



HAL
open science

**About the Sorption of P(v) on Fe(iii) Oxyhydroxides:
Comments and Corrections to the Paper by Xu, Zhu
and Xiong [Water, Air & Soil Pollution 233:454 (2022)]**

Véronique Deluchat, Jean-Claude Bollinger

► **To cite this version:**

Véronique Deluchat, Jean-Claude Bollinger. About the Sorption of P(v) on Fe(iii) Oxyhydroxides: Comments and Corrections to the Paper by Xu, Zhu and Xiong [Water, Air & Soil Pollution 233:454 (2022)]. Water, Air, and Soil Pollution, 2024, 235 (7), pp.463. 10.1007/s11270-024-07241-y . hal-04655203

HAL Id: hal-04655203

<https://hal.science/hal-04655203>

Submitted on 21 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Discussion**

2 **About the sorption of P(V) on Fe(III) oxyhydroxides: Comments**
3 **and corrections to the paper by Xu, Zhu and Xiong [*Water, Air &***
4 ***Soil Pollution* 233:454 (2022)]**

5

6 Véronique Deluchat • Jean-Claude Bollinger

7

8 V. Deluchat • J.-C. Bollinger

9 Laboratoire E2Lim (Eau et Environnement Limoges), UR 24133

10 Faculté des Sciences & Techniques

11 Université de Limoges, 87060 Limoges (France)

12 e-mail: veronique.deluchat@unilim.fr; jean-claude.bollinger@unilim.fr

13

14

15 Submitted: 25 October 2023 / Accepted: 3 June 2024

16 ***Water, Air & Soil Pollution* 235: 463 (2024).**

17 DOI: 10.1007/s11270-024-07241-y

18

19 **Abstract**

20 Many papers deal with the characterization of various sorption supports, tested with numerous
21 contaminants. However, the results concerning the same “sorbate/sorbent” system are often
22 very different. In sorption studies, there are regularly misleading calculations concerning (i)
23 both kinetic and isothermal modeling by linear (instead of nonlinear) equations; and (ii)
24 calculation of thermodynamic parameters for sorption processes. It should also be noted that
25 it is often impossible to compare the results of such studies and their interpretations. Indeed,
26 according to the context of the studies (natural environment, wastewater, industrial system...),
27 the experimental conditions are very different. Moreover, while studies could be dedicated to
28 similar species, both sorbent and sorbate, the keywords associated to these papers can be
29 different and authors can miss a published paper, making their bibliography incomplete.
30 Therefore, we remind how to use correct procedures to perform these calculations in a
31 valuable way; in our opinion, it is a source of confusion for the scientific community if
32 inappropriate methods continue to be used. Moreover, we would like to encourage scientists
33 to pay attention to the choice of keywords, and to suggest editors of scientific journals to
34 increase the number of keywords. This is illustrated here with recent papers dealing with the
35 sorption of P(V) on Fe(III) oxyhydroxides.

36

37 **Keywords** Phosphate sorption • Iron oxyhydroxide • Kinetics modelling • Isotherm
38 modelling • Thermodynamic parameters • Scientific mistakes.

39

40 **1 Introduction**

41 In order to fight against the eutrophication of waterbodies, several methods have been
42 proposed in recent years to limit the amount of P(v) input, a very harmful element for the life
43 of plants and animals (LeMoal et al., 2019). This can be done, among other methods (Jia et
44 al., 2023; Zheng et al., 2023), by precipitating the polluting phosphate with a calcium salt, as
45 this is the case in natural pond systems (Moutin et al., 1992) or by adding aluminum salts as
46 experienced in eutrophic lakes (Auvray et al., 2006; de Barros et al., 2023). Other types of
47 phosphate removal can be achieved with Fe(III) salts or solid (natural) compounds (Lanet et
48 al., 2021 ; Wang et al., 2024).

49 Within such a framework, Xu, Zhu and Xiong have recently published in this journal a study
50 on phosphate removal by sorption on several isomeric Fe(III) oxyhydroxides: goethite,
51 akageneite and lepidocrocite (Xu et al., 2022); however, 6 years earlier Sleiman et al. (2016)
52 had published a paper on a similar subject, which Xu et al. (2022) seem not to have been
53 aware of, as they do not cite it.

54 The internal structure of both papers is of course traditional: after a description of the
55 preparation of the solid sorbents and their characterization by various physicochemical
56 methods, the sorption kinetics and isotherms of P(v) batch studies were modelled and
57 discussed. Only Xu et al. (2022) have also calculated the thermodynamic parameters for the
58 sorption process.

59 Unfortunately, although the misuse of linearized kinetic, isotherm or thermodynamic
60 equations, was pointed out in several papers, they seem to have been very often read but only
61 rarely used. This is the case in the paper by Xu et al. (2022), when the nonlinear data
62 treatments were privileged by Sleiman et al. (2016).

63 To complete this comparative work, we must also mention a different paper, published almost
64 simultaneously by Kalaitzidou et al. (2022), which describes the sorption of P(v) on various

65 Fe(III) oxyhydroxides, either commercial or synthesized in the laboratory. According to the
66 respective dates of publication for Kalaitzidou et al. (2022) (05 April 2022) and submission
67 for Xu et al. (2022) (10 May 2022), it seems that the latter authors could not have been aware
68 of this newly published article, which is also considered here.

69 In this Discussion paper, we will mainly comment on (i) the similarities and differences
70 between these three papers; (ii) the erroneous use of linearization in sorption studies.

71 However, we would like to emphasize at the outset that these critical comments do not
72 undermine the scientific value of the works by Xu, Zhu and Xiong or by Kalaitzidou,
73 Zouboulis and Mitrakas.

74

75

76 **2 Discussion**

77

78 2.1 Experimental part

79 2.1.1 *Preparation and solid-state characterization of sorbents*

80 It is not surprising that for the studies considered here, solid Fe(III) oxyhydroxide materials
81 were prepared by methods derived from those described by Schwertmann and Cornell in their
82 famous book (Schwertmann & Cornell, 1991; Cornell & Schwertmann, 2003). However, it
83 should be noted in passing that this widely known and used work is misquoted by Xu et al.
84 (2022) who refer to a ‘book review’ of the 1991 edition, and also by Sleiman et al. (2016)
85 who give two different citations from the two editions, each time referring only to the name of
86 the first author (their references 27 and 33).

87 More specifically, it is noted that Xu et al. (2022) prepared different samples of goethite α -
88 FeOOH, akageneite β -FeOOH and lepidocrocite γ -FeOOH with slightly different recipes,
89 whereas Kalaitzidou et al. (2022) used mainly commercial samples of akageneite, goethite

90 and a binary iron(III)/manganese(IV) oxyhydroxide (Fe-MnOOH), and also samples of
91 schwertmannite $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n \text{H}_2\text{O}$ and lepidocrocite prepared from Fe(II) sulphate
92 thanks to an oxidation-precipitation reaction. The case of Sleiman et al. (2016) is more
93 original: while working mainly on the removal of P(v) by zero-valent iron (ZVI), they
94 decided to compare the behavior of the experimentally obtained iron oxidation byproducts
95 with that of genuine iron oxides or oxyhydroxides, such as magnetite Fe_3O_4 ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$),
96 maghemite $\gamma\text{-Fe}_2\text{O}_3$, goethite and lepidocrocite.
97 In **Table 1**, we have summarized all the useful information about the solid-state
98 characterization methods applied by each research team, as well as the experimental
99 conditions for studying the sorption of phosphate on these solid sorbents.
100 To go into more details, Sleiman et al. (2016) characterized the obtained ZVI oxidation
101 byproducts with XRD and FTIR, which allowed them to discover mainly lepidocrocite.
102

103

104 **Table 1.** Comparison of the three studies of P(v) sorption onto Fe(III) oxyhydroxides (more detailed information could be found in the
 105 corresponding original papers).

106

	Xu et al., 2022	Sleiman et al., 2016	Kalaitzidou et al., 2022
Solid preparation ^a	L, G, A: modified from Cornell & Schwertmann	ZVI oxidation byproducts (= L) L, G: Cornell & Schwermann	G, A: commercial sorbing phases L: oxidation/precipitation reaction
Solid characterization	XRD, FESEM, FTIR	XRD, FTIR, Raman	None
pH_{pzc}	Zeta potential	Potentiometric and zeta potential	Potentiometric and zeta potential
P(v) analysis	Ammonium molybdate (700 nm)	Molybdate/ascorbate (880 nm)	Molybdate/SnCl ₂ (690 nm)
Kinetic studies	solid = 1.0 g/L; PO ₄ = 20 mg/L; NaNO ₃ 0.01 mol/L; T = 28°C; pH = (5; 7; 9)	solid = 1.5 g/L; PO ₄ = 10 mg/L; pH _{init} = 7.2; T = 20°C	solid = 200 mg/L; PO ₄ = 10 mg/L; pH = 7; T = (10; 20; 35) °C
Isotherm studies	solid = 1.0 g/L; PO ₄ = 2–50 mg/L; NaNO ₃ 0.01 mol/L; t = 24 h; pH = 7; T = 28°C	solid = 1.5 or 1 g/L; PO ₄ = 2–20 or 2–100 mg/L; t = 24 h; pH = (4.2; 7.2; 9.2); T = 20°C	solid = 75–350 mg/L; PO ₄ not given; t = 24 h; pH = 7; T = (10; 20; 35) °C
Thermodynamic parameters	Yes (T = 15; 25; 35; 45 °C)	None (only at T = 20°C)	Yes (T = 10; 20; 35 °C)
Loaded solids analysis	FTIR, XPS	FTIR, Raman	None

107

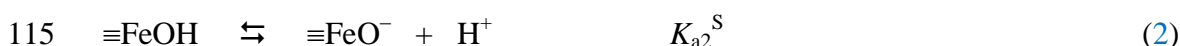
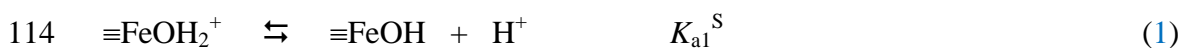
108

^a L = lepidocrocite ; G = goethite ; A = akageneite

109

110 2.1.2 *pH at the point of zero charge (pH_{pzc} or PZC)*

111 It is now well established that, when pH changes in the surrounding solution, oxides and
112 hydroxides undergo changes in their surface charges, due to surface
113 protonation/deprotonation reactions:



116 where $\equiv\text{FeOH}$ represents an Fe atom on the solid surface with its hydroxyl group. Various
117 ligands (including anions such as P(V) species) can then interact with these surface charges to
118 form surface coordination complexes at the solid/water interface (Stumm et al., 1980; Sigg &
119 Stumm, 1981). The potentiometric determination of solid surface charges allowed to easily
120 obtain the point of zero charge (pH_{pzc} or PZC) where the solid sorbent in aqueous suspension
121 has a global zero charge; taking into account the electroneutrality of the solid surface, one can
122 demonstrate that:

$$123 \text{pH}_{\text{pzc}} = \frac{\text{p}K_{a1}^S + \text{p}K_{a2}^S}{2} \quad (3)$$

124 Therefore, the solid is expected to be positively charged at pH < pH_{pzc} and negatively charged
125 at pH > pH_{pzc}.

126 The behavior of surface charges on a solid can also be determined from zeta potential
127 measurements, leading to the ‘isoelectric point’ IEP; due to different physicochemical
128 processes, one often finds some discrepancies between the two values, pH_{pzc} and IEP.

129 Recent critical compilations (Kosmulski, 2016, 2018, 2020, 2021, 2023) report the values
130 obtained for different samples of Fe(III) oxyhydroxides, for which one can choose the
131 following ranges for either pH_{pzc} or IEP (which show a generally consistent agreement): 7.5–
132 9.7 for goethite, 6.4–7.2 for akageneite and 7.4–7.7 for lepidocrocite. As the presently
133 discussed papers are concerned, it should be noted that all three used both the potentiometric

134 titration method and zeta potential measurements for their samples. However, Kalaitzidou et
135 al. (2022) did not report the values obtained, and Sleiman et al. (2016) performed their
136 measurements only on the by-products of ZVI oxidation. As for Xu et al. (2022), if all their
137 zeta potential results are given in their Figure 5b, one can only question their comment that
138 “the pH_{pzc} of five isomeric FeOOH adsorbents were about 4.0”, because if this is true for
139 akageneite and one of their goethite samples, one can read from this Figure 5b the value pH_{pzc}
140 ≈ 4.5 for lepidocrocite and for their other goethite sample. However, these values seem to
141 contradict those reported above.

142 In any case, it seems to us that in the discussed papers, the surface charge status of the studied
143 oxyhydroxides under the experimental pH conditions is somewhat confused.

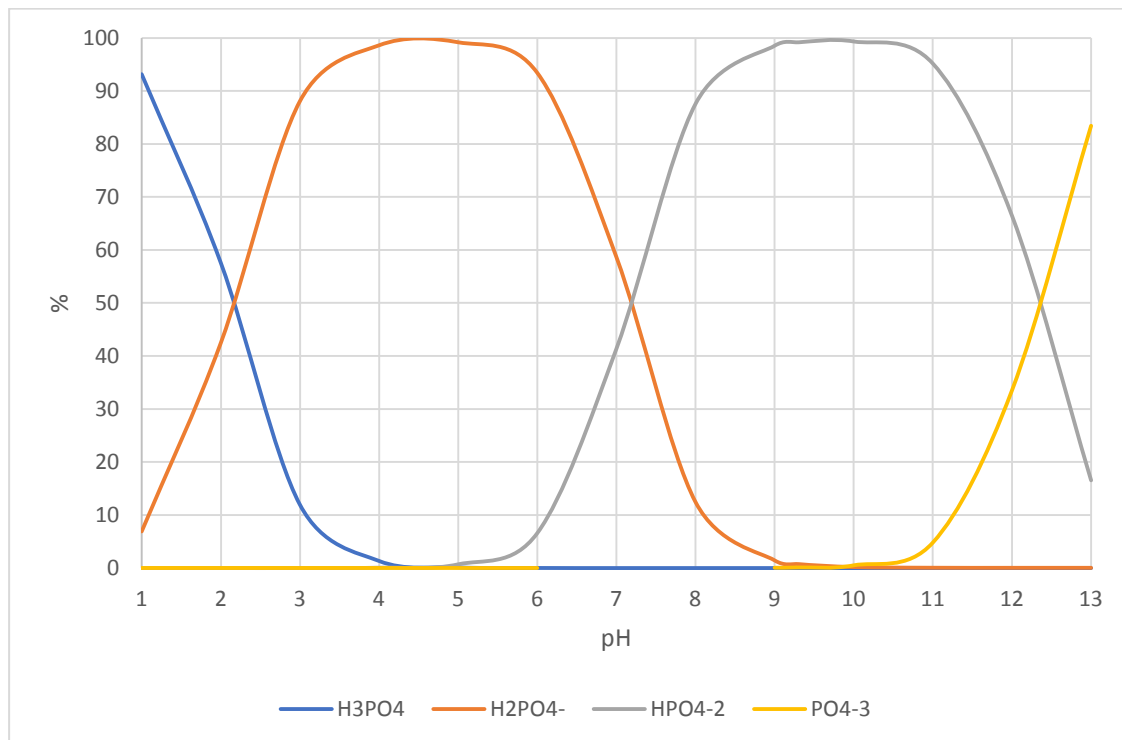
144 2.1.3 *P(v) analysis*

145 Sleiman et al. (2016) determined the concentration of P(v) with the official colorimetric
146 method ISO-6878:2004(E) (ISO, 2004; it is identical to the standard methods recommended
147 by US-EPA and APHA), based on the blue complex obtained from the ascorbic acid
148 reduction of 12-molybdophosphoric acid (Nagul et al., 2015; Worsfold et al., 2016; Zhu
149 & Ma, 2020); the selected wavelength is $\lambda_{\text{max}} = 880$ nm. However, Xu et al. (2022) chose a
150 value of $\lambda_{\text{max}} = 700$ nm for their spectrophotometric analysis by their ‘ammonium molybdate’
151 method: therefore, their results can be assumed to be about 30% less sensitive than if
152 measured at 880 nm, as specified in the ISO standard subsections 4.4.3.2 and 4.4.3.3 (ISO,
153 2004). As far as the analytical method used by Kalaitzidou et al. (2022) is concerned, it is the
154 colorimetric method using SnCl_2 , with measurements at $\lambda_{\text{max}} = 690$ nm.

155 On the other hand, it should be remembered that inorganic P(v), although measured and
156 expressed as ‘ $\text{PO}_4 \text{ g L}^{-1}$ ’ does not exist as this species in the pH range of common waters
157 (Figure 1). Thus, although the solutions of Sleiman et al. (2016) have a fixed $\text{pH} = 7.2 = \text{pK}_{\text{a}2}$
158 where $[\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}] = 50\%$, for Xu et al. (2022) at $\text{pH} = 7.0$ the speciation is

159 calculated as $[\text{H}_2\text{PO}_4^-] = 61.3\%$ and $[\text{HPO}_4^{2-}] = 38.7\%$. When other pH values are chosen for
 160 their kinetic studies, the discrepancies are even more significant: at pH = 5.0, $[\text{H}_2\text{PO}_4^-] =$
 161 99.3% , $[\text{HPO}_4^{2-}] = 0.6\%$ and $[\text{H}_3\text{PO}_4] = 0.1\%$; at pH = 9.0, $[\text{HPO}_4^{2-}] = 98.4\%$, $[\text{H}_2\text{PO}_4^-] =$
 162 1.6% and $[\text{PO}_4^{3-}] = 0.04\%$ (**Figure 1**). Kalaitzidou et al. (2022) also worked at pH = 7.0,
 163 either in distilled water (buffered with BES) or in artificial natural water reconstituted
 164 according to a National Sanitation Foundation (NSF) standard, where the speciation of P(v)
 165 was calculated and given in their Figure 1; from our own calculations with the software
 166 *Visual-MINTEQ 3.1* (Gustafsson, 2021), we obtained: $[\text{H}_2\text{PO}_4^-] = 45.8\%$, $[\text{HPO}_4^{2-}] = 38.5\%$,
 167 $[\text{CaHPO}_4(aq)] = 7.7\%$ and $[\text{MgHPO}_4(aq)] = 5.6\%$.
 168 It will then be difficult to compare these sorption experiments with each other because the
 169 composition of the solutions will be very different.

170
171
172



173
174 **Figure 1.** Calculated speciation diagram of P(v) as H₃PO₄ (T = 298 K; I = 1.10⁻³ mol L⁻¹).
175

176

177 2.2 Sorption data treatment

178

179 Here we will mainly focus on the treatment of data from sorption experiments; authors and
180 readers can then be reminded of the general advice previously given in the literature (Tran et
181 al., 2017; Hubbe, 2022; Pourret et al., 2022). In particular, unlike Kalaitzidou et al. (2022)
182 who performed their experiments in triplicates and Sleiman et al. (2016) who worked with
183 duplicated measurements, Xu et al. (2022) should have added information on the number of
184 replicates for all experiments (including preparation of the solid sorbent materials and the
185 determination of the P(v) concentration), and hence the corresponding standard deviation.
186 Consequently, all figures with experimental data points should include their respective error
187 bars, for example when plotting the sorbed amount q_t ($\text{mg}\cdot\text{g}^{-1}$), defined in Equation (4):

$$188 \quad q_t = \frac{(C_0 - C_t) \times V}{m} \quad (4)$$

189 where C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial concentration of P(v) in solution, C_t ($\text{mg}\cdot\text{L}^{-1}$) is the
190 concentration of P(v) at time t (min), m (g) is the dry mass of the sorbent, and V (L) is the
191 volume of the P(v) solution.

192 In addition, Xu et al. (2022) chose to represent the fundamental kinetic and isotherm
193 equations in a linearized manner, although it is well known that such a data handling can
194 greatly alter the values of the resulting parameters, sometimes leading to poor results from
195 correct data (González-López et al., 2022). This problem arises because transformations of
196 nonlinear equations into linear forms implicitly change their error structure and may also
197 violate standard least-squares error variance and normality assumptions. Today, with the
198 general availability of personal computers, this is no longer necessary.

199 2.2.1 Kinetic modelling

200 The first part of any sorption study involves kinetic experiments and their data processing.
201 The most common models are the pseudo-first-order (PFO or Lagergren model) and the
202 pseudo-second-order (PSO): as mentioned above, Xu et al. (2022) used the linearized forms:

$$203 \quad \ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \quad (5)$$

$$204 \quad \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2} \quad (6)$$

205 but Kalaitzidou et al. (2022) were satisfied only by the PSO linearized model. In these
206 Equations (5) and (6), respectively, k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the corresponding
207 rate constants. It should be noted that these units were not given in the paper by Xu et al.
208 (2022) with their corresponding equations, and that the unit for k_1 in their Table 1 is wrong:
209 $\text{g} \cdot \text{min}^{-1}$ instead of min^{-1} .

210 In fact, several recent studies (Simonin, 2016; Lima et al., 2021; González-López et al., 2022)
211 have emphasized that nonlinear regression (NLLS) is more appropriate than linear regression
212 to obtain the correct parameters of kinetic models. Therefore, in the present case, we should
213 replace the linear regression analyses from Equation (5) and Equation (6) above with the full
214 nonlinear $q_t = f(t)$ forms of the PFO and the PSO Equations (7) and (8), respectively:

$$215 \quad q_t = q_e \cdot [1 - \exp(-k_1 \cdot t)] \quad (7)$$

$$216 \quad q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \quad (8)$$

217 Consequently, in the discussed paper (Xu et al., 2022) the contents of their Figure 1(d, e)
218 should be deleted and those of their Table 1 should be changed to new values calculated from
219 the NLLS method; as for Kalaitzidou et al. (2022), for similar reasons, the data in their Table
220 4 should also be deleted and recalculated.

221 However, on their side, Sleiman et al. (2016) correctly applied the nonlinear kinetic Equations
222 (7) and (8) to describe their results. Although the experimental conditions in these three
223 papers were very similar (see the compiled data in our **Table 1** above), the three research

224 teams obtained contradictory results: for Xu et al. (2022) and for Kalaitzidou et al. (2022), the
 225 better model is the PSO (erroneously attributed to Lagergren by the first group of
 226 researchers), but the PFO was chosen by Sleiman et al. (2016). In fact, it was shown by Lima
 227 et al. (2021) that although experimental data from a large number of kinetic results from the
 228 literature were better fitted to the linear PSO model, more than 50% of these data were better
 229 fitted to the nonlinear PFO model; furthermore, it was also shown that high values of R^2 in
 230 linear fitting are not a good statistical tool for establishing a kinetic model.
 231 Since the computational methods for handling experimental sorption kinetic data are different
 232 (and in some cases not in accordance with good practice), it is therefore difficult to derive
 233 useful information about the actual type of kinetics taking place (PFO or PSO), which is
 234 shown in our **Table 2**.

235 2.2.2 Isotherm modelling

236 Similarly, of course, for the Langmuir isotherm equation (original linearized equation in the
 237 paper by Xu et al., 2022):

$$238 \quad \frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \quad (9)$$

239 the nonlinear form

$$240 \quad q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (10)$$

241 is also better to apply here (Tran et al., 2017; González-López et al., 2022). However, if the
 242 Freundlich isotherm equation (original equation for Xu et al., 2022)

$$243 \quad q_e = K_F \cdot C_e^{1/n} \quad (11)$$

244 is correctly nonlinear, its data treatment was obtained as the linearized form, as shown in their
 245 original Figure 2c (Xu et al., 2022).

246 **Table 2.** Comparison of the parameters calculated in the studied papers for P(V) sorption onto some selected Fe(III) oxyhydroxides samples:
 247 Kinetics.

248

	Xu et al., 2022	Sleiman et al., 2016 ^a	Kalaitzidou et al., 2022
Data treatment	linear	non-linear	linear
Temperature	28°C	20°C	20°C
pH	7	7.2	7 (buffered)
Goethite sample	synthetic	synthetic	commercial (Bayoxide)
<i>PFO model^b</i>			
q_e (mg PO₄/g solid)	6.19 ; 5.90	No data	Not studied
k₁ (min⁻¹)	3.1×10^{-3} ; 3.1×10^{-3}	No data	
<i>PSO model^c</i>			
q_e (mg PO₄/g solid)	6.26 ; 5.87	4.2	No data
k₂ (g mg⁻¹ min⁻¹)	4.5×10^{-3} ; 10.5×10^{-3}	0.9	No data
Lepidocrocite sample	synthetic	synthetic	synthetic
<i>PFO model^b</i>			
q_e (mg PO₄/g solid)	5.70	No data	Not studied
k₁ (min⁻¹)	3.2×10^{-3}	No data	
<i>PSO model^c</i>			
q_e (mg PO₄/g solid)	5.66	6.09	No data
k₂ (g mg⁻¹ min⁻¹)	8.7×10^{-3}	3	No data

249

250 *a* original data given as mg P have been changed to mg PO₄

251 *b* our equation (7)

252 *c* our equation (8)

253 **Table 3.** Comparison of the parameters calculated in the studied papers for P(V) sorption onto some selected Fe(III) oxyhydroxides samples:
 254 Isotherms.

255

	Xu et al., 2022	Sleiman et al., 2016 ^a	Kalaitzidou et al., 2022
Data treatment	linear	non-linear	linear
Temperature	28°C	20°C	20°C
pH	7	7.2	7 (buffered)
Goethite sample	synthetic	synthetic	commercial (Bayoxide)
<i>Langmuir model^b</i>			
q_{max} (mg PO₄/g solid)	8.09 ; 6.56	6.48	18.7
K_L (L mg⁻¹)	0.396 ; 1.270	0.603	15.64
<i>Freundlich model^c</i>			
K_F^d	3.02 ; 4.51	4.03	17.2
1/n	0.273 ; 0.104	0.1	0.109
Lepidocrocite sample	synthetic	synthetic	synthetic
<i>Langmuir model^b</i>			
q_{max} (mg PO₄/g solid)	7.36	9.6	41.7
K_L (L mg⁻¹)	0.713	1.3	13.3
<i>Freundlich model^c</i>			
K_F^d	3.60	5.20	36.6
1/n	0.211	0.13	0.101

256

257 *a* original data given as mg P have been changed to mg PO₄

258 *b* our equation (10)

259 *c* our equation (11)

260 *d* unit for K_F is (mg PO₄/g solid)/(mg PO₄/L)^{1/n}

261 Again, we believe that their original Figure 2(b, c) could be deleted, as the direct isotherm
262 curves $q_e = f(C_e)$ in their Figure 2a are sufficiently informative. In addition, the parameters
263 given in their original Table 2 should be recalculated using the NLLS method; then the
264 authors could better discuss their results in comparison with the available literature. Although
265 the Langmuir isotherm seems to better describe their experimental data (R^2 parameter close to
266 1), this seems to be in contradiction with their Figure 2a where no plateau is apparent at
267 higher C_e values (Xu et al., 2022).

268 In the study by Kalaitzidou et al. (2022), overall the Freundlich isotherm seems to describe
269 the experimental data better than the Langmuir model, regardless of the solid sorbent, the
270 aqueous medium (distilled water or NSF water) or the temperature (283K; 293K or 308K),
271 see their Table 4 and their Figure S1 (in their Supplementary Materials file).

272 For their part, Sleiman et al. (2016) correctly treated their data with the nonlinear forms of the
273 Langmuir (Equation (10) above) and Freundlich models; however, it should be noted that they
274 introduced the Freundlich exponent as n , not $1/n$ as in Xu et al. (2022) and in our Equation
275 (11) above.

276 Given the comments above, it is therefore difficult to compare the results of these three
277 studies, which is highlighted in our **Table 3**. In fact, the q_{\max} values obtained by Xue et al.
278 (2022) and Sleiman et al. (2016) are in a similar range, whereas the values obtained by
279 Kalaitzidou et al. (2022) are two to four times higher.

280 2.2.3 Thermodynamic parameters

281 Thermodynamics is often considered as an essential part of the discussion of the mechanism
282 of sorption experiments; therefore, correct basic knowledge and calculations must be
283 emphasized.

284 The calculation of the thermodynamic parameters for P(v) sorption on the solid Fe(III)
285 oxyhydroxide sorbents is, of course, based on the classical thermodynamic relationships:

286 $\Delta G^\circ = \Delta H^\circ - RT\Delta S^\circ$ (12)

287 $\Delta G^\circ = -RT \ln(K_{Eq}^0)$ (13)

288 where ΔG° ($\text{kJ}\cdot\text{mol}^{-1}$) is the standard Gibbs energy change, ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$) and ΔS° ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) are the standard enthalpy and entropy changes, respectively; R ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the universal gas constant, T (K) is the absolute temperature and K_{Eq}^0 (dimensionless) is the thermodynamic equilibrium constant for the process under consideration.

292 Starting from Equation (13), it is now possible to calculate all the thermodynamic equilibrium parameters using the famous van't Hoff equation. The *linear* form of the van't Hoff equation:

294 $\ln K_{Eq}^0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$ (14)

295 (as applied by Xu et al., 2022 and by Kalaitzidou et al., 2022) may be acceptable when the number of experimental points is small, as is the case in the original papers (data at only 4 or 3 temperatures, respectively); however, it is important to remember that this linearization artificially maximizes the calculated confidence in the estimated parameters, although the *nonlinear* adjustment (Lima et al., 2019; Lima et al., 2020)

300 $K_{Eq}^0 = \exp\left[\frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R}\right) \times \frac{1}{T}\right]$ (15)

301 is obviously more representative of the true results (González-López et al., 2022). Finally, in any case, the comments in the original papers on the sign, magnitude and significance of the thermodynamic parameters should be moderated with reference to Salvestrini et al. (2014).

304 However, contrary to the claim of Xu et al. (2022), the distribution coefficient K_c calculated from their equation noted:

306 $K_c = C_{Ae} / C_e$ (16)

307 cannot be considered as the sorption equilibrium constant, as pointed out by Tran (2022a); according to their original quotations, “ C_e and C_{Ae} (mg/L) are the equilibrium concentrations of P in solution and on adsorbent, respectively”. But it should be remembered that the unit for

310 the concentration C_{Ac} of P(V) sorbed on the solid should be mg per g of solid (or, better, mol
311 per g of solid), not mg per L of solution; then, the unit for K_c becomes

$$312 \{K_c\} = \{\text{mg/L of solution}\} / \{\text{mg/g of solid}\} = \{\text{g of solid}\} / \{\text{L of solution}\} \quad (17)$$

313 Since one can only take the logarithm of a dimensionless parameter, when calculating an
314 equilibrium constant the only unit for the amount of substance should be mole (not g or mg or
315 anything else) before taking the logarithm of the thermodynamic equilibrium constant K°_{Eq}
316 (unitless). Although this should be a well-known topic (Salvestrini et al., 2014; Tran et al.,
317 2017; Lima et al., 2019; Tran et al., 2021), it is too often forgotten.

318 Therefore, it is impossible to introduce the distribution coefficient K_c defined in Equation (16)
319 into Equation (13) to calculate the thermodynamic parameters (Lima et al., 2019; Tran et al.,
320 2021), and the data published by Xu et al. (2022) in their original Figure 3 and Table 3 should
321 be considered as not significant, and likewise the authors' claim that “These results suggested
322 that P adsorption by five FeOOH adsorbents was endothermic, spontaneous, and random”
323 should be taken with caution, especially because Salvestrini et al. (2014) recalled that,
324 contrary to a current and erroneous claim, the sign of ΔG° cannot inform us about the
325 spontaneity of the process under non-standard conditions.

326 Sleiman et al. (2016), who only worked at one experimental temperature (20°C), were
327 therefore unable to calculate the thermodynamic parameters.

328 For Kalaitzidou et al. (2022), the information given in their paper seems to us somewhat
329 confusing, while they introduced an equilibrium sorption constant K_{ads} , “calculated from the
330 equilibrium constant of Langmuir K_L , when expressed as L/mol of phosphates”, but without
331 any other explanation about such a conversion of K_L to K_{ads} . Therefore, we prefer to give them
332 the benefit of the doubt and consider the data in their original Figure 2 and Table 3 as
333 acceptable. On the other hand, one can see from their Table 2 that the Freundlich model
334 seems to be more efficient in representing the experimental data: $R^2(\text{Freundlich}) >$

335 R^2 (Langmuir); that's why they should have used K_F (and not K_L) to calculate ΔG° . But it
336 should be noted that Tran (2022a) recently explained that K_F from Equation (11) cannot be
337 introduced into Equation (13) as the equilibrium constant, nor can it be transformed into any
338 useful value.

339

340 2.3 About the sorption mechanism

341

342 In order to fully describe the experimental data corresponding to the sorption of a chemical
343 species (here: phosphate ions) onto a solid (here: an iron(III) oxyhydroxide), it is important to
344 be able to identify the mechanism of this liquid/solid sorption process.

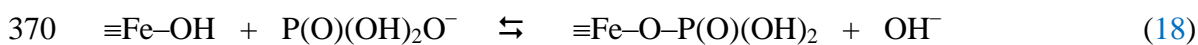
345 For this purpose, some scientific works have simply extrapolated some kinds of sorption
346 kinetics results; however, Tran (2022b) recently discussed that it is wrong to claim that a
347 pseudo-second-order or an Elovich kinetic equation would imply a chemisorption mechanism.
348 Similarly, it is often considered (as recalled in Tran et al., 2021) that the calculation of the
349 standard enthalpy of sorption allows to discriminate between chemisorption ($\Delta H^\circ \geq 200$
350 $\text{kJ}\cdot\text{mol}^{-1}$) and physisorption ($\Delta H^\circ \leq 60 \text{ kJ}\cdot\text{mol}^{-1}$), when the common range for ΔG° is (-80 to
351 $-400 \text{ kJ}\cdot\text{mol}^{-1}$) for chemisorption and (-20 to $0 \text{ kJ}\cdot\text{mol}^{-1}$) for physisorption (as cited by
352 Anastopoulos & Kyzas, 2016). In this case, it is clear that these considerations can be biased
353 if the calculations of the thermodynamic parameters are incorrect, as discussed above.

354 Whatever questions we may have about it, it is interesting to return to the comments of
355 Kalaitzidou et al. (2022) regarding their calculated thermodynamic parameters (their Table 3):
356 in distilled water, they obtained either endothermic or exothermic chemisorption or
357 physisorption of P(v), depending on the nature of the solid sorbent, although in the artificial
358 NSF water the process is mainly an endothermic physisorption. Their explanation seems

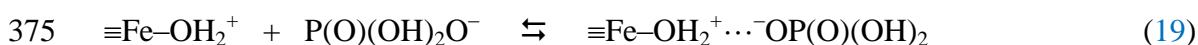
359 valuable, since in the latter case they considered the competitive influence of calcium
360 phosphate soluble complexes.

361 In fact, only advanced physicochemical and spectroscopic methods can provide access to the
362 types of surface bonds between P(v) and FeOOH; the more dedicated spectroscopic methods
363 for such a purpose are Fourier-Transform Infrared (FTIR), X-ray photoelectron (XPS), P and
364 Fe K-edge X-ray absorption near edge structure (XANES), Fe Mössbauer, ³¹P nuclear
365 magnetic resonance, and Raman spectroscopies.

366 After P(v) sorption on their ZVI oxidation byproduct (i.e.: mainly lepidocrocite), Sleiman et
367 al. (2016) observed that new peaks appeared in either the corresponding FTIR or Raman
368 spectra, clearly indicating the formation of *inner*-sphere complexes after an exchange between
369 the surface hydroxyl groups and the P(v) species (here represented as H₂PO₄⁻):



371 On the contrary, from the new FTIR peaks observed in P(v)-loaded FeOOH (in the case of
372 goethite and akageneite), Xu et al. (2022) claimed the formation of *outer*-sphere complexes
373 corresponding to electrostatic interactions between P(v) ions and the surface $\equiv\text{Fe}-\text{OH}_2^+$
374 species (appearing as described in our Equation (1) above):



376 But their XPS data for goethite rather suggested a surface exchange reaction like Equation
377 (18).

378 Thus, these two studies seem to be contradictory and the sorption mechanism of P(v) on
379 FeOOH is not clearly identified. However, it is reasonable to assume that both types of
380 complex formation (inner and outer) can occur simultaneously. Incidentally, it should be
381 noted that none of these articles has demonstrated or imagined the formation of a FePO_{4(s)}
382 precipitate from Fe(III) ions released by partial dissolution of FeOOH.

383

384

385 **3. Conclusion**

386

387 The removal of excess P(V) from aqueous media has long been an important issue, and in the
388 context of sustainable development its sorption on various types of iron ores has been
389 proposed, among others (Jørgensen et al., 2017; Ofoegbu, 2019; Wang et al., 2021; Xia et al.,
390 2023; Wang et al., 2024). While the use of Fe(III) oxides, hydroxides and oxyhydroxides has
391 been well documented in the scientific literature, here we have discussed several fundamental
392 errors and information omissions in a recent paper by Xu et al. (2022) and also in another
393 paper published simultaneously by Kalaitzidou et al. (2022). Furthermore, we have compared
394 their data and results with an older paper on the same topic (Sleiman et al., 2016).

395 However, a comparison of these three studies shows that their results are either not
396 comparable or very different (even contradictory), in particular because the experimental
397 conditions are different (temperature, pH, phosphate concentration range, amount of solid).
398 Thus, precise data on the behavior of P(V) sorption on Fe(III) oxyhydroxides remain to be
399 obtained.

400 Although many studies have already drawn attention to these all-too-common problems, we
401 unfortunately have to remind that the data treatment of sorption experiments should clearly
402 avoid the use of linearized model equations. This is the only way to obtain reliable and
403 accurate results.

404 It is of course important to emphasize that this ‘Discussion’ paper and its comments should be
405 read in the spirit in which they are intended, i.e. as constructive criticism to produce better
406 scientific papers in the future and to avoid the dissemination of unwanted and overlooked
407 errors in the scientific literature, as discussed for example in several recent critical papers
408 cited above.

409 Finally, we tried to speculate why the Sleiman et al. (2016) paper seems to have been ignored
410 by both Xu et al. (2022) and Kalaitzidou et al. (2022), even though it contains similar
411 experiments? It seems that this may be due to the fact that the main goal of Sleiman et al.
412 (2016) was to characterize the behavior of zerovalent iron oxidation byproducts during water
413 treatment for phosphate removal: thus the title of their paper and the corresponding keywords
414 did not sufficiently emphasize the studies (kinetics, isotherms) on the sorption of P(v) on
415 Fe(III) oxyhydroxides. It is therefore recommended that authors of scientific papers carefully
416 choose their title description and related keywords.

417

418 **Data availability** All data discussed in the present study are either present in the cited
419 papers, or available in the form of tables and/or figures.

420

421 **Statements and Declarations**

422 **Author contribution** All authors contributed equally to this study. All authors read and
423 approved the final manuscript.

424 **Funding** No funding was received to assist with the preparation of this manuscript.

425 **Financial interest** Authors have no relevant financial or non-financial interests to disclose.

426 **Conflict of Interest** The authors declare that they have no conflict of interest.

427

428 **References**

- 429 Anastopoulos, I., & Kyzas, G.Z. (2016). Are the thermodynamic parameters correctly
430 estimated in liquid-phase adsorption phenomena? *Journal of Molecular Liquids*, 218, 174–
431 185. <http://dx.doi.org/10.1016/j.molliq.2016.02.059>
- 432 Auvray, F., van Hullebusch, E.D., Deluchat, V., & Baudu, M. (2006). Laboratory
433 investigation of the phosphorus removal (SRP and TP) from eutrophic lake water treated

434 with aluminium. *Water Research*, 40, 2713–2719.
435 <https://doi.org/10.1016/j.watres.2006.04.042>

436 Cornell, R.M., & Schwertmann, U. (2003). *The iron oxides: structure, properties, reactions,*
437 *occurrences, and uses*; second edition. Wiley-VCH, Weinheim. ISBN:9783527302741.

438 de Barros, I.R., Benincá, C., & Zanoelo, E.F. (2023). Kinetics of the precipitation reaction
439 between aluminium and contaminant orthophosphate ions. *Environmental Technology*,
440 published online 16 August 2023. <https://doi.org/10.1080/09593330.2023.2246643>

441 González-López, M.E., Laureano-Anzaldo, C.M., Pérez-Fonseca, A.A., Arellano, M., &
442 Robledo-Ortíz, J.R. (2022). A critical overview of adsorption models linearization:
443 Methodological and statistical inconsistencies. *Separation & Purification Reviews*, 51,
444 358–372. <https://doi.org/10.1080/15422119.2021.1951757>

445 Gustafsson, J.P. (2021). Visual MINTEQ 3.0, a free equilibrium speciation model, v. 3.1.
446 KTH, Department of Land and Water Resources, Stockholm, Sweden. Freely
447 downloadable at: <http://vminteq.lwr.kth.se/download/>

448 Hubbe, M.A. (2022). Insisting upon meaningful results from adsorption experiments.
449 *Separation & Purification Reviews*, 51, 212–225.
450 <https://doi.org/10.1080/15422119.2021.1888299>

451 ISO (2004). International Standard ISO-6878. Water quality – Determination of phosphorus –
452 Ammonium molybdate spectrometric method (Second edition, 2004-06-01).

453 Jia, Y., Sun, S., Wang, S., Yan, X., Qian, J., & Pan, B. (2023). Phosphorus in water: A review
454 on the speciation analysis and species specific removal strategies. *Critical Reviews in*
455 *Environmental Science & Technology*, 53, 435–456.
456 <https://doi.org/10.1080/10643389.2022.2068362>

457 Jørgensen, C.A., Jensen, H.S., & Egemose, S. (2017). Phosphate adsorption to iron sludge
458 from waterworks, ochre precipitation basins and commercial ferrihydrite at ambient

459 freshwater phosphate concentrations. *Environmental Technology*, 38, 2185-2192.
460 <https://doi.org/10.1080/09593330.2016.1250819>

461 Kalaitzidou, K., Zouboulis, A., & Mitrakas, M. (2022). Thermodynamic study of phosphate
462 adsorption and removal from water using iron oxyhydroxides. *Water (Switzerland)*, 14,
463 1163. <https://doi.org/10.3390/w14071163>

464 Kosmulski, M. (2016). Isoelectric points and points of zero charge of metal (hydr)oxides: 50
465 years after Parks' review (Historical perspective). *Advances in Colloid & Interface Science*,
466 238, 1–61. <http://dx.doi.org/10.1016/j.cis.2016.10.005>

467 Kosmulski, M. (2018). The pH dependent surface charging and points of zero charge. VII.
468 Update (Historical perspective). *Advances in Colloid & Interface Science*, 251, 115–138.
469 <https://doi.org/10.1016/j.cis.2017.10.005>

470 Kosmulski, M. (2020). The pH dependent surface charging and points of zero charge. VIII.
471 Update (Historical perspective). *Advances in Colloid & Interface Science*, 275, 102064.
472 <https://doi.org/10.1016/j.cis.2019.102064>

473 Kosmulski, M. (2021). The pH dependent surface charging and points of zero charge. IX.
474 Update. *Advances in Colloid & Interface Science*, 296, 102519.
475 <https://doi.org/10.1016/j.cis.2021.102519>

476 Kosmulski, M. (2023). The pH dependent surface charging and points of zero charge. X.
477 Update. *Advances in Colloid & Interface Science*, 319, 102973.
478 <https://doi.org/10.1016/j.cis.2023.102973>

479 Lanet, P., Deluchat, V., & Baudu, M. (2021). Relevant design parameters for a reactor used in
480 P removal with ZVI-based materials. *Journal of Industrial & Engineering Chemistry*, 104,
481 8–21. <https://doi.org/10.1016/j.jiec.2021.08.005>

482 Le Moal, M., Gascuel-Oudou, C., Ménesguen, A., Souchond, Y., Étrillard, E., Levain, A.,
483 Moatar, F., Pannard, A., Souchu, P., Lefebvre, A., & Pinay, G. (2019). Eutrophication: A new

484 wine in an old bottle? (Review). *Science of the Total Environment*, 651, 1–11.
485 <https://doi.org/10.1016/j.scitotenv.2018.09.139>

486 Lima, E.C., Gomes, A.A., & Tran, H.N. (2020). Comparison of the nonlinear and linear forms
487 of the van't Hoff equation for calculation of adsorption thermodynamic parameters (ΔS°
488 and ΔH°). *Journal of Molecular Liquids*, 311, 113315.
489 <https://doi.org/10.1016/j.molliq.2020.113315>

490 Lima, E.C., Hosseini-Bandegharai, A., Moreno-Piraján, J.C., & Anastopoulos, I. (2019). A
491 critical review of the estimation of the thermodynamic parameters on adsorption equilibria.
492 Wrong use of equilibrium constant in the Van't Hoof equation for calculation of
493 thermodynamic parameters of adsorption. *Journal of Molecular Liquids*, 273, 425–434.
494 <https://doi.org/10.1016/j.molliq.2018.10.048>

495 Lima, E.C., Sher, F., Guleria, A., Saeb, M.R., Anastopoulos, I., Tran, H.N., & Hosseini-
496 Bandegharai, A. (2021). Is one performing the treatment data of adsorption kinetics
497 correctly? *Journal of Environmental Chemical Engineering*, 9, 104813.
498 <https://doi.org/10.1016/j.jece.2020.104813>

499 Moutin, T., Gal, J.Y., El Halouani, H., Picot, B., & Bontoux, J. (1992). Decrease of phosphate
500 concentration in a high rate pond by precipitation of calcium phosphate: Theoretical and
501 experimental results. *Water Research*, 26, 1445–1450. [https://doi.org/10.1016/0043-
502 1354\(92\)90063-A](https://doi.org/10.1016/0043-1354(92)90063-A)

503 Nagul, E.A., McKelvie, I.D., Worsfold, P., & Kolev, S.D. (2015). The molybdenum blue
504 reaction for the determination of orthophosphate revisited: Opening the black box
505 (Review). *Analytica Chimica Acta*, 890, 60–82.
506 <https://dx.doi.org/10.1016/j.aca.2015.07.030>

507 Ofoegbu, S.U. (2019). Technological challenges of phosphorus removal in high-phosphorus
508 ores: Sustainability implications and possibilities for greener ore processing (Review).
509 *Sustainability*, 11, 6787. <https://doi.org/10.3390/su11236787>

510 Pourret, O., Bollinger, J.-C., Hursthouse, A., & van Hullebusch, E.D. (2022). Sorption vs
511 adsorption: The words they are a-changin', not the phenomena (Discussion). *Science of the*
512 *Total Environment*, 838, 156545. <http://dx.doi.org/10.1016/j.scitotenv.2022.156545>

513 Schwertmann, U., & Cornell, R.M. (1991). *Iron oxides in the laboratory: Preparation and*
514 *characterization*. Wiley-VCH, Weinheim, New York. ISBN: 3.527. 26991.6.

515 Salvestrini, S., Leone, V., Iovino, P., Canzano, S., & Capasso, S. (2014). Considerations
516 about the correct evaluation of sorption thermodynamic parameters from equilibrium
517 isotherms. *Journal of Chemical Thermodynamics*, 68, 310–316.
518 <https://doi.org/10.1016/j.jct.2013.09.013>

519 Sigg, L., & Stumm, W. (1981). The interactions of anions and weak acids with the hydrous
520 goethite (α -FeOOH) surface. *Colloids & Surfaces*, 2, 101–107.
521 [https://doi.org/10.1016/0166-6622\(81\)80001-7](https://doi.org/10.1016/0166-6622(81)80001-7)

522 Simonin, J.P. (2016). On the comparison of pseudo-first order and pseudo-second order rate
523 laws in the modeling of adsorption kinetics. *Chemical Engineering Journal*, 300, 254–263.
524 <https://doi.org/10.1016/j.cej.2016.04.079>

525 Sleiman, N., Deluchat, V., Wazne, M., Courtin, A., Saad, Z., Kazpard, V., & Baudu, M.
526 (2016). Role of iron oxidation byproducts in the removal of phosphate from aqueous
527 solution. *RSC Advances*, 6, 1627–1636. <https://doi.org/10.1039/c5ra22444f>

528 Stumm, W., Kummert, R., & Sigg, L. (1980). A ligand exchange model for the adsorption of
529 inorganic and organic ligands at hydrous oxide interfaces. *Croatica Chemica Acta*, 53,
530 291–312.

531 Tran, H.N. (2022 *a*). Improper estimation of thermodynamic parameters in adsorption studies
532 with distribution coefficient K_D (q_e/C_e) or Freundlich constant (K_F): Considerations from
533 the derivation of dimensionless thermodynamic equilibrium constant and suggestions.
534 *Adsorption Science & Technology*, 2022, 5553212. <https://doi.org/10.1155/2022/5553212>

535 Tran, H.N. (2022 *b*). Is it possible to draw conclusions (adsorption is chemisorption) based on
536 fitting between kinetic models (pseudo-second-order or Elovich) and experimental data of
537 time-dependent adsorption in solid-liquid phases? *Recent Innovations in Chemical*
538 *Engineering*, 15, 228–230. <https://doi.org/10.2174/2405520416666221202085740>

539 Tran, H.N., Lima, E.C., Juang, R.S., Bollinger, J.C., & Chao, H.P. (2021). Thermodynamic
540 parameters of liquid–phase adsorption process calculated from different equilibrium
541 constants related to adsorption isotherms: A comparison study. *Journal of Environmental*
542 *Chemical Engineering*, 9, 106674. <https://doi.org/10.1016/j.jece.2021.106674>

543 Tran, H.N., You, S.J., Hosseini-Bandegharai, A., & Chao, H.P. (2017). Mistakes and
544 inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical
545 review. *Water Research*, 120, 88–116. <https://doi.org/10.1016/j.watres.2017.04.014>

546 Wang, Q., Liao, Z., Yao, D., Yang, Z., Wu, Y., & Tang, C. (2021). Phosphorus
547 immobilization in water and sediment using iron-based materials: A review. *Science of the*
548 *Total Environment*, 767, 144246. <https://doi.org/10.1016/j.scitotenv.2020.144246>

549 Wang, S.-X., Huang, Y.-X., Wu, Q.-F., Yao, W., Lu, Y.-Y., Huang, B.-C., & Jin, R.C. (2024).
550 A review of the application of iron oxides for phosphorus removal and recovery from
551 wastewater. *Critical Reviews in Environmental Science & Technology*, 54, 405–423.
552 <https://doi.org/10.1080/10643389.2023.2242227>

553 Worsfold, P., McKelvie, I., & Monbet, P. (2016). Determination of phosphorus in natural
554 waters: A historical review. *Analytica Chimica Acta*, 918, 8–20.
555 <https://dx.doi.org/10.1016/j.aca.2016.02.047>

556 Xia, L., Vangansbeke, A., Lauryssen, F., & Smolders, E. (2023). Screening redox stability of
557 iron rich by-products for effective phosphate immobilisation in freshwater sediments.
558 *Journal of Environmental Management*, 337, 117728.
559 <https://doi.org/10.1016/j.jenvman.2023.117728>

560 Xu, S., Zhu, S., & Xiong, H. (2022). Phosphate adsorption removals by five synthesized
561 isomeric α^- , β^- , γ^- FeOOH. *Water Air & Soil Pollution*, 233, 454.
562 <https://doi.org/10.1007/s11270-022-05916-y>

563 Zheng, Y., Wan, Y., Zhang, Y., Huang, J., Yang, Y., Tsang, D.C.W., Wang, H., Chen, H., &
564 Gao, B. (2023) Recovery of phosphorus from wastewater: A review based on current
565 phosphorous removal technologies. *Critical Reviews in Environmental Science &*
566 *Technology*, 53, 1148–1172. <https://doi.org/10.1080/10643389.2022.2128194>

567 Zhu, X., & Ma, J. (2020). Recent advances in the determination of phosphate in
568 environmental water samples: Insights from practical perspectives. *Trends in Analytical*
569 *Chemistry*, 127, 115908. <https://doi.org/10.1016/j.trac.2020.115908>

570
571