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Abstract: An extensive experimental work is reported that aims to assess the efficiency in manganese (Mn) removal from aqueous solution by carbonyl iron microparticles using magnetic separation techniques. A set of batch experiments are performed to explore the effect of pH, adsorbent concentration, surface coating and contact time for achieving the highest Mn removal efficiency. Mn removal efficiency is extremely high (> 98%) for pH values larger than 9 as a result of the chemisorption of Mn oxides onto magnetic microparticles. In contrast, Mn removal efficiency for pH < 9 was significantly reduced as Mn remains as a soluble cation. In this manuscript we demonstrate that the efficiency clearly increases when increasing the adsorbent concentration and when using MnO_x(s) coated magnetic particles instead of bare particles. Desorption rates from Mn-loaded magnetic particles at different pHs were always lower than 15%. Furthermore, Mn removal efficiency remained at a very high value (> 95%) when reused particles were employed in the adsorption process

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Dear Editor,

It is our pleasure to submit the manuscript entitled “*Manganese removal by magnetic microparticles for improving water quality*” for publication as an article in *Water Research*. This manuscript is authored by Ana Funes, Juan de Vicente, Luis Cruz-Pizarro and Inmaculada de Vicente. The data, analysis and conclusions of the manuscript represent original and unpublished work. We agree to cover any costs, if needed, associated with the publication of the manuscript in *Water Research*. Please, find enclosed a list with names and addresses of potential reviewers.

Thank you very much for your efforts in overseeing our manuscript through the review processes.

Looking forward to hear from you,

Sincerely yours,

Inmaculada de Vicente

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HIGHLIGHTS

- Magnetic techniques with iron microparticles are used for removing Mn from aqueous solution.
- Mn removal efficiency is extremely high (> 98%) for pH > 9.
- However for pH < 9 Mn removal efficiency was significantly reduced.
- An increase in the efficiency was observed when increasing the adsorbent concentration and when coating magnetic particles.
- Low desorption rates and high removal efficiency of reused particles were measured.

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2 **Article type:** Research article

3

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5

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26 **Abstract**

27 An extensive experimental work is reported that aims to assess the efficiency in
28 manganese (Mn) removal from aqueous solution by carbonyl iron microparticles using
29 magnetic separation techniques. A set of batch experiments are performed to explore the
30 effect of pH, adsorbent concentration, surface coating and contact time for achieving the
31 highest Mn removal efficiency. Mn removal efficiency is extremely high (> 98%) for
32 pH values larger than 9 as a result of the chemisorption of Mn oxides onto magnetic
33 microparticles. In contrast, Mn removal efficiency for $\text{pH} < 9$ was significantly reduced
34 as Mn remains as a soluble cation. In this manuscript we demonstrate that the efficiency
35 clearly increases when increasing the adsorbent concentration and when using $\text{MnO}_x(\text{s})$
36 coated magnetic particles instead of bare particles. Desorption rates from Mn-loaded
37 magnetic particles at different pHs were always lower than 15%. Furthermore, Mn
38 removal efficiency remained at a very high value (> 95%) when reused particles were
39 employed in the adsorption process.

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44 **Keywords:** Manganese removal, magnetic particle, water quality, magnetic separation
45 gradient

46

47 **Introduction**

48 Manganese (Mn) is a common trace metal in the earth's crust essential for the
49 metabolism (Aschner and Aschner, 2005). However, at high concentrations, Mn is a
50 neurotoxicant (Carrière et al., 2011) that can impair water quality intended for human
51 consumption. Mn is usually found in water supplies due to natural processes that take
52 place in the aquatic ecosystem such as dry deposition of pollutants, transport of
53 materials by surface runoff and groundwater inflow or dissolution of Mn-bearing
54 sediments (Zaw and Chiswell, 1999). During thermal stratification period in eutrophic
55 lacustrine aquatic ecosystems, oxygen concentration at the hypolimnion is reduced due
56 to microbial oxidation of the organic matter . When hypoxic conditions are present (<16
57 % oxygen saturation) at the sediment/water interface, redoxcline moves upwards in
58 sediment column and Mn reduces to the soluble ion Mn(II) that goes into solution
59 (Balzer, 1982; Baden et al., 1995). Thus, Mn(II) can enter to the water supply network
60 where is oxidized -in contact to the air (Aziz and Smith, 1992), metal surfaces (Davies
61 and Morgan, 1989; Sung and Morgan, 1981), microorganisms or chemical products
62 used for disinfection (Sly, 1990), before or after water treatment- to its insoluble form
63 causing undesirable aesthetic, cosmetic and technical effects (Environmental Protection
64 Agency, EPA, 1992). Some of these effects are the accumulation of Mn oxides
65 (MnOx(s)) deposits within distribution pipelines, staining of laundry and clothes or the
66 addition of unpleasant metallic taste when concentrations are above $100 \mu\text{g L}^{-1}$ (Roccaro
67 et al., 2007; Bamforth et al., 2006; Tekerlekopoulou et al., 2008). Moreover, it has been
68 reported that a chronic exposure to Mn can pose a threat for human health, specifically;
69 it may induce to neurological diseases, like manganisme, a Parkinson's-like disorder
70 (Elsner and Spangler, 2005).

71

72 Mn concentration in drinking waters broadly ranges from 1 to 100 $\mu\text{g L}^{-1}$, being more
73 usual values below 10 $\mu\text{g L}^{-1}$ (Keen and Lonnerdal, 1986). In the European framework,
74 the Directive 98/83/CE that regulates drinking water quality sets a maximum Mn
75 concentration of 50 $\mu\text{g L}^{-1}$. This value is similar to the Secondary Maximum
76 Contamination Level (SMCLs) established by the EPA as a guideline for water
77 treatment industry (EPA, 2012). On the other hand, World Health Organization (WHO)
78 suggests a health-based value of 400 $\mu\text{g L}^{-1}$ at which there is no adverse effects for
79 human health (WHO, 2011). Nowadays, a large number of water resources all over the
80 world are being affected by Mn concentrations that exceed 400 $\mu\text{g L}^{-1}$ such as Greece,
81 Japan or Australia, among others (Frisbie et al., 2012).

82

83 In order to meet the quality standards for drinking water, a wide variety of physical and
84 chemical methods, or combinations of both of them, have been employed to reduce Mn
85 concentration of polluted waters. Since Mn remains as soluble cation in a wide pH
86 range (4.5 to 8) it is a difficult and costly process to remove it from solution (Bamforth,
87 2006). Up to now, natural adsorbents have been used, including activated carbons
88 (Jusoh et al., 2005; Emmanuel and Veerabhdra Rao, 2009), zeolites (Taffarel and
89 Rubio, 2009; Erdem et al., 2004) and kaolinites (Yavuz et al., 2003). On the other hand,
90 the oxidation of Mn(II) as MnOx(s) onto oxide – coated filter media, such greensand (a
91 MnO₂-coated commercial clay) and the use of strong oxidizing chemicals like
92 potassium permanganate, ozone, chlorine or dioxide chlorine for oxidation and
93 precipitation of Mn with subsequent filtration are common techniques used in water
94 treatment plants (Gantzer et al., 2009; Kohl and Medlar, 2006). Finally, biological
95 treatments usually involve the use of Mn-oxidizing bacteria coated beds that promote
96 Mn biofiltration under oxic conditions and its removal from the solution (Pacini et al.,

97 2005; Burguer et al., 2008; Tekerlekopoulou et al., 2008). Most of these techniques are
98 not profitable since in many cases exists high operational cost, insufficient adsorption
99 capacity, difficulties of separation and regenerations of the adsorbents or formation of
100 undesirable by-products that can alter water quality (Yong-Mei et al., 2010;
101 Katsoyiannis et al., 2004).

102

103 In recent years, the application of magnetic particles for removing contaminants from
104 the aqueous effluents has attracted special attention (Ngomsik et al., 2005). This
105 technology involves the separation of the adsorbent (magnetic particles) from the
106 medium in which is immersed by applying a gradient magnetic separation, once the
107 contaminant is adsorbed on its surface. Magnetic field generated by a magnet exerts a
108 force on magnetic particles proportional to the volume of the particles, magnetic
109 susceptibility of the particles, magnetic induction and magnetic field strength (de
110 Vicente et al., 2010; Merino-Martos et al., 2011). A recent example of the application of
111 this innovative technology is the use of magnetic particles for Phosphorous (P) removal
112 from aqueous solutions, the main cause of eutrophication (de Vicente et al., 2010). In
113 this study, authors reported a high efficient removal process (> 80%) in a wide pH range
114 (5-9). Other authors have used functionalized magnetic nanoparticles as adsorbents for
115 the removal of heavy metals such as Cu^{+2} , Hg^{+2} , Cd^{+2} , Ag^{+} , Ni^{+2} , Pb^{+2} from the aqueous
116 solution (Huang and Chen, 2009; Yong-Mei, 2010; Song et al., 2011; Ge et al, 2012) or
117 for the extraction of trace metals present in biological samples with excellent results
118 (Huang and Hu, 2008). In particular, Song et al. (2011) studied the kinetic of adsorption
119 of Mn on polyrhodanine-coated magnetic nanoparticles at pH 4 (initial Mn
120 concentration was 80 mg L^{-1}). These authors evidenced that Mn adsorption mechanism
121 was quite fast as equilibrium state was reached within just 2 hours.

122

123 For making best use of magnetic particles, and in particular, for guaranteeing the
124 colloidal stability of the particles in the medium and for preventing their degradation in
125 contact to oxygen or other chemicals, magnetic particles are frequently coated with
126 organic or inorganic core-shell structures or dispersed in polymers-containing matrices
127 such as silica or carbon (Lu et al., 2007). Moreover, shells provide the ability to
128 functionalize the magnetic particles by specific ligands such as catalysts or special
129 functional groups that enhance the affinity with the adsorbate (Philippova et al., 2011;
130 Zhang et al., 2011). MnOx(s) minerals occur as coating or fine-grained aggregates in
131 soils and aquatic ecosystems and play an important role in chemical reactions (Post,
132 1999). They are thought to be important resources for metalloids immobilization by
133 mechanisms as adsorption or surface precipitation (della Puppa et al., 2013). MnOx(s)
134 have a large surface area and a low pH_{pzc} (2.8 - 4.5) which result in a negative surface
135 charge in a wide range of environmental conditions (Posselt et al., 1968; Feng, 2007).

136

137 Therefore, magnetic separation of precipitated Mn could be considered as a promising
138 technology for water quality treatment. Among the most outstanding advantages of
139 using these particles, it can be suggested: (i) high adsorption capacity due to high
140 specific surface of the adsorbents, (ii) easy and efficient recovery of the adsorbents from
141 the solution due to magnetic properties, minimizing alterations of water quality, (iii) the
142 reusability of the adsorbents contributing to economic cost savings (iv) the possibility to
143 functionalize the particles for specific purposes (de Vicente et al., 2010; Singh et al.,
144 2011; Zhang et al., 2011). Even more, due to their advantages as cation adsorbents, we
145 hypothesize that covering the surface of magnetic particles with MnOx(s) can be an
146 excellent optimization strategy for Mn removal from aqueous solutions.

147

148 In this context, the main aim of this study was to assess the suitability of using bare and
149 $\text{MnO}_x(\text{s})$ coated magnetic particles for Mn adsorption and its subsequent removal from
150 aqueous solution by applying a high gradient magnetic separation technique. For this
151 purpose, a set of batch experiments were carried out in order to determine the optimum
152 conditions (e.g. pH and contact time) for an efficient Mn removal. In addition, the Mn
153 desorption from Mn-loaded magnetic particles, at different pH, and the reusability of
154 magnetic particles was tested.

155

156 **Materials and Methods**

157 **3.1 Materials**

158 Iron (Fe) microparticles were supplied by BASF SE (grade CC, Germany) and used as
159 adsorbents. The bulk composition of the particles consists essentially of iron (more than
160 99.5 %). All chemicals were obtained from Panreac (Spain), except Mn stock solution
161 ($\text{Mn}(\text{NO}_3)_2$) which was supplied by Merck (Germany). All suspensions were prepared
162 by using deionized and filtered water (Milli-Q Academic, Millipore, France).

163

164 **3.2 Characterization of magnetic particles**

165 A LEO Gemini 1530 field-emission scanning electron microscope (FESEM) was used
166 to estimate the size and morphology of the bare magnetic particles. The samples were
167 prepared by drying a drop of a magnetic dispersion onto a glass substrate. After that, a
168 thin coating of carbon was applied. To elucidate whether Mn is oxidized and/or
169 adsorbed onto bare magnetic particles surface after an adsorption experiment at pH 9,
170 surface morphology and qualitative chemical composition of the particles after
171 adsorption tests was investigated using an Auriga Cross Beam (FIB)[®] workstation (Carl

172 Zeiss SMT, Inc.) adapted to a field emission high resolution scanning electron
173 microscope (FESEM) and equipped with energy-dispersive X-ray analysis (EDX)
174 (INCA 300, Oxford Instruments). Spectra were obtained in a range of 0 – 20 keV.
175 Quantitative chemical composition of magnetic particles surface (before and after
176 adsorption tests) was analyzed using a Kratos Axis Ultra-DLD X-ray photoelectron
177 spectrometer. The wide spectrum (pass energy of 160 eV) and individual spectra (pass
178 energy of 20 eV) were obtained using an electrostatic lens. The samples were prepared
179 for a microscopic inspection immediately after an adsorption experiment. Adsorption
180 experiments typically comprised a 1 g L⁻¹ of bare magnetic particles stock suspension
181 and 100 mg L⁻¹ of Mn stock solution that are then mixed at pH 9. After adsorption of
182 Mn, samples were dried for 24 h at 60 °C and analyzed.

183

184 The magnetization measurements of the bare magnetic particles were carried out at
185 room temperature (25 °C ± 5° C) as a function of the applied external magnetic field
186 strength with a QuantumDesign (San Diego, CA) MPMS-XL5.0 Tesla Magnetometer.
187 The external field was swept from -1500 to 1500 kA/m.

188

189 Electrophoretic mobility of bare magnetic particles was determined using a zetameter
190 (Zetasizer Nano Z, Malvern instruments, Germany) at 25 °C ± 5 °C using the Laser
191 Doppler Micro-electrophoresis technology. Briefly, suspensions with bare magnetic
192 particles and 3 mM NaHCO₃ were first agitated with an orbital shaker for 24 h at the
193 desired pH value. After this time, pH value was readjusted just before measurement and
194 the suspensions were made up to 50 mL of volume. To minimize sedimentation of
195 magnetic particles under gravity, prior to the test, the samples were sonicated for 5

196 minutes. Each mobility data point reported in this work is the average of three
197 measurements in the course of 10 to 40 “runs”.

198

199 **3.3 Preparation of magnetic colloidal dispersions**

200 The stock dispersion of bare magnetic particles was prepared by adding 5 g of Fe
201 particles to 100 mL of Milli-Q water, obtaining a final concentration of 50 g L⁻¹ of
202 magnetic particles. This stock suspension was thoroughly sonicated for 5 min to
203 minimize colloidal aggregation and sedimentation under gravity.

204

205 Dispersions of MnOx(s) coated magnetic particles were also formulated. For this
206 purpose, a volume of 1 mL of bare magnetic particles stock suspension (50 g L⁻¹) were
207 shaken (150 rpm, in a horizontal shaker) for 24 h with 3 mM NaHCO₃ at room
208 temperature 25 °C ± 5 °C. 2 mL of Mn stock solution (1000 mg L⁻¹) was added to the
209 suspension and pH value was adjusted to pH = 9 with 1N NaOH. After 24 h of
210 agitation, pH was readjusted and suspension was made up to 50 mL of volume. The
211 appearance of black-brown precipitates indicated presence of MnOx(s) (Lloyd et al.,
212 1983). A magnetic separation gradient of approximately 12400 kAm⁻² (PASCO
213 scientific; EM-8641) was applied to the suspension for 5 min and all the supernatant
214 was removed. MnOx(s) loaded magnetic particles were washed twice with 1N NaOH
215 and 3 times with 3mM NaHCO₃. MnOx(s) coated magnetic particles were then dried in
216 an oven at 60 °C for 24 h and stored.

217

218 **3.4 Kinetic stability of magnetic suspensions**

219 Turbidity measurements were performed using a Turbiscan MA 2000 (Formulation,
220 Toulouse, France) in order to investigate the formation of MnOx(s) precipitates in

221 solution and the kinetic stability of iron suspensions. In a typical essay, the dispersion is
222 placed in a cylindrical plastic cell which is scanned from the bottom to the top with an
223 incident near infrared light source ($\lambda_{\text{air}} = 850 \text{ nm.}$). A transmission sensor (180° from the
224 incident radiation) receives the light transmitted through the sample and, a
225 backscattering sensor (45° from the incident radiation) detects the light backscattered by
226 the sample, obtaining transmission and backscattering data every 40 μm (Wulff-Pérez et
227 al., 2009). Turbiscan software provides curves that correspond to transmission data as a
228 function of sample height (mm) at a certain time. The measurements are repeated over
229 time, resulting in several overlaid curves that provide information about the stability of
230 dispersion over time. Measurements consisted in analyzing the optical transmission of
231 the samples at different conditions (presence or absence of magnetic particles and Mn)
232 and at different pH values (7 and 9).

233

234 **3.5 Oxidation and adsorption experiments**

235 To determine Mn oxidative removal by O_2 (that is, in the absence of magnetic particles),
236 the following experiment was carried out at room temperature ($25 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$). 0.1 mL of
237 a Mn stock solution (1000 mg L^{-1}) was mixed with 40 mL of 3mM NaHCO_3 and pH
238 value was adjusted in the range of 6-10 by adding 1N NaOH or HCl. The solution was
239 left under shaking (150 rpm, in a horizontal shaker) for 24 h (after that time, black-
240 brown precipitates indicated the presence of MnOx(s) in solution) and pH value was
241 readjusted. Suspension was made up to 50 mL of volume and left to sediment for 5
242 minutes. After that, the supernatant was pipetted off and filtered (Whatman GFF) to be
243 analyzed for Mn concentration following the spectrophotometric procedure using 1-(2-
244 pyridyl-azo)-2-naphthol (PAN) colorimetric method, which is a slight modification of

245 that proposed by Goto et al. (1977). Finally, Mn oxidative removal only by O₂ was
246 calculated as follows:

247

$$248 \quad Mn_R(\%) = \frac{C_o - C_e}{C_o} 100 \quad (1)$$

249

250 where C_o is Mn initial concentration (mg L⁻¹) and C_e is Mn equilibrium concentration
251 (mg L⁻¹), that is, at the end of shaking time.

252

253 The effect of pH on Mn removal/adsorption by bare magnetic particles was tested in
254 batch mode at room temperature. To achieve this goal, adsorption experiments were ran
255 as follows: (i) A mixture of 1 mL of magnetic particles stock solution (50 mg L⁻¹) and
256 40 mL of 3 mM NaHCO₃ was shaken (150 rpm) for 24 h. (ii) 0.1 mL of Mn stock
257 solution was added to the magnetic suspension and pH was adjusted to different values
258 (6-10) by adding 1N NaOH or HCl. Suspensions were shaken (150 rpm) for 24 h. After
259 that time, pH was readjusted and made up to 50 mL of volume with 3 mM NaHCO₃.
260 (iii) Magnetic separation was later carried out for each magnetic suspension. It consisted
261 on applying a magnetic field gradient for 5 min (PASCO scientific; EM-8641) (de
262 Vicente et al., 2010). Supernatant was pipetted off and filtered to measure Mn
263 concentration in solution with the above mentioned spectrophotometric procedure. The
264 similar methodology was repeated for different pHs in the range from pH 6 to pH 10.
265 The efficiency of Mn removal process by magnetic particles, Mn_R , is defined as the
266 relationship between adsorbed Mn concentration and initial Mn concentration according
267 to equation (1).

268

269 The kinetics of the adsorption process by bare magnetic particles at pH = 9 was also
270 measured in order to determine the necessary time to reach the equilibrium conditions at
271 room temperature. For such study, firstly, 1 mL of magnetic particles stock solution (50
272 mg L⁻¹) was immersed into 40 mL of 3mM NaHCO₃ and shaken for 24 h. Later, 2 mL
273 of Mn stock solution (1000 mg L⁻¹) were added (making a Mn final concentration of 40
274 mg L⁻¹) and pH value was adjusted to 9. All suspensions were left for shaking (150 rpm)
275 during different contact times: 1, 2, 5, 10 and 24 h, and the volume was made up to 50
276 mL with 3mM NaHCO₃. A magnetic field gradient was applied for 5 min and Mn
277 concentration was determined as previously mentioned. Mn adsorbed per unit amount
278 of adsorbent, q (mg g⁻¹), was estimated using the following expression:

279

$$280 \quad q = \frac{C_o - C_e}{M_a} V \quad (2)$$

281

282 where M_a is the mass of adsorbent in grams (in our case, 0.05 g of magnetic particles)
283 and V is the total volume of suspension (L).

284

285 To ascertain the influence of adsorbent concentration (bare magnetic particles) in Mn
286 removal and adsorption capacity, q , different volumes (2 and 4 mL) of a magnetic
287 particles stock suspension (50 g L⁻¹) were put in contact with a Mn concentration of 2
288 mg L⁻¹ in the pH range of 7-9 as in a typical adsorption experiment. Afterwards, a
289 magnetic separation gradient was applied and Mn concentration was determined.

290

291 The effect of pH on Mn removal by MnOx(s) coated magnetic particles was studied as
292 follows: a suspension of 1 g L⁻¹ of MnOx(s) coated magnetic particles was left under

293 shaking (150 rpm) with 40 mL of 3mM NaHCO₃ for 24 h. Afterwards, 0.1 mL of a
294 manganese stock solution (1000 mg L⁻¹) was added and pH value was adjusted in the
295 range from pH 6 to pH 9 with 1N NaOH. After 24 h stirring, pH value was readjusted
296 and the suspension was made up to 50 mL. Finally, a magnetic separation gradient was
297 applied and Mn concentration was measured.

298

299 **3.6 Desorption study**

300 Desorption of Mn from the iron particles was also investigated. For this purpose, firstly,
301 an adsorption experiment with 1 g L⁻¹ of magnetic particles and 100 mg L⁻¹ Mn was
302 carried out at pH 9. Magnetic particles were later separated from the solution by
303 applying a magnetic field gradient and the supernatant was extracted. After the
304 adsorption experiment, recovered magnetic particles (with adsorbed Mn) were left for
305 shaking with 40 mL 3mM NaHCO₃ during 24 h. Then, pH was adjusted to different
306 values (6, 7, 8 and 9) and suspensions were shaken for 24 h. Once pH value was
307 readjusted, suspensions were made up to 50 mL with 3mM NaHCO₃. After application
308 of magnetic field gradient, Mn concentration was measured in the supernatant as it was
309 described in section above. Percentage of desorbed Mn, d , was calculated with the
310 following expression:

311

$$312 \quad d(\%) = \frac{C_d}{C_i} 100 \quad (3)$$

313

314 where C_d represents desorbed Mn concentration and C_i is initial Mn concentration.

315

316 **3.7 Reusability of magnetic particles**

317 In order to evaluate the adsorption capacity of reused magnetic particles, an adsorption
318 experiment was carried out using an initial Mn concentration of 100 mg L⁻¹ at pH 9 and
319 at room temperature. Two different sets of desorption experiments were later
320 performed. In the first one, magnetic particles with adsorbed Mn were washed 2 times
321 with 1N NaOH and 3 times with 3mM NaHCO₃. The magnetic particles were dried at
322 60 °C for 24 h and then reused in a new adsorption experiment. In the second
323 experiment, magnetic particles with adsorbed Mn were directly reused, that is, without
324 washing the particles previously.

325

326 **3.8 Statistical analysis**

327 All experiments reported in this study were carried out in triplicates. Comparisons of
328 means were performed using one-way ANOVA test and then Tukey's HSD test was
329 applied, considering significant differences when $p < 0.05$. In order to verify ANOVA
330 assumptions, data were transformed to logarithmic in some cases. Shapiro-Wilk test to
331 check normality and a Bartlett's test to check homogeneity of variances were
332 performed. Statistical analysis was done using R software (R Development Core Team,
333 2012).

334

335 **Results and Discussion**

336 **4.1 Characterization**

337 A SEM image of the bare magnetic particles used in this work is shown in Figure 1a.
338 The micrograph shows that magnetic particles used as adsorbents are quasi-spherical in
339 shape and very polydisperse in size. The mean particle size is 3.8-5.5 µm as specified
340 by the manufacturer (BASF SE). Particle size has important implications for adsorption
341 capacity and magnetic separation techniques. Small particles have higher specific

342 surface area, and thus, more adsorption capacity than larger particles. However, for such
343 small particles it is necessary to apply a higher magnetic separation gradient. On the
344 other hand, large particles tend to sediment faster under gravity. Recently, it has been
345 reported in the literature that micron-sized iron particles present a reasonably large P
346 adsorption capacity and are easy to separate using conventional high gradient magnetic
347 separation techniques (de Vicente et al., 2010).

348

349 Bare magnetic particles (before adsorption test) are constituted of iron (> 97 %), as it
350 has been reflected by atomic absorption analysis of the bulk (data not shown). However,
351 other chemical elements (carbon, oxygen and nitrogen) are also present in smaller
352 amounts in the bulk (below 3 %) as a result of the thermal decomposition process that
353 was employed in the fabrication of the particles from pentacarbonyl iron. Table 1 shows
354 the surface chemical composition of the particles as obtained by XPS. Both, before and
355 after adsorption test, more than 80% of the surface chemical composition is represented
356 by C and O probably coming from surface oxidation and environmental “adventitious”
357 contamination.

358

359 The magnetization curve for bare magnetic particles used in this work is shown in
360 Figure 2. As observed in the figure, particles behave as soft magnetic materials with
361 negligible coercitive field and remnant magnetization; magnetization becomes zero
362 when removing the field. As a consequence, they are expected to be reutilized after
363 adsorption and accordingly, particles should easily redisperse when removing the
364 magnetic field.

365

366 Table 2 shows the electrophoretic mobility of the magnetic particles as a function of pH.
367 The results show that magnetic particles are negatively charged in the pH range studied
368 (pH = 6-10). Data reveal that the magnitude of the surface charge increases when
369 increasing pH value, as it is usual for inorganic oxides. Magnetic particles employed in
370 the present study exhibit an oxidized surface layer with amphoteric functional groups (-
371 OH) which determine the surface charge of magnetic particles depending on pH
372 (Hunter, 1993). As a consequence, it is expected that the electrokinetic properties of the
373 particles may play a role in the adsorption capacity.

374

375 **4.2 Manganese oxidative removal by O₂**

376 Because Mn oxidation by O₂, and its subsequent removal from the solution, may occur
377 within the pH range of interest in lakes ecology, it is important to assess the impact of
378 pH on Mn oxidation. Our results demonstrate a strong dependence of Mn removal on
379 pH values (see squares in Figure 3). Remarkably, up to 100% of Mn removal is
380 achieved for pH levels higher than 9, which is presumably due to the formation of large
381 precipitates that become entrapped by the filters employed in the adsorption process as
382 described in section 3.5. By contrast, significantly lower Mn removal efficiencies (<
383 20%) were obtained when pH was below 8.5.

384

385 Mn precipitation was also monitored by using turbidity measurements. In Figure 4 we
386 show the transmission profiles in reference mode (by subtracting the curve at time zero)
387 along the tube for different times up to 80 minutes. Figure 4a clearly shows that both
388 sedimentation and flocculation processes are occurring in Mn solutions at pH 9. The
389 sedimentation (gravity-driven particle migration) process is observed as a result of the
390 variations of the optical transmission profiles at the bottom and the top of the sample. In

391 other words, it is evidenced by an increase in the transmission at the top of the sample
392 due to a decrease of the concentration of the dispersed phase (clarification) and by a
393 concomitant decrease in the transmission at the bottom of sample (sedimentation). In
394 addition, the flocculation of the dispersed phase is manifested by an increase of optical
395 transmission (decrease of the backscattering) over the whole height of the sample. As a
396 way of illustration, Figure 4b shows the temporal variation in the transmission data (in
397 %), averaged in a middle height (between 15 mm and 25 mm from the bottom) of the
398 sample tube, at two different pH values (7 and 9). As it can be observed, temporal
399 changes in transmission were almost negligible at pH 7 in accordance with a stable
400 solution that is not aggregating. On the contrary, transmission values at pH 9
401 experienced a marked temporal increase from 5% to 50% after 60 min as a result of the
402 oxidation of dissolved Mn by O₂ and the eventual precipitation of the Mn oxides.

403

404 The oxidation of dissolved Mn by O₂ has been thoroughly studied by Hem (1981).
405 According to this author, under laboratory conditions Mn is oxidized by O₂ in the range
406 of pH 7-9 resulting in different Mn oxyhydroxides species which precipitate. The Mn
407 oxidation reaction is slow (but not negligible) when the pH value of the solution is < 9
408 (Sung and Morgan, 1981) and it becomes autocatalytic when pH is close to 9 (Kessic
409 and Morgan, 1975).

410

411 **4.3 Mn removal by bare iron microparticles**

412 Next, we aimed to evaluate the use of bare magnetic microparticles for Mn uptake from
413 aqueous solutions. The effect of pH on Mn removal, Mn_R , by bare magnetic particles is
414 shown in Figure 3 (circles) together with results from section 4.2 without magnetic
415 particles in solution. As it can be observed, Mn removal dramatically increased when

416 increasing pH. The same tendency in Mn uptake has been found by other authors when
417 using adsorbents with similar surface composition (iron oxides) such as lepidocrocite
418 (γ -FeOOH), akaganeite (β -FeOOH) and goethite (α -FeOOH) (Sung and Morgan, 1981;
419 Kanungo, 1994; Davies and Morgan, 1989; Stumm, 1993). No significant differences in
420 Mn removal were observed ($p > 0.05$) neither between pH 6 and 8 nor between pH 9
421 and 10; while significant differences were found between pH 8 and 9. Even more,
422 significant differences in Mn removal have been also detected between pH 8.5 and 9.
423 Such an abrupt increase in Mn removal in a narrow pH range (from 8.5 to 9) was
424 similar to that described in previous studies. In fact, Kanungo (1994) observed that Mn
425 removal increased from 0 to 90 % when pH increased in 0.2 units using akaganeite (β -
426 FeOOH), an iron oxihydroxide, as adsorbent in a 0.1 M KNO₃ solution. He also found
427 that the Mn removal efficiency was larger than 98% for pH higher than 9. Our results
428 were also consistent with those found by Han et al. (2012) who estimated a Mn uptake
429 by hematite of 98.2 % when pH was 8.66.

430

431 When comparing the Mn removal in the absence and in the presence of iron particles,
432 we can observe that the particle effect was negligible at pH 9, as Mn removal was close
433 to 100% in both cases and it strongly decreased for pH lower than 9 (c.f. Figure 3). We
434 found that only at pH 8.5, Mn removal was significantly higher in the presence of
435 magnetic particles than in the absence of these particles. An opposite tendency was
436 observed at pH 10, when a significantly higher Mn removal efficiency was measured in
437 the absence than in the presence of magnetic particles.

438

439 As a result of the striking differences in Mn removal efficiency depending on pH, next
440 we analyzed in more detail the adsorption mechanism at high pH (higher than 9) and at
441 intermediate pH (between 6 and 9).

442

443 ***4.3.1 Adsorption at high pH ($pH \geq 9$)***

444 As it was stated above, Mn ions precipitate in solution rather quickly at pH higher than
445 9. In fact, the kinetic isotherm has shown that Mn removal in the presence of bare
446 magnetic particles was extremely fast (see Figure 5). Hence, the precipitates do form in
447 less than 1 hour and so, the time period required for the system to reach equilibrium is
448 very short. These results are similar to those obtained by Song et al. (2011) when using
449 polyrhodanine-encapsulated magnetic nanoparticles for Mn adsorption at $pH = 4$. This
450 fast removal may be due to the catalytic and autocatalytic mechanisms of Mn oxidation
451 favoured by suitable pH conditions (see section above) and it represents an important
452 advantage for using magnetic particles as it makes the whole process less time-
453 consuming reducing economic costs.

454

455 The effect of the presence of bare magnetic particles on $MnOx(s)$ precipitation and
456 sedimentation process is shown in Figure 6. It represents the time evolution of the
457 sedimentation front H at a constant value of transmission for three different systems:
458 bare magnetic particles (squares); Mn solutions (circles) and magnetic particles
459 dispersed in Mn solutions (triangles). In all cases the sedimentation front experienced a
460 marked decrease over time reaching a constant value of $\approx 20\%$ after 10 min that is in
461 accordance with a sedimentation process. Importantly, remarkable differences among
462 the systems studied came up. On the one hand, the sedimentation of bare magnetic
463 particles occurred very fast. Actually, the iron particles started to sediment immediately

464 after positioning the tube in the Turbiscan device (in less than 1 min). On the other
465 hand, the sedimentation of MnOx(s) was the slowest and became noticeable after
466 approximately 5 minutes probably due to the lower density of the MnOx(s) precipitates
467 if compared to the iron particles. The turbidity results also evidenced that the
468 sedimentation rate of MnOx(s) was affected by the presence of bare magnetic particles.
469 Results suggest that magnetic particles may affect MnOx(s) precipitation in two
470 possible ways: Mn is precipitated on bare magnetic particles surface and sediment
471 together, or bare magnetic particles drag along MnOx(s) formed in solution towards the
472 bottom of the tube.

473

474 Davies and Morgan (1989) proposed an adsorption-oxidation model to explain the Mn
475 oxidation mechanism by O₂ on metal oxides surface that seems to be applied in our
476 case. In their model, Mn is firstly adsorbed on binding-sites (-OH) of oxide surfaces.
477 Then, Mn(II) adsorbed is oxidized as Mn (III) or Mn (IV) and precipitates on metal
478 oxides surface at neutral or alkaline conditions. Lloyd et al. (1983) found that Mn
479 oxidizes on iron oxides when pH is 8.5. These pH conditions are required since the
480 reaction of Mn oxidation is favorable at high pH values and very slow when pH values
481 are low. The catalytic effect of metal oxides surfaces on Mn oxidation process has been
482 reported in the literature (Davies and Morgan, 1989; Coughlin and Matsui, 1976;
483 Goldberg and Arrhenius, 1958; Wilson, 1981; Sung and Morgan, 1981). Some of these
484 authors have found that Mn oxidation rate by O₂ was increased by the presence of metal
485 oxides in the solution.

486

487 The magnetic particles may serve as a site for the oxidation of Mn and accordingly, they
488 promote a faster removal of Mn by the application of magnetic field gradients. This

489 process was expected from the negative charge of the iron particles as inferred from
490 electrokinetic measurements (Table 2), and it was also confirmed from SEM
491 micrographs combined with EDX analyses. In Figure 1b it can be observed a SEM
492 image where magnetic particles are clearly covered by MnOx(s) precipitated on their
493 surfaces. This finding is also reinforced by the results obtained by using EDX analysis
494 (Figure 7) which showed that large aggregates consisting only of overlapping MnOx(s)
495 layers were precipitated on preferential sites of magnetic particle surfaces. In addition,
496 quantitative chemical composition of magnetic particles after an adsorption experiment,
497 by using XPS technique, is presented in Table 1. The presence of high atomic
498 concentrations of Mn and O suggests the presence of important amounts of MnOx(s)
499 and support HRSEM-EDX results. These results are in agreement with those from Junta
500 & Hochella (1994) when studying Mn(II) oxidation on hematite surface. These authors
501 argued that Mn(II) adsorption-oxidation process occurs initially at the most reactive
502 sites of the adsorbent surface generating a thin layer. Once MnOx(s) are formed, these
503 sites become the most reactive sites (more than initial substrate) to continue the
504 adsorption-oxidation process (Lloyd et al., 1983) resulting in the continuous formation
505 of MnOx(s) layers. Since MnOx(s) precipitates growth is faster at the more reactive
506 sites, large aggregates of MnOx(s) can be formed by overlapping layers. The fact that
507 MnOx(s) surfaces accelerate Mn(II) oxidation process by O₂ (autocatalytic) has been
508 reported by Coughlin and Matsui (1976) and Morgan (2005). It must be pointed out that
509 the pH at which Mn adsorption begins is strongly dependent on the type of adsorbate
510 (Bleam and McBride, 1985).

511

512 A photograph of the experimental setup for a typical experiment at pH 9, is shown in
513 Figure 8, and demonstrates that most of the precipitates become attracted to the

514 magnets. This means that the majority of MnOx(s) (represented as black-brown
515 precipitates) were chemisorbed onto magnetic particles surfaces and retained by
516 magnetic separation gradient, and only a minor proportion was precipitated as MnOx(s)
517 in solution due solely to the oxidation by O₂. The reason behind this observation is that,
518 under these conditions (pH = 9; 100 mg Mn L⁻¹), Mn oxidation and precipitation occur
519 easier on surfaces oxides than in solution (Davies and Morgan, 1989).

520

521 In summary, we can conclude that at high pH values: (i) Mn removal mechanism
522 basically consisted in chemisorption in which adsorption capacity is continuously
523 regenerated due to the formation of MnOx(s) layers by autocatalytic oxidation. (ii)
524 There exist two types of possible adsorption surfaces, only if conditions of required pH
525 for Mn oxidation are suitable: magnetic particles and MnOx(s) surfaces. MnOx(s)
526 surfaces can be formed by adsorption and oxidation on magnetic particles surfaces or in
527 solution due to Mn oxidative removal by O₂.

528

529 ***4.3.2 Adsorption at intermediate pH levels (6 ≤ pH ≤ 9)***

530 For these intermediate pH values, Mn oxides form at a very low rate and they hardly
531 precipitate onto the magnetic particles at the studied concentration levels (c.f. Figures 3
532 and 4b). Nevertheless, the presence of magnetic particles resulted in a slight increase in
533 Mn removal at pH = 8.5 (see circles in Figure 3).

534

535 Therefore, in this section we aim to asses if increasing magnetic particles concentrations
536 may enhance Mn removal from aqueous solutions. In Figure 9 we show that Mn
537 removal remained low for pH ≤ 8 independently on iron concentrations. However, at pH
538 = 8.5, Mn removal increased when increasing iron concentration. In particular, our

539 results have shown that, at pH = 8.5, the percentages of Mn removal notably increased
540 when adding 2 g L⁻¹ (46%) instead of 1 g L⁻¹ (27%), while no significant differences in
541 Mn removal were observed between adding 2 and 4 g L⁻¹.

542

543 Also, we focused on identifying the optimum adsorbent doses, since it is an important
544 factor to maximize the interactions between the adsorbent and adsorbate (Zhou et al.,
545 2009). In Table 3, it is shown the effect of adsorbent concentration on Mn removal
546 efficiency (%) and adsorption capacity, q (mg g⁻¹) at pH 8.5. As observed, when
547 adsorbent concentration increased Mn removal efficiency (%) increased, but magnetic
548 particles adsorption capacity (q) decreased. An increase in adsorbent doses results in
549 higher removal efficiency due to an enhancement of available binding sites for Mn
550 adsorption-oxidation, but further increase in doses does not imply a significant increase
551 in Mn removal. The reduction in adsorption capacity can be due to the aggregation of
552 magnetic particles, resulting in a reduction of surface area and thus, the availability of
553 binding sites (Yong-Mei et al., 2010). Thus, our results may suggest that the product of
554 these two parameters (Mn removal × q) could be used to find out the optimum
555 concentration of adsorbent for achieving the highest efficiency. In our case, 2 g L⁻¹ of
556 magnetic particles is the most suitable concentration since it provides higher value for
557 Mn removal efficiency and adsorption capacity than the other concentrations.

558

559 **4.4 Adsorption of Mn by MnOx(s) coated iron microparticles**

560 In order to further increase Mn removal efficiency at pH values lower than 9, we tested
561 the effect of coating iron particles with MnOx(s). The main reasons for selecting
562 MnOx(s) as coating of iron particles were as follows: (i) MnOx(s) can enhance the
563 affinity between Mn and magnetic particles since they are highly selective surfaces for

564 Mn adsorption (Junta and Hochella, 1994) and (ii) MnOx(s) coatings remain as stable
565 precipitates on surfaces magnetic particles over a wide pH range, as it was described in
566 section 4.3.

567

568 In Figure 3, Mn removal by MnOx(s) coated magnetic particles is represented as a
569 function of pH. Our results show a very remarkable increase in Mn removal when
570 magnetic particles were coated with MnOx(s) compared to bare magnetic particles. As a
571 way of example, Mn removal efficiency was larger than 80% when pH was ≥ 7 and the
572 largest value ($> 90\%$) was achieved for pH 8 and 9. These results are in agreement with
573 those obtained by Taffarel and Rubio (2010) when using Mn oxide coated zeolite.
574 These authors found a Mn uptake close to 70% at pH 7 and 85% when pH was 8.

575

576 The significant enhancement in Mn removal efficiency when comparing MnOx(s)-
577 coated with bare magnetic particles can be due to the microporous structure of MnOx(s)
578 supplying a higher surface area and thus, more available surface binding sites (Taffarel
579 and Rubio, 2010). In addition, Junta and Hochella (1994) reported that MnOx(s) are
580 highly selective surfaces for Mn adsorption.

581

582 The progressive increase in Mn removal as the suspension becomes more alkaline can
583 be explained by an increase in the number of adsorption sites. In aqueous solution,
584 MnOx(s) present a hydroxylated surface whose charge is strongly pH dependent and a
585 pH_{pzc} (point of zero charge) between 2.0 and 4.5 (Kanungo and Parida, 1984; Posselt et
586 al., 1968). As pH value increases, surface negative charge increases due to
587 deprotonation of surface functional groups (-OH) and cations are attracted to the surface
588 by electrostatic forces. On the contrary, at low pH, dominant H^+ ions in solution occupy

589 the binding-sites of adsorbent resulting in a net positive surface charge that prevent
590 cation adsorption (Song et al., 2011; Sen et al., 2002; Huang and Chen, 2009).

591

592 **4.3 Desorption**

593 Batch desorption experiments were carried out to evaluate the effect of pH on Mn
594 desorption from Mn-loaded magnetic particles surfaces. Such study provides an
595 important insight into the reversibility of the adsorption process in a range of pH that
596 covers those found in natural waters. As observed in Figure 10, Mn desorption rate
597 increased when reducing pH value from 9 to 6. Significant differences ($p < 0.05$) were
598 observed in Mn desorption rate between pH 6 and 8 and pH 7 and 9. Nevertheless, it
599 must be pointed out that Mn desorption rate was always relatively low ($< 15\%$) even
600 when pH was near pH = 6. These results support the idea that MnOx(s) formed on
601 magnetic particles surface at pH 9 are stable complexes that hardly go back to solution
602 in a wide pH range. Similar results were found by Lloyd et al. (1983) when studying the
603 desorption of Mn previously oxidized at pH 8.5 and 9 from iron oxides. This finding
604 confirms the convenience of using magnetic particles for Mn removal from aqueous
605 solutions.

606

607 **4.4 Reutilization**

608 Finally, we study the possibility of reusing magnetic particles for Mn removal and so,
609 reducing economic investments. As it can be observed in Table 4, no significant
610 differences ($p > 0.05$) in Mn removal efficiency between bare magnetic particles and
611 reused magnetic particles neither with nor without previous washing were observed. In
612 fact, Mn removal efficiency was in all cases higher than 98%. Therefore, we can
613 conclude that there was not any reduction in Mn adsorption capacity of reused magnetic

614 particles even if the adsorbent was not washed. Again, this result is consistent with the
615 above mentioned continuous formation of MnOx(s) selective surfaces for Mn(II)
616 adsorption, which was supported by isotherm results, and HRSEM and EDX analysis.
617 However, it should be noted that the use of magnetic particles in successive removal
618 processes without washing may affect to magnetic properties of magnetic particles and
619 colloidal stability.

620

621 **Conclusions**

- 622 1. For pH values higher than 9, both in the presence and in the absence of bare
623 magnetic particles, Mn was removed from aqueous solution by an oxidation and
624 precipitation process with an efficiency of 98%. When particles are present,
625 most of the MnOx(s) were precipitated on magnetic particles surface and
626 therefore could be easily removed from solutions by magnetic field gradients.
627 Only a minor proportion of Mn was precipitated as MnOx(s) in solution due to
628 oxidation by O₂. At these pH values, Mn removal mechanism consists of two
629 steps: First, Mn adsorbs and oxidizes onto magnetic particles surfaces. Second,
630 MnOx(s) precipitated on adsorbent surface become the most reactive sites for
631 Mn adsorption and its subsequent oxidation, causing a continuous regeneration
632 of adsorption capacity. In addition, Mn can be adsorbed and precipitated onto
633 MnOx(s) formed in solution due to the oxidation by O₂.
- 634 2. For intermediate pH values (7-8.5), no effect of increasing adsorbent
635 concentration on Mn removal efficiency was observed, except for pH=8.5,
636 where an increase in adsorbent concentration from 1 to 2 g L⁻¹ caused an
637 increment in Mn removal from 27% to 46%. In fact, at this pH, our results
638 suggest that the product of Mn removal percentage and Mn adsorption capacity

639 (q) could be used as a proxy for finding out the optimum concentration of
640 adsorbent for achieving the highest efficiency (2 g L^{-1} of magnetic particles in
641 our case).

642 3. Apart from increasing magnetic particle concentration (which would cause more
643 economic cost), the use of $\text{MnO}_x(\text{s})$ -coated magnetic particles was the best
644 alternative for improving Mn removal efficiency at intermediate pH values (7-9)
645 evidenced that. In this sense, Mn removal efficiency was drastically improved at
646 all pH values, being higher than 80% for pH between 7 and 9.

647 4. Desorption experiments of Mn-loaded magnetic particles, at different pH values
648 (6-9), revealed that Mn adsorbed onto magnetic particles was a highly stable
649 compound. Accordingly, very low desorption rates (always lower than 15%)
650 were measured.

651 5. For economic reasons, the possibility of reusing magnetic particles for Mn
652 removal was explored. Our experimental results suggest that Mn removal
653 efficiency was very similar (and always higher than 98%) both when employing
654 bare magnetic particles and reused ones. These results were consistent with the
655 explanation provided for the Mn removal, that was based on the autocatalytic
656 adsorption-oxidation of Mn on magnetic particles.

657

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662

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Tables

Table 1. Surface chemical composition of bare magnetic particles before and after adsorption tests by XPS technique. Initial conditions: 1 g L⁻¹ of magnetic particles; 100 mg Mn L⁻¹; pH = 9.

Chemical element	Atomic concentrations (%)	
	Before adsorption test	After adsorption test
Fe	2.78	3.53
C	30.83	65.93
O	49.79	22.53
Si	6.70	1.27
Mn	0.00	6.74

Table 2. Electrophoretic mobility of bare iron particles as a function of pH value.

pH	Electrophoretic mobility ($\mu\text{m cm V}^{-1} \text{s}^{-1}$)	Standard Deviation
6	-2.446	0.010
6.5	-2.77	0.04
7	-3.01	0.05
8	-3.59	0.06
8.5	-3.73	0.08
9	-3.91	0.04
10	-4.22	0.07

Table 3. Mn removal (Mn_R) and adsorption capacity (q) as a function of magnetic particles concentration. 2 mg Mn L^{-1} ; $\text{pH} = 8.5$.

	Without particles	1 g L^{-1}	2 g L^{-1}	4 g L^{-1}
Mn_R (%)	15.81	27.37	46.28	50.78
q (mg Mn /g Fe)	-	0.60	0.50	0.27
$Mn_R \times q$	-	16.48	23.19	13.96

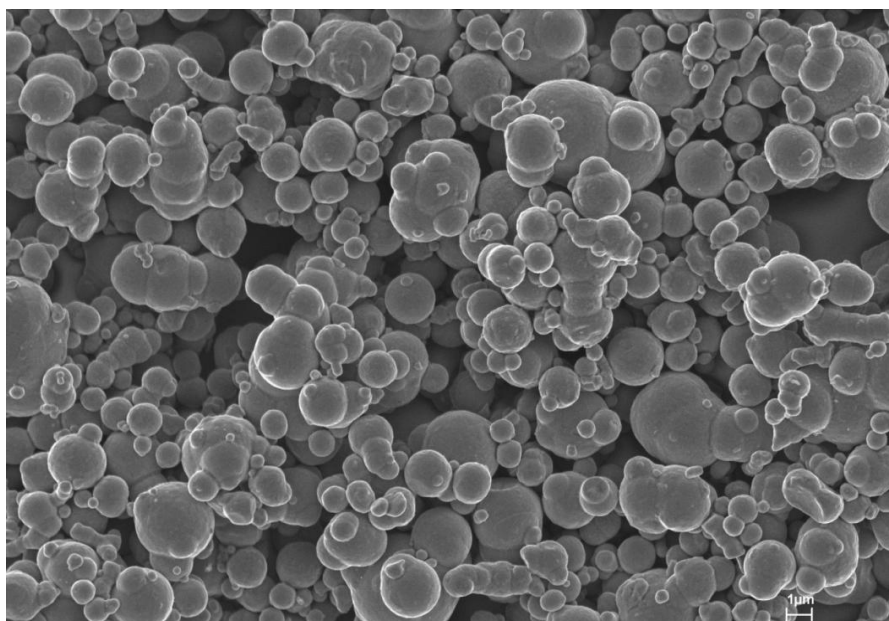
Table 4. Mn removal (Mn_R) by initial (bare) and reused particles (with and without washing). Initial conditions: 1 g L^{-1} magnetic particles; 100 mg Mn L^{-1} ; $\text{pH} = 9$.

	Mn_R (%)	Standard Deviation (%)
Initial Particles	98.96	0.66
Reused particles (with washing)	99.50	0.32
Reused particles (without washing)	99.38	1.04

Figures

Figure 1. HRSEM micrographs of magnetic particles. a) Magnetic particles before the adsorption experiment. b) Magnetic particles after Mn adsorption experiment. Initial conditions: 100 mg Mn L^{-1} ; $\text{pH} = 9$. Please, note that EDX analysis of Spectrum 1 and 2 regions are shown in Figure 7.

a)



b)

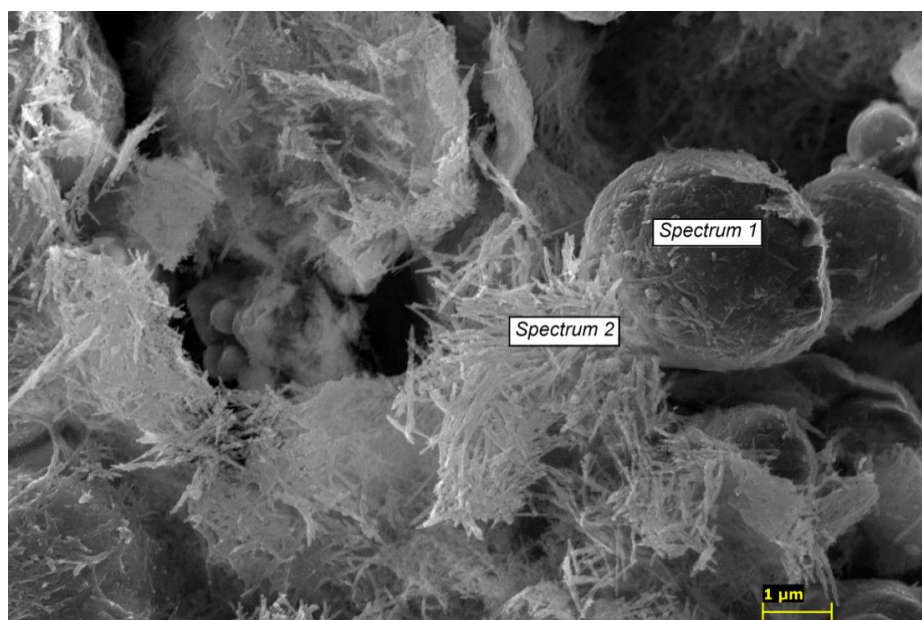


Figure 2. Hysteresis curve of the magnetic particles. M: particle magnetization, H: magnetic field strength.

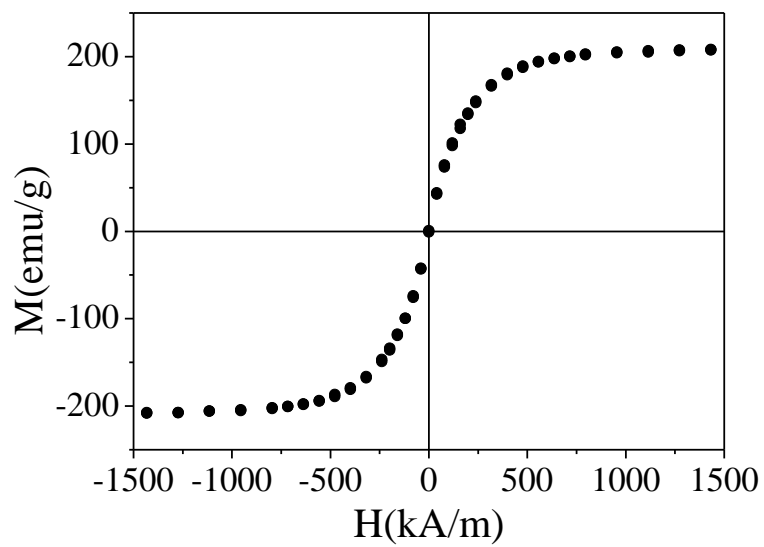


Figure 3. Effect of pH on Mn removal efficiency, Mn_R . The standard deviation is represented by vertical bars. Squares: without magnetic particles in suspension. Circles: with bare iron particles. Triangles: with MnOx(s) coated iron particles. Initial conditions: 1 g L^{-1} magnetic particles; 2 mg Mn L^{-1} . In both, with and without bare magnetic particles, Mn removal only takes place when Mn oxidizes, that occurs at pH higher than 9. By contrast, MnOx(s) coated iron particles clearly enhance Mn removal at all pH values.

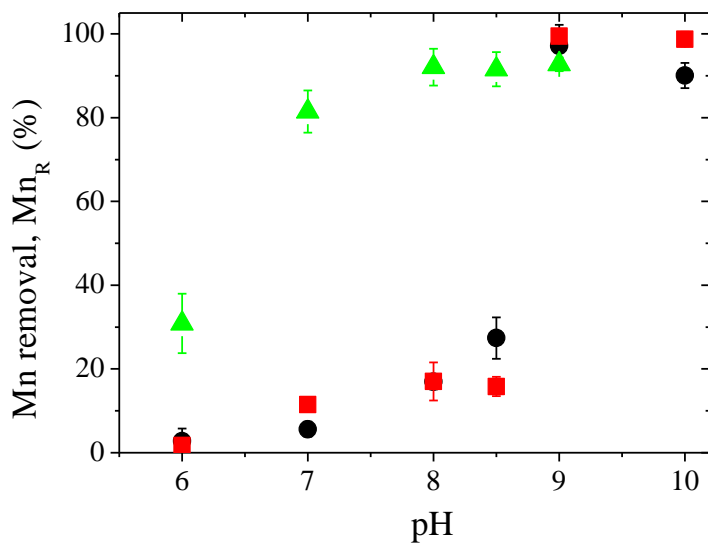
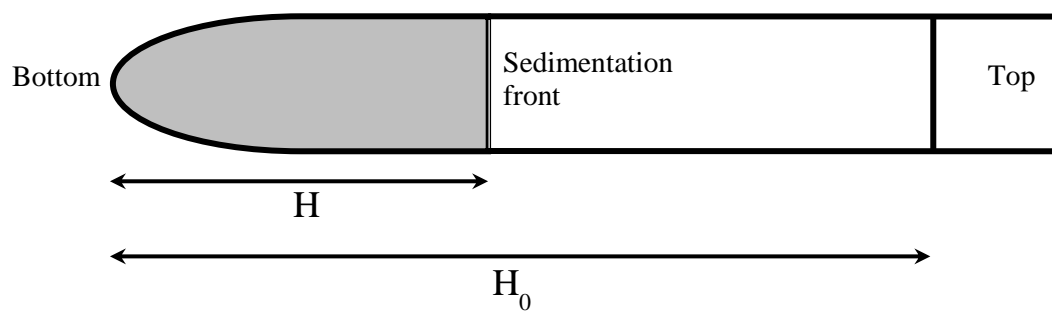
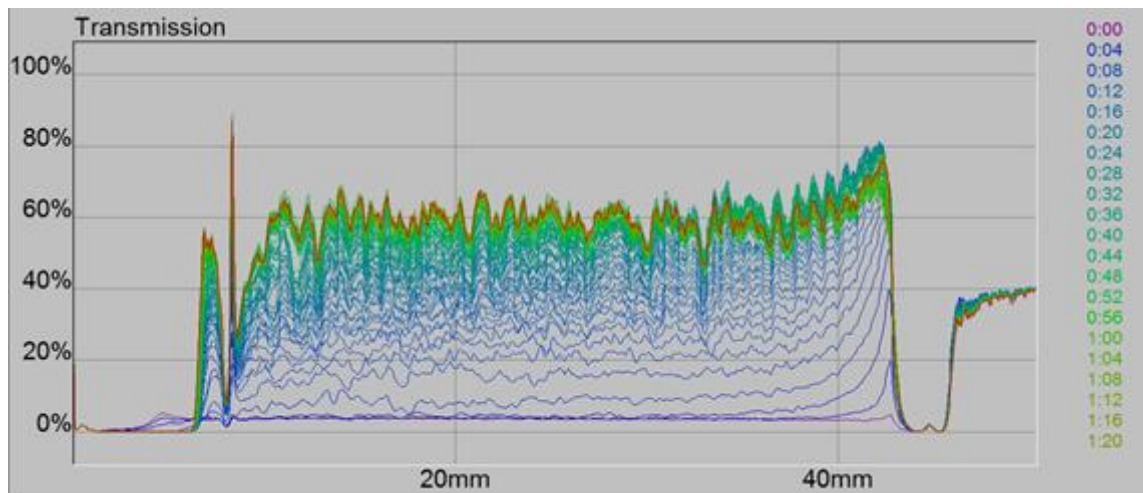


Figure 4. Turbidity measurements of Mn solutions (without particles). a) Transmission (%) as a function of the height of measuring cell (mm) in reference mode (subtracting the curve at time zero). Each curve represents a transmission measure every 4 minutes. Initial conditions: 400 mg Mn L⁻¹; pH = 9. b) Averaged transmission (between 15 mm and 25 mm from the bottom) as a function of time at two different pH (pH =7 and pH = 9). Initial conditions: 400 mg Mn L⁻¹; Changes in transmission over time come from the formation and sedimentation of MnOx(s) precipitates.

a)



b)

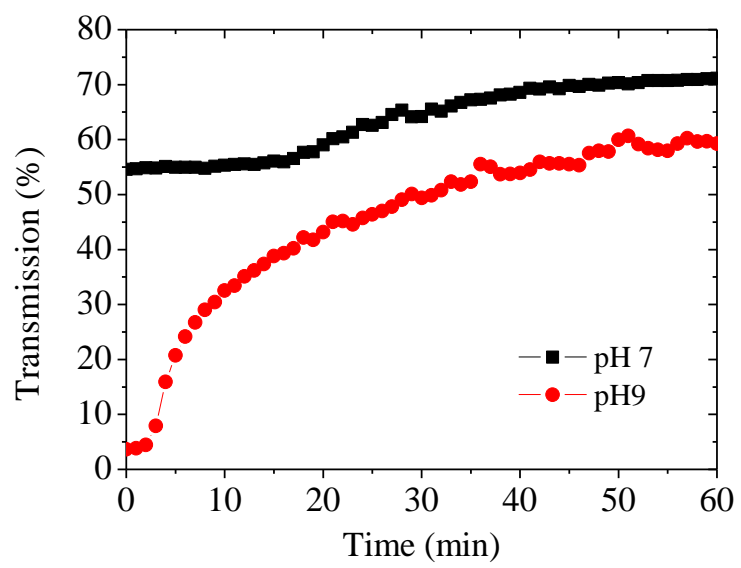


Figure 5. Kinetic isotherm. Initial conditions: 40 mg Mn L⁻¹, pH = 9. The standard deviation is represented by vertical bars

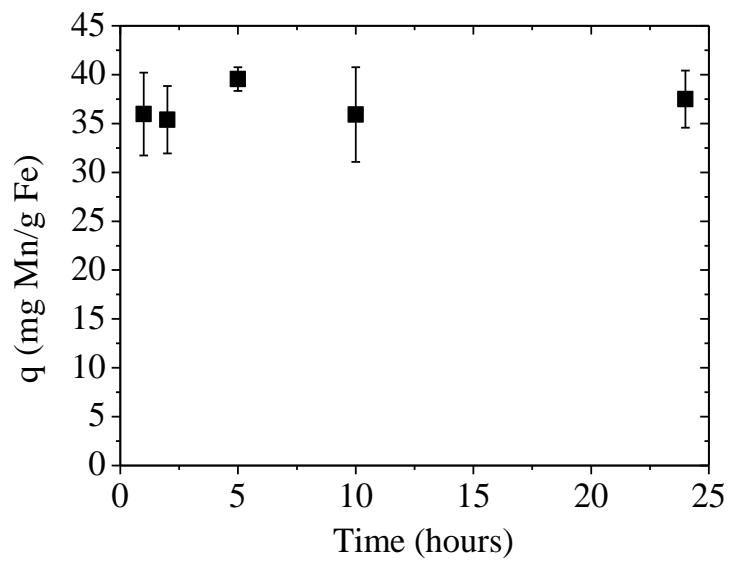


Figure 6. Sedimentation ratio of bare iron suspensions (Fe), Mn solutions (Mn) and magnetic iron particles dispersed in Mn solutions (Fe + Mn). H = sediment front as determined at a constant value of transmission (around 30 %). H_0 = initial sample height (at time zero). Initial conditions: 1 g L^{-1} magnetic particles. 400 mg Mn L^{-1} . $\text{pH} = 9$.

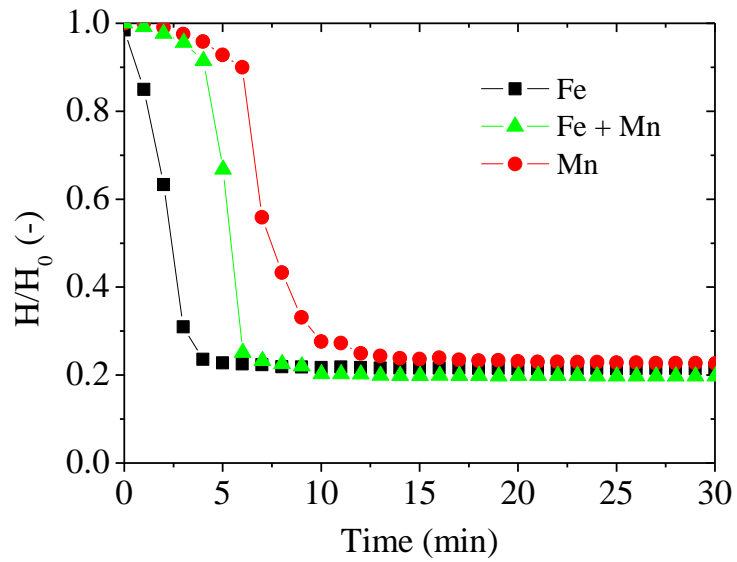
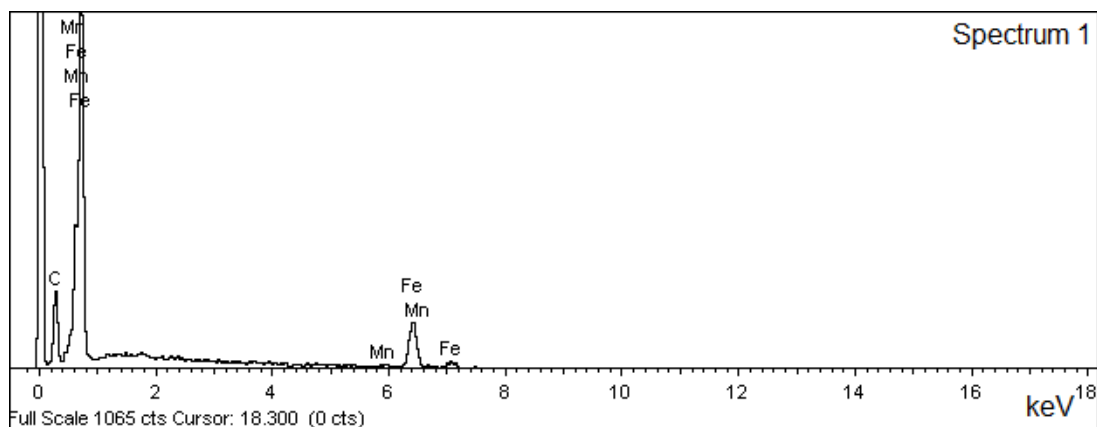


Figure 7. EDX analysis of magnetic particles after a typical Mn adsorption experiment. a) and b) indicate elemental composition of two different substrates. a) Spectrum 1 belongs to a magnetic particle coated by precipitated Mn oxides. Note that in this spectrum, both Fe and Mn are present. b) Spectrum 2 belongs to a deposit of MnOx(s) clumps preferentially accumulated over a specific area of the magnetic particle. Note that in this case, only Mn and O are present. Initial conditions: 1 g L⁻¹ magnetic particles; 100 mg Mn L⁻¹; pH = 9.

a)



b)

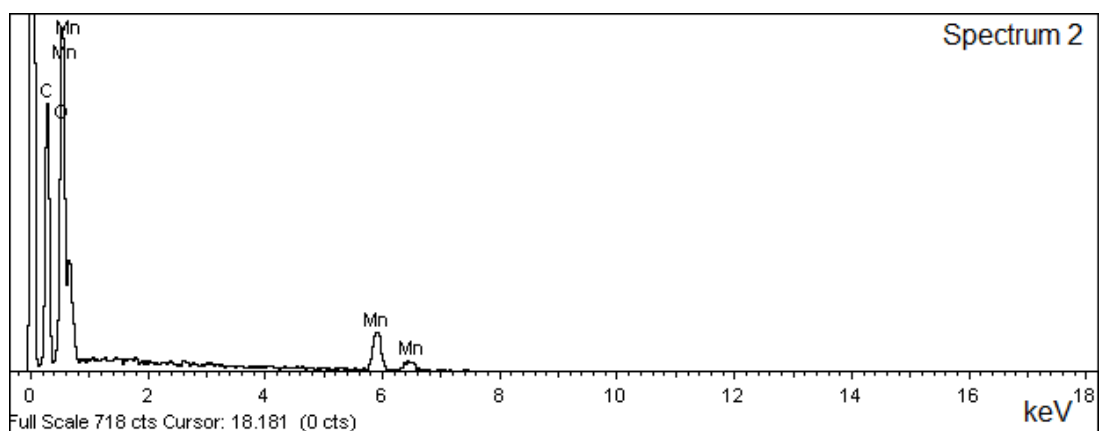


Figure 8. Experimental set-up showing the magnetic field gradient separation technique for a typical experiment at pH = 9. At this pH value most of Mn oxides are precipitated on magnetic particles and retained by magnetic field gradient generated by the magnets. A non-negligible amount of Mn is precipitated in solution evidenced by brown coloration of solution. Initial conditions: 1 g L^{-1} magnetic particles; 100 mg Mn L^{-1} .

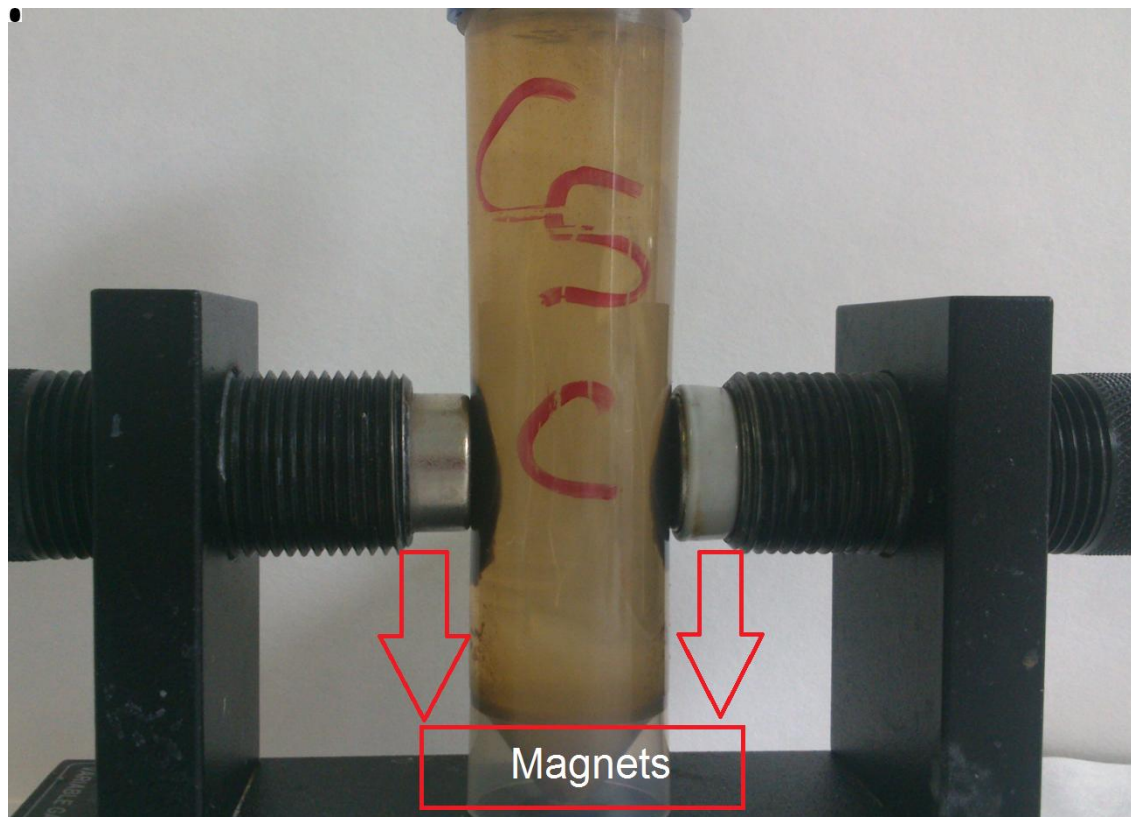


Figure 9. Mn removal efficiency Mn_R (%) as a function of magnetic particles concentration at different pH values, for an initial 2 mg Mn L^{-1} concentration. Triangles: no magnetic particles; Circles: 1 g L^{-1} ; inverse triangles: 2 g L^{-1} ; Squares: 4 g L^{-1} .

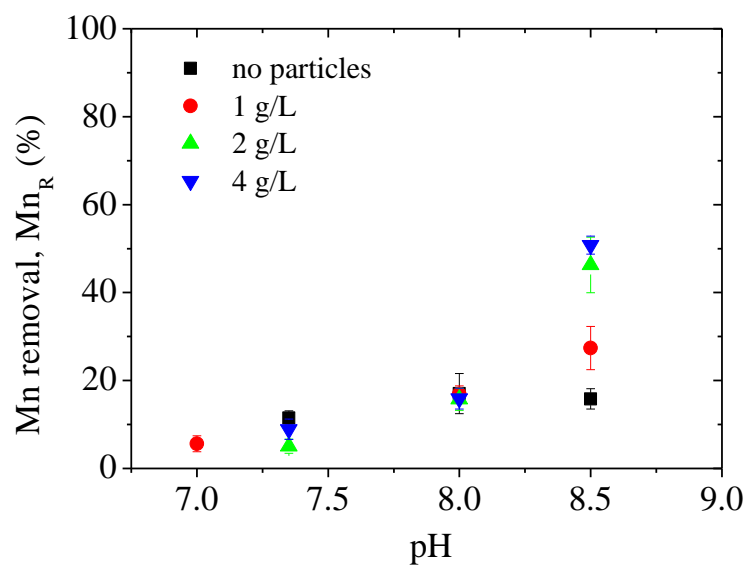


Figure 10. Desorption of Mn (%) from Mn-loaded magnetic particles as a function of pH. The standard deviation is represented by vertical bars. Initial conditions: 1 g L⁻¹ magnetic particles; 100 mg Mn L⁻¹; pH = 9. Significant differences at p < 0.05 between pH are indicated with letters.

