

The specific surface area (area per unit mass or volume) of the minerals was determined by a multi-point BET method with \(N_2\) adsorption, using Belsorp mini-II equipment from Bel Japan Inc. This method consists of modelling the portion of the isotherm that corresponds to the end of the adsorption of the first layer of the gas. Finally, the surface area is determined using t-plot method by considering the volume of \(N_2\) adsorbed for the total coating of the solid. The results for the BET surface area of each mineral are presented in Table 2.

2.3. Electrophoretic mobility measurements

Measurements were performed with a Zetaphoremetre IV, model Z3000 apparatus. An electric field of 80 ± 1 V cm\(^{-1}\) was employed during the zeta potential determinations. They were carried out in an indifferent electrolyte solution (KCl) of concentration 10\(^{-2}\) M at pH from 2 to 12. The pure mineral powder of size fraction below 5 \(\mu m\) was added to deionised water to prepare a dilute suspension used for the measurements. The suspension was then passed through an ultrasonic bath to be well disaggregated and then kept constantly under stirring. The pH value was adjusted through the addition of analytical grade HCl or KOH solutions. For each pH value the electrophoretic mobility was determined from at least 100 particles and the Zeta Potential was calculated by the Smoluchowski equation. The experiments were repeated twice, and
the results were averaged. The standard deviation was calculated using the average of all values.

2.4 Adsorption studies

The adsorption determination was made by a TOC (Total Organic Carbon) analysis using a Shimadzu analyser TOC-VCSH and its value is the difference between the TC (Total Carbon) and IC (Inorganic Carbon). For the tests, 1 g of each mineral was placed in a 100 mL volume flask with total depressants concentrations ranging from 25 to 300 mg L\(^{-1}\). After 1 h of conditioning on a digital horizontal shaker at 23 ± 2 °C, the solid-liquid separation was performed in a centrifuge at 10,000 G and the liquid phase was then passed through the TOC analyser. The quantity of reagent adsorbed was then determined from the difference between the initial (\(C_0\)) and residual (\(C_e\)) concentrations. All the adsorption tests were made in duplicate and the standard deviation presented were calculated from the average value of adsorption quantity results.

2.5 Theory

2.5.1 Adsorption isotherms models

Two well-known adsorption isotherms models, namely Freundlich [36] and Langmuir [37], were used to explain the adsorption of the reagents onto the surface of the iron oxides.

2.5.2 Freundlich isotherm

\[ q_e = K_F C_e^{1/n} \] (1)

Eq. 1 can be rearranged into linear form as:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \] (2)

where \(q_e\) is the amount of reagent (mg) adsorbed per unit area of iron oxide (m\(^2\)) at equilibrium; \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)) of reagent; \(K_F\) is the Freundlich adsorption isotherm constant (mg\(^{1/n}\) L\(^{1/n}\)g\(^{-1}\)) that indicates the adsorption capacity of the adsorbent and \(n\) is also the Freundlich adsorption isotherm constant which represents an indication of the deviation from linearity. A plot \(\log q_e\) against \(\log C_e\) gives a straight line of slope \(1/n\) and intercept \(K_F\) by means of which the constants can be determined.

2.5.2.1 Langmuir isotherm.

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \] (3)

Eq. 3 can also be linearized into:

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_a q_m C_e} \] (4)

where \(q_m\) is the value of \(q_e\) at saturation and, \(K_a\) is Langmuir’s adsorption isotherm constant (L mg\(^{-1}\)), which is related to the energy of adsorption. By plotting \(1/q_e\) against \(1/C_e\), the constants \(q_m\) and \(K_a\) can be determined from intercept and slope of the straight line, respectively.

2.5.3 Error analysis

The best-fitting isotherm, when linearization is used, has been very often determined with the use of the coefficient of determination \(r^2)\). Ho proved that this coefficient is not appropriate for comparing which model fits best the experimental data and suggested the Chi-square test \((\chi^2)\) as a method that does not present significantly impact with the different equations’ forms [38]. Chi-square test considers the experimental and model calculated data and can be determined by:

\[ \chi^2 = \sum \left( \frac{(q_{ec} - q_{ec})^2}{q_{ec}} \right) \] (5)

where \(q_{ec}\) is the same value of \(q_e\) coming from the experiments and \(q_{ec}\) is the same equilibrium capacity of the adsorbent calculated according to the model. The lowest the value of \(\chi^2\)-test, the best, proving that experimental data fit well into the model.

3 Results and discussion

3.1 Electrophoretic mobility measurements

Fig. 2 shows the zeta potential of the iron oxides as a function of pH. From the same figure one can see that the isoelectric points (IEPs) of hematite and magnetite were achieved at pH values of 6.2 and 5.4, respectively. Table 3 shows reported values obtained by other researchers for those minerals.
3.2. **Effect of pH on adsorption**

The effect of pH in the range 5–11 on the adsorption of the reagents on the iron oxides surfaces was investigated (Fig. 3).

Almost no adsorption was observed for CMC into hematite and magnetite surfaces. Humic acid and dextrin showed better affinity for these minerals, but corn stalk is by far the best performer. According to the electrophoretic measurements (Fig. 2) at pH 7 both iron oxides present negative surface charge and positive at pH 5. Since humic acid and CMC are anionic polymers and at lower pH values, the carboxylic acidic groups become protonated and less negatively charged [46], a higher adsorption was expected at a pH value below their IEP. This behaviour was slightly observed for humic acid, however CMC showed almost no adsorption with the initial concentration used for the pH tests. Based on the pH value that showed the highest adsorption for each polymer, the equilibrium adsorption isotherms presented later were determined at pH 7 for all the adsorbates except for humic acid which was obtained at pH 5, this is exactly the same behaviour observed in a previous study using the same polymers onto silicates minerals [1].

3.3. **Adsorption isotherms**

Adsorption isotherms are a powerful tool to determine how adsorbates molecules interact with adsorbents surfaces. The understanding of the relationship between experimental data and proposed models can be extremely useful for these interpretations.

The experimental data were fitted in two different models: the Freundlich one used to describe heterogeneous systems, assuming that sites of adsorption with different adsorption free energy occur in parallel, not restricting the formation of multiple layers [36] and the Langmuir one, which are used to homogeneous systems in which constant adsorption free energies are observed [37]. From the linearization of the experimental data it is possible to determine all the constants for each model and evaluate the fitting quality of each one (Figs. 4–11).

Freundlich constant $K_F$ has a linear correlation with the adsorption capacity of the adsorbent, which means that the greater this constant, the greater adsorption capacity. Freundlich constant $n$ can also indicates the type of adsorption that takes place. When $n = 1$, the isotherm is linear, and the adsorption sites are homogenous (as in Langmuir model); when $n < 1$, the presence of more adsorbate in the adsorbent enhances the free energies of further adsorption; finally, when $n > 1$, the added adsorbates are bound with weak free energies.
Table 4 – R-values isotherm classification.

<table>
<thead>
<tr>
<th>R value</th>
<th>Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = 0</td>
<td>Irreversible</td>
</tr>
<tr>
<td>0 &lt; R &lt; 1</td>
<td>Favourable</td>
</tr>
<tr>
<td>R = 1</td>
<td>Linear</td>
</tr>
<tr>
<td>R &gt; 1</td>
<td>Unfavourable</td>
</tr>
</tbody>
</table>

Fig. 5 – Freundlich model linearization for corn starch adsorption on hematite and magnetite.

The Langmuir model in other hand is used most of the time to predict if an adsorption system is favourable or not under specific experimental conditions. Trying to classify the shape of the isotherms by groups, Langmuir, 1918, introduced the concept of a dimensionless equilibrium parameter (R):

\[ R = \frac{1}{1 + K_L C_i} \]  

(6)

From the values obtained by the Eq. 6, the classification can be done as presented in Table 4.

All the obtained values of Freundlich and Langmuir model’s parameters are depicted in Table 5 for both minerals investigated.

Both n and R values indicate that the adsorption of the reagents on the surface of these two minerals is favourable. Considering only the values of \( r^2 \), there would be experimental data that would fit better into the Freundlich model and others that would fit better into the Langmuir one. However, as stated in section 2.5.2, \( \chi^2 \) - test is a better method of error than \( r^2 \) analysis and from the values shown on Table 5, it is clear that Freundlich model fits best in all the experimental data.

The experimental equilibrium adsorption isotherms of CMC, corn starch, dextrin and humic acid on hematite and magnetite are presented in Figs. 12–15. The circles and squares represent the experimental data and the lines the model that best fit this data – Freundlich model.

The values of the Freundlich constant \( K_F \) are higher for corn starch, showing that this polymer has more adsorption capacity than the others. Corn starch has high affinity with iron oxides, through initial hydrogen bonds [47] leading to the for-
formation of chemical complexes [6,27]. This high affinity due to the formation of complexes was not observed in this study for the other polymers. Humic acid adsorption is related to an ionic interaction between minerals and reagents rendering the adsorption quite stable. Dextrin results were unexpected since this polymer should have the same trend of corn starch, this shows that chain length plays an important role in the adsorption mechanisms of polymers. CMC adsorption was low on both iron oxides surfaces mainly due to the influence of the substitution degree that was low which leads to a low solubility of this polymer. The difference in magnitude between the adsorption of corn starch onto hematite and magnetite seems to be related to the differences between their crystalline structures. While in hematite the oxygens ions are arranged in a hexagonal with Fe$^{3+}$ ions occupying octahedral sites, in magnetite the oxygen ions are arranged in a cubic with Fe$^{3+}$ ions distributed between octahedral and tetrahedral sites and Fe$^{2+}$ ions in octahedral sites. Weissenborn et al. [27] demonstrated that the amyllopectin has a strong complexing ability for Fe$^{3+}$ in the solution for a molar ratio of 5.6:1 and 100:1 and suggested to translate the complexation of iron(III) in solution to the complexation of iron(III) atoms on the surface of hematite. Thus, the presence of iron(II) in octahedral position in the magnetite structure may impact the adsorption behaviour of the starch on the magnetite surface. The conformational effects between the hydroxyl groups of polymers and the interatomic distance on the magnetite need to be considered and may restrict also complexation on the magnetite surface.

The mechanism of polysaccharides adsorption has been the object of study of several researchers over the years. Hydrogen bonding stands out between the others for being reported by several researchers [9,48,49]. Hydrophobic interactions [32,50,51] and chemical complexation [6,26,27,52] were also proposed. Nakatani [53] found that glucose adsorbed much more strongly on a basic alumina surface than on an acid one, this fact associated with other researchers findings [54], made possible the proposition of an acid-base interaction between polysaccharides and minerals, meaning that these interactions are responsible for determining the adsorption mechanism as hydrogen bonding or chemical complexation, depending on the basicity of the minerals surface.

In the present study, humic acid showed a slightly difference in the amount adsorbed when pH is varied. The same behaviour was reported by several studies leading with humic substances [24,25,33,55–57]. The increase or decrease in the amount adsorbed related to the pH value is consistent with the proposition of a complexation-ligand exchange mechanism for humic substances [57] and also with the possibility of a protonation of surface hydroxyls to form complexes [33]. In general, an anion adsorption at oxides surfaces involves ligand exchange with surface Fe-O $H^+_2$ and Fe–OH groups, whereby the carboxylate groups displace surface
Analysing all possible explanations for the adsorption mechanisms of humic substances, what is clear is that different mechanisms can coexist in an adsorption process. Some authors have even quantified the contribution of those mechanisms (e.g., van der Waals interactions, ligand exchange and cation bridging) for the whole process [46,58].

It is also worth noting that the constant $n$ has a value greater than 1 for all studied cases, indicating that all equilibrium adsorption isotherms are associated with a weak bound process, even those that may have higher adsorption energies.

The observed variations in the adsorption mechanisms of polymers reported by several authors over the years can be explained by the differences in terms of heterogeneity of samples and in the intrinsic variations of the conditions of each experiment.

From this study it was possible to prove by the modelling of experimental isotherms that Freundlich model fits better the adsorption of these polymers on the surface of hematite and magnetite. Freundlich model constant $n$ indicates that hydrogen bonding is the main adsorption mechanism present in these interactions. However, as previously discussed, the coexistence of adsorption mechanisms is a widely studied subject and our experimental results combined with the literature review allows us to state that in the polysaccharides (corn starch, CMC and dextrin) and humic substance (humic acid) adsorption by iron oxides (hematite and magnetite), the coexistence of adsorption mechanisms is clearly what happens at different degrees and intensities.
4. Conclusions

The equilibrium adsorption data were fitted to two isotherm models and the results showed that for all experiments the Freundlich model fits better the experimental data than the Langmuir one. It is proved here that the $\chi^2$-test is a better tool to analyse the fit of models when compared to $r^2$. The value of $K_f$ indicates that corn starch has a higher adsorption capacity in both iron oxides, which is expected given the widely use of this polymer in the mineral processing industry.

The adsorption mechanism that most contributes to the adsorption process in all experiments was likely hydrogen bonding, proved by the value of the constant $n$ being greater than 1 in all cases, indicating that the adsorbates are bound with weak free energies. However, the coexistence of adsorption mechanisms is for us what best explains the process itself, in addition to explaining the differences found between theories over the years.

REFERENCES


