Natural Sources of Iron and Manganese in Groundwater of the Lower Kelantan Basin, North-eastern Coast of Peninsula Malaysia: Water Quality Assessment and an Adsorption-based Method for Remediation

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Abstract

Transition metals contamination in groundwater is often a consequence of effluent discharge from industrial activities but may also be the result of natural processes. In the former case contamination hazard can be mitigated at source by adopting improved protocols for waste disposal. For the situation where dissolved metals enter groundwater systems by mechanisms such as silicate rock weathering, an economic method of water treatment is required, because of the need for continuous purification. Shallow groundwater resources in the lower Kelantan Basin show anomalously high concentrations of iron and manganese. In some cases, other transition metals and metalloids such as arsenic are also present at elevated levels. The basin is predominantly drained by the Kelantan, Semerak, Kemsin, and Pengkalan Datu rivers these fluvial systems flow towards the northwest before discharging into the South China Sea. The groundwater is acidic to alkaline (pH 5.14 to 8.75) and is dominated by Na-HCO₃ hydrochemical facies. Coupled mineral stability and aqueous geochemical models are used to establish the source of iron and manganese in the groundwater. High concentrations of dissolved iron and manganese are related to Na-Cl groundwater types. Geochemical modeling of Fe²⁺/Fe³⁺ and S²⁻/SO₄²⁻ redox pairs shows the state of redox disequilibrium in the groundwater. Redox conditions control mineral precipitation and dissolution of iron oxy-hydroxides, acid volatile sulphides and subordinate influence from pH fluctuations governs the stability of iron bearing carbonates. Speciation modelling results show the presences of ferric iron complexes and aqueous sulphides, despite supersaturation with respect to hematite, goethite, and pyrite. Dissolved manganese in the groundwater possibly originated from the dissolution of amorphous oxide-hydroxides and siderite, having substituted for iron as a minor impurity. The vadose-phreatic zone boundary in the shallow unconfined aquifers fluctuation in response to seasonal recharge patterns. This cyclic process induces a concomitant fluctuation in redox state, influencing the stability of redox sensitive phases. The shallow sediments of the Kelantan Basin host high concentrations of iron and manganese bearing minerals that are subject to reductive dissolution during recharge events. Additionally, meteoric recharge is characteristically acidic, destabilizing iron bearing carbonates phases such as siderite and ankerite. Naturally occurring metals contamination in potable groundwater supplies requires an economical method of remediation to avoid environmental and human health risks. Synthesized magnetic nano-particles created by a one-step method shows effective removal capacity of high iron and manganese concentrations in the groundwater samples at room temperature. The result of this work show that the primary sources of transition metals contamination in potable groundwater is a consequence of natural processes. It is proposed that the nano particulate adsorption method that has recently been developed will provide for an economical method of purification treatment.

1. Introduction

Groundwater is an indispensable resource on a global basis. Almost every region depends on groundwater to a lesser or greater extent (Xing et al., 2013), for drinking water, domestic usage, and industry. Due to societal development, many anthropogenic factors such as urbanization, industry, and

mining activities have affected the quality of groundwater from the discharge of polluting contaminants, such as transition and heavy metals, which present a human health risk (Bouchard et al., 2011; Rahim et al., 2010). The consumption of groundwater with high concentrations of iron and manganese can cause accumulation in body tissues potentially increasing susceptibility to various diseases (Avigliano and Schenone, 2015) such as kidney failure and damage to neurological systems.

Iron is a common solute in groundwater with concentrations often controlled by drainage basin mineralogy and climatic conditions. High concentrations of iron can have a negative impact on groundwater quality. Iron is predominantly present in the more soluble reduced, uncomplexed divalent species as Fe^{2+} (Sawyer and McCarty, 1967) and also occurs in some waters in the oxidized low solubility ferric complexed form, e.g., $\text{Fe}(\text{OH})_3$. The occurrence of dissolved Fe^{2+} generally indicates reducing conditions, which is the case for most groundwater a few inches below the vadose-phreatic boundary (Casey, 2009). Iron can also be present in groundwater complexed in carbonate ($\text{Fe}(\text{HCO}_3^+)$) and chloride (FeCl^+) species (Khozyem et al., 2019; French, 1971). The natural occurrence of manganese in groundwater is commonly due to the elemental substitution in iron bearing minerals or pure manganiferous phases, such as manganite or rhodochrosite. Similar to iron, both pH and redox potential (Eh) control the speciation and migration of manganese in aquifers. Mafic rocks, some limestones, and shale, are common sources of both iron and manganese bearing minerals, from which, both elements are released into groundwater as a consequence for chemical weathering processes (Schwertmann, 1989). Higher concentrations of manganese generally occur in acidic groundwater under reducing conditions (McMahon et al., 2018; Homoncik et al., 2010). Manganese is dominantly present as the more soluble divalent form at lower Eh and pH conditions. Elevated manganese concentrations in groundwater can also be derived from anthropogenic sources, such as sewage effluent and industrial wastewater (Lee and Bennett 1998). Initial investigations in Malaysia focused on groundwater resources were conducted by the geological survey, now the Mineral and Geoscience Department in partnership with the Hydrogeological agency from Germany in 1971–1975 (Hussin et al., 2014).

Nanotechnology has recently created a new pathway from scientific advances in the development of materials with super-functional properties at the nano-scale. Adsorption remediation is of one the most significant methods for the removal of heavy metals contamination in water. There is a range of magnetic nanoparticles with different compositions that has been developed (Khan et al., 2020; Guo et al., 2015).

This study provides a new understanding of the sources and distribution of iron and manganese in the lower Kelantan Basin groundwater. The natural background sources of these metals are established from field data and interpretation of geochemical modelling results to understand the contribution derived from natural and anthropogenic sources. In the cases where natural sources contribute to the high metals concentrations, an economical method of water treatment is required. Nano-magnetic particulate removal of dissolved metals has been shown to be an effective and potentially cheap method (Usman et al., 2020).

2. Geology And Hydrogeology

The study areas are located within the Lower Kelantan Basin in the north-eastern part of Kelantan State, Malaysia (Fig. 1). The sampling areas include Pasir Mas, Bachok, Tumpat, and Kota Bharu. The Lower Kelantan Basin is dominated by quaternary alluvial sediments (Sefie et al., 2018; Macdonald, 1967). According to Ang and Mohamad (1996), the alluvium consists of several layers of gravel and sand, which constitute the aquifers. The first (shallow) aquifer lies at approximately 12 to 20 m below surface. The second (middle) aquifer is approximately 20–50 m below surface, and the third (deep) aquifer system is approximately 50 m below surface. The clay layer operating as an aquitard above the first aquifer can be up to 6–8 m thick. Intrusive basement underlies the alluvium in the northern part of the basin and in the southern and western parts of the basin the unconsolidated sediments are underlain by sedimentary bedrock or metasedimentary basement, comprised of sandstone, shale, slate, and phyllite, (Sefie et al., 2018; Bachik 1989). The deeper aquifer consists of coarse sand with fine to medium gravel, the middle aquifer dominated by light Gray, medium to coarse sand, and the shallow aquifers consist of fine, light brown sand with shelly material and Grey clays.

The study area is predominantly drained by the Kelantan, Semerak, Kemsin, and Pengkalan Datu rivers. According to Sefie et al., (2018), the Kelantan river is almost 350 km long and has a drainage basin covering about 85 percent of Kelantan state. All these river systems flow towards the northwest before discharging into the South China Sea. In the study area, land use is distributed between rural, industrial, and urban zones. All the aquifers in the area appear to be recharged by vertical infiltration from the first layer aquifer under normal hydraulic gradients. Recharge is significant throughout the aquifer layers (shallow, middle, deep) during the wet season and are interconnected operating as a single sub-regional to regional groundwater system (Sefie et al., 2018). These systems are heterogeneous and anisotropic, are mostly unconfined and very variable vertically and horizontally due to mixed depositional processes (Noor, 1979). The groundwater salinity of the Kelantan Basin has been altered due to the dilution effect from losing river discharge into the aquifers. Hydraulic conductivity in the basin ranges from 28 to 337 m/day, with 0.06 as an average specific yield. The area of study is equatorial and has a tropical climate with an average temperature of 27 °C. The annual evapotranspiration rate is approximately 1510 mm. According to Sefie et al., (2018), the rainfall pattern is monsoonal, which begins in October and normally continues until March with intense rainfall and strong winds towards the coastal areas. Mean rainfall during the monsoon is around 900 mm, recorded for 34% of the annual rainfall. The dry periods start from February lasting to April.

3. Methods

Upper alluvium layer samples were obtained using a hand auger method from 5 to 9 m depth. A sub-section of the alluvium samples was used for analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES), thin-section petrography, field emission electron microscopy (FESEM) coupled with energy dispersive X-ray (EDX) analysis, and X-ray diffraction (XRD).

Groundwater samples were taken from thirty (30) wells within the lower Kelantan Basin area after stabilization of field parameters (water level, pH, Eh, EC, temperature, and salinity). The multi-parameter (model 8329) meter was calibrated in the laboratory and field using standards, for EC (12.88 $\mu\text{S}/\text{cm}$, 1413 $\mu\text{S}/\text{cm}$, and 147 $\mu\text{S}/\text{cm}$ solutions), Eh (420 mV), pH (buffer solutions 4.01, 7.0, and 10.1). A positive pressure submersible pump was used for obtaining the groundwater samples. Aqueous Fe^{2+} and S^{2-} concentrations were measured in the field using the phenanthroline (APHA, 1998) and methylene blue (APHA, 1998) methods, respectively, with a field spectrophotometer (Hach DR/2400 version 1.04, USA). Groundwater samples for cations were filtered in the field before preservation with 2% analytical grade concentrated nitric acid. Anion samples were immediately placed in a cooler at 4 °C. Dissolved Fe^{3+} was calculated by difference using preserved samples and laboratory derived values for total Fe (Fe^{t}) and the field data for Fe^{2+} . Cation concentrations were measured by ICP-OES (5300DV/PerkinElmer, USA) using appropriate calibration standards and nitric acid was used for blank preparation. Anion concentrations were analyzed by ion chromatography (AQF-2100H, Shirley, USA) with appropriate calibration standards.

Mineral saturation states for the groundwater samples were calculated using the PHREEQC geochemical modeling software. Aqueous speciation reactions, thermodynamic and redox equilibria, and comparative mineral saturation states were calculated with the Geochemists Workbench (GWB) software (standard version, 12.0). Thermodynamic equilibrium and redox disequilibrium constraints were imposed where applicable.

Magnetite coated with graphene oxide nanoparticles (Fe_3O_4 -GO NPs) was synthesized and characterized (see Usman et al. 2020 for details). These NPs were tested used for the removal of iron and manganese from groundwater samples collected from the study site as part of this research program.

4. Results And Discussion

4.1 Upper layer alluvium mineralogy and geochemistry

The upper layer aquifer is shallow and unconfined (Fig. 1b), with a depth ranging from 5 to > 9 m. Field lithological descriptions are differentiated into 4 groups: sand; fine-medium to coarse sand with some gravel, sandy clay; poorly sorted-medium to coarse grained, clay, and mottled clay with very little sand. The color ranges from brown, red, light grey, to dark grey. The mineral composition comprises finely distributed iron-ore minerals associated with quartz and clay minerals dominated by kaolinite and chlorite (Fig. 2a). The surface morphological analysis indicates mineral dissolution with an abundance of authigenic clay (Fig. 2b – e). The EDX fields of view pick up a significant amount of iron and potassium (Table 1), indicating that iron occurs in iron-rich chlorite. The concentrations of hematite, goethite, and siderite are associated with clay dominated samples. High iron concentrations are associated with chlorite phases, and iron oxy-hydroxides (Fig. 2a Tables 1 and 2).

Reported geochemical studies on Peninsular Malaysia sediments predominantly focused on clay minerals and major elements, showing that the region has experienced extensive chemical weathering

(Liu et al., 2016, 2012; Wang et al., 2011). Clay minerals are common weathering products derived from silicate rock weathering processes (Chamley, 1997; Holtzapffel, 1985). Most of the cemented iron-oxyhydroxides forming the ferricrete horizons in the upper layer quaternary alluvium most probably result from chemical weathering of exhumed mafic rocks, erosion, and subsequent deposition in alluvial soils. The mineralogical and geochemical composition of the basin bedrock and alluvial drift are typical of lateritic profiles formed in tropical climates (Saghravani et al., 2015). Lateritic profiles are often the consequence of primary mineral dissolution and leaching of more soluble elements, leaving residual iron and alumina rich soils. Excessive, late stage leaching results in pure bauxite deposits with the removal of iron under highly reducing conditions.

Frequently, organic matter is observed in shallow clay layers. In the coastal areas, bicarbonate rich groundwater in the presence of high dissolved iron concentrations promotes the formation of calcareous soils hosting siderite (Curtis and Coleman, 1986); ferrous calcites and dolomites are also common authigenic minerals in iron rich groundwater zones. Soluble iron is also commonly sequestered in iron oxy-hydroxides (goethite and hematite) under oxidizing conditions and in sulphides (pyrite and marcasite) in the presence of H_2S . In many cases both the oxidized and reduced minerals coexist as a consequence of redox disequilibrium.

Under reducing conditions, siderite is the stable phase in association with groundwater of low sulphate concentration and is considerably influenced by the partial pressure of carbon dioxide (Hodgkinson et al., 2008; Lim et al., 2004). Ankerite is often associated with siderite and would provide a potential sources for both iron and manganese under acidic groundwater conditions.

Petrographic mineral composition relationships and the results of mineral stability saturation modeling indicate that siderite may be one of the sources of iron and manganese in the groundwater (Fig. 5). All the alluvium samples show high concentrations of amorphous iron bearing minerals and iron-chlorites in the quaternary upper layer alluvium, Some of the samples, e.g., PD 374 are dominated by iron oxy-hydroxides (Fig. 2a). Energy-dispersive X-ray analysis results indicate significant quantities of chlorite, kaolinite, and subordinate Illite (Table 1). Clays are sensitive to fluid chemistry and have a high cation exchange capacity. In this regard, it may be possible that both iron and manganese are sorbed to the surface of clays and other phyllosilicates, such as chlorite. Both mineral groups have low cation exchange capacity, but chlorite is of more significance than kaolinite (Eylem et al., 1989).

4.2 Groundwater Chemistry

4.2.1 Major cations and anions

Groundwater occurrence in the lower Kelantan Basin is hosted in unconfined, semi-confined, and confined aquifers, overlain by both marine and non-marine deposits. Groundwater types in both aquifers show significant chemical heterogeneity but are mainly sodic (Figs. 3 and 4, Table 3).

The pH range observed for groundwater in the study area is between 5.14 and 8.75 (Table 3), which is close to the acceptable World Health Organisation range of 6.5 to 8.5 (WHO 2004). The wide range in pH values plays a significant role in mineral stability and solubility of metals in solution. It is also a contributing factor in soluble metals toxicity levels (Saha 2019). The range in groundwater temperature is between 27.1 and 31.0 °C. Electrical conductivity (EC) of the groundwater in the basin ranges from 4.21 to 1899 $\mu\text{S}/\text{cm}$. The field EC data as a proxy for salinity of the groundwater in the study area shows that it can be considered fresh ($< 1000 \mu\text{S}/\text{cm}$) and only sample PD 357 is moderately brackish (1899 $\mu\text{S}/\text{cm}$). The average abundance of cations is $\text{Na}^+ > \text{Ca}^{++} > \text{Mg}^{++}$, while for anions $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{--2}$ and all are low in sulphate.

The concentration of Na^+ varies from 1.52 to 878.30 mg/l (Table 4). The highest concentration is from the 2nd layer aquifer (PD 70) in Pengkalan Chepa, Kota Bharu, which exceeds the maximum acceptable limits for sodium in drinking water (WHO) (Table 4). The 1st layer of quaternary alluvium in the Kelantan Basin contains feldspar including albite (Fig. 2a, Table 2). The results indicate that sodium in the groundwater of the 1st layer aquifer and probably in 2nd and 3rd layer aquifers is the result of silicate rock weathering and incongruent dissolution of albite with some possible contribution from halite dissolution. The concentrations of potassium are less than sodium and likely due to the greater stability and slower weathering rate of K feldspar (Saha et al., 2019). The mean concentration of K^+ in the studied groundwater of Kelantan Basin is 8.54 mg/l, whereas the minimum content of K^+ is 0.45 mg/l at Pasir Mass area (PD 418) and the maximum concentration is 48.0 mg/l at Golok, Pusu 40/Pasir Mass area (PD 335). Five groundwater samples were above the maximum acceptable limit for potassium in drinking water, recommended by WHO (Table 4).

The minimum concentration of Ca^{++} is 0.07 mg/l, maximum is 43.98 mg/l, and the average concentration value is 13.09 mg/l. More than 50% of the analyzed samples were above the permissible limit (7.50 mg/l) for the Malaysian Ministry of Health (MMOH), but all the samples were within the accepted limit for Ca^{++} in drinking water provided by WHO. According to Nag, (2009). The Ca^{++} concentration in groundwater generally varies from 10 to 100 mg/l. Carbonate rocks are the main sources of Ca^{++} , i.e., dolomites, calcite and sometimes siderite and ankerite, which are unstable under acidic groundwater conditions. Ganyaglo et al., (2010) reported, the chemical breakdown of pyroxenes and calcic-plagioclase feldspars may also contribute Ca^{++} to groundwater.

Magnesium content is derived from the dissolution of ferromagnesian minerals (biotite micas, amphiboles, pyroxenes, and olivines) and dolomite. Magnesium is hosted in the structures of secondary minerals, such as serpentine, montmorillonite, and chlorite (Nag 2009). These secondary minerals can limit the concentration imparted to groundwater if found through the incongruent dissolution of the primary silicate phases. Carbonate dissolution is primarily congruent under acid aqueous conditions and these minerals typically control the solution concentration of Ca^{++} and Mg^{++} and sometimes F^{++} and Mn^{++} .

The minimum concentration of magnesium is 0.13 mg/l, the maximum is 30.27 mg/l and the average values are 8.04 mg/l. The magnesium concentration level in all the samples is below the maximum acceptable limit of MMOH and WHO for drinking water (Table 4).

The concentration of chloride in groundwater can be a consequence of industrial contamination or domestic sewage from the discharge of salts. High Cl^- values are also imparted to groundwater from seawater inundation and the dissolution of evaporates. Generally, the chloride concentration in groundwater is below 30 mg/l, but in arid regions it is commonly greater than 1000 mg/l (Nag 2009). Chloride concentrations in groundwater of the lower Kelantan Basin range from 1.83 to 1704.90 mg/l, with an average concentration of 159.08 mg/l.

Chloride is a subordinate component in the two shallowest aquifers and only becomes dominant over bicarbonate in aquifer 3. This is characteristics of freshwater influence from recharge to the shallower unconfined and semi-confined aquifers. The highest concentrations were observed in samples from the boreholes of Pengkalan chepa (PD 70 and 66), Kota Bharu, Bris Kubur, and Beoh (PD 96, 98, 100, and 357) and Bachok (Table 4). Chloride is below the permissible limit of WHO and MMOH standards in all the samples analyzed.

The low concentrations of sulfate in groundwater are most likely derived from the dissolution of sulfur-bearing minerals. Oxidation of pyrite and marcasite hosted by organic rich shales releases sulfate into groundwater (Rahman et al., 2013). Sulfate concentrations in the study area vary from < 0 to 9.37 mg/l, with an average value of 1.17 mg/l.

Bicarbonate is the dominant anion in most of the samples are within a range in concentration of 10 to 316 mg/l, and a mean value of 75.89 mg/l. There are potentially multiple sources of bicarbonate and a combination of recharge water composition, silicate rock weathering and carbonate mineral dissolution contribute the signature (Khashogji and El Maghraby 2013).

4.2.2 Iron and manganese occurrence

Iron and manganese are redox sensitive and despite the generally slow rates of reaction, seasonal wetting and drying of shallow aquifers promotes precipitation and dissolution of both oxidized and reduced minerals. The boundary between the vadose and phreatic zones fluctuates, which in turn determines the concentration and distribution of the metals. Almost all compositionally sub-mature and immature rocks contain Fe and Mn, either bound in minerals phases or as surface species. Chemical weathering induced by meteoric recharge and fluctuations in pH mobilize Fe and Mn both mineral dissolution and cation exchange.

Most groundwater in the sampling areas (Kota Bharu, Pasir Mass, Bachok, Pasir Puteh, and Tumpat) was highly contaminated with Fe and Mn (Table 4). The range of Fe and Mn concentrations was detailed by Sefie et al., (2018). The most seriously contaminated areas are Beris Kubur, Kampung Kok Bedullah, Pengkalan and Chepa. The mean Fe concentrations in the groundwater of Beris Kubur, Kampung Kok Bedullah, and Pengkalan Chepa were 66.73, 35.18, and 27.72 mg/l, while Mn is 0.733, 0.580, and 0.519.

The Fe and Mn concentration level in the shallow groundwater of Kampung Belukar Luas (PD 000354) is much lower than the other locations and lower than the national and international standard permissible limits for drinking water.

Based on the MMOH standard for drinking water, many samples obtained from Kota Bharu area exceeded the limits for Fe and Mn and 93.75% and 6.25 % showed elevated Fe and Mn concentrations based on WHO standard limits for trace metal concentrations in drinking water. Almost all of the groundwater samples collected from Pasir Mass exceeded both MMOH and WHO aqueous Fe standards of 1.0 and 0.30 mg/l for groundwater. For Mn only 20% of the samples exceeded the MMOH standard limits and none of the samples contaminated with Mn exceeded the permissible limit of 0.5 mg/l specified by WHO. The groundwater samples collected from Bachok areas showed that more than 85% were contaminated with Fe based on MMOH standard, while all of the samples exceeded the WHO standard limits.

More than 28% of the samples analysed for Mn contamination in the groundwater samples of Bachok, exceeded both MMOH and WHO limits. The groundwater samples from Kampung Bukit Gedombak (PD 000313) in Pasir Puteh and Kampung Kok Bedullah (PD 000329) in Tumpat district are also highly contaminated with Fe (Table 4). The Mn concentrations at Kampung Kok Bedullah is 0.58 mg/l, which exceeded the permissible limits.

4.3 Solubility and mineral phase equilibria

Although thermodynamic data is largely based on pure phases for mineral equilibrium modelling, the relationships are useful for understanding mineral stability and water-rock interaction in the sub-surface. In the absence of mineralogical data for aquifer media, the relationships are subjective, but can still provide a good basis for conceptual models. Well constrained conceptual models offer the most probable mechanisms that control the source of components in groundwater and the controls on solution concentration.

Equilibrium speciation, saturation simulations were conducted for the collected samples. Redox disequilibrium states were calculated using measured redox couples for $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{S}^{2-}/\text{SO}_4^{2-}$. Mineral saturation states showed super-saturation for pyrite, hematite, goethite, and ferrihydrite (Fig. 5). Iron sulfides show a range of saturation states, with a pattern of decreasing supersaturation (pyrite) and increasing undersaturation (Mackinawite) with decreasing pH. Generic sulphides were close to or at equilibrium for a broad range of pH. Siderite and mackinawite are close to or at equilibrium but move towards undersaturation with pH reduction (Fig. 5). Jarosite and melanterite are undersaturated.

The redox state of aqueous systems has to be considered relative to the topic of study. Stating that a system is oxidizing or reducing must be in reference to the influence of redox state on the solubility of minerals and gases of interest. In this case it is the availability of iron and manganese. Probe measured values of Eh are subjective even when corrected to SHE values. The measurement of dominant redox couple components is arguably a more meaningful measure of redox state. In this study dissolved

sulphide and ferric iron were measured in the field using colorimetry. Sulphide is extremely volatile and only present in low concentrations in most groundwaters. Sulphide concentrations for a number of samples in this study were zero or below detection (Table 3). Data for those samples showing measurable values were used to calculate redox couples and compare with the same that were calculated for ferric/ferrous iron.

The data show that field measured Eh values corrected to SHE are largely meaningless for evaluating redox sensitive speciation. Comparison of the calculated $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{S}^{2-}/\text{SO}_4^{2-}$ redox couples shows the general state of redox disequilibrium apparent in most of the samples. Analyses from PD 95 and PD 419 do, however, show an equilibrium state (Table 3).

The relationship between the XRD and the modelled results is subjective, as the evidence for the presence of hematite and siderite is limited. This could be due to background interference obscuring the iron bearing phases, which is a common problem if XRD facilities do not have the capacity to improve the signal to noise ratio. Both minerals were observed from thin-section petrography data, which concurs with the modelled state of redox disequilibrium that would allow for the coexistence of siderite and iron oxy-hydroxides (Fig. 6).

The data are subjective but given the state of disequilibrium illustrated by the measured redox couples and the apparent stability of both ferric and ferrous minerals, it seems plausible that reductive dissolution could be an active process contributing dissolved iron and manganese to the groundwater system. Iron activity-pH and iron activity-sulphate activity plots (Fig. 7) show that the majority of the groundwater samples reside in the aqueous ferrous iron stability range.

4.4 Remediation of iron and manganese

Synthesized nanoparticles (NPs) composed of magnetite coated with graphene oxide (Fe_3O_4 -GO NPs) and naked graphene oxide (GO) were used for the removal of high concentrations of iron and the effective removal efficiency compared. The Fe_3O_4 -GO NPs were selected over the GO particles for the remediation studies, due to the more efficient removal of contaminants by the former. The synthesis of Fe_3O_4 -GO NPs and GO and the characterization results are detailed in Usman et al., 2020.

4.5 Removal of iron and manganese

Removal of Fe and Mn was conducted on thirty groundwater samples. Figure 8 is the schematic presentation of adsorption of Fe and Mn onto the magnetic nanoparticles (Fe_3O_4 -GO). The removal condition factors that influence the removal efficiency of Fe_3O_4 -GO NPs for Fe and Mn: sorbents dosage, groundwater pH, and contact time. The removal optimization was done in triplicate. 10 mg/l of adsorbent, 15 ml of groundwater sample, and 1 h shaking time were used as the optimization factors for the removal process.

For useful utilization as a polluted groundwater remediation method, the Fe_3O_4 -GO NPs should have recyclable and be effective removal efficiency to be commercially viable. Desorption and regeneration

capabilities of the adsorbent reduces the cost of the entire remediation process. Fe₃O₄-GO NPs reusability and regeneration performed extremely well, with reusability efficiency of 86% and 82% for Mn and Fe after the six cycles (Usman et al., 2020).

4.5.1 Adsorption of the trace metals onto Fe₃O₄-GO NPs

The major mechanisms that control removal efficiency using Fe₃O₄-GO based on the pH conditions are (a) changing of the speciation of cations at higher pH, and (b) altering of the surface charge for the Fe₃O₄-GO NPs. The effective adsorption of Fe and Mn ions at pH ≥ 5 can be ascribed to alteration of the surface charge of the Fe₃O₄-GO NPs and at pH < 4, surfaces of both Fe₃O₄ and GO develop a positive charge (Tayyebi et al., 2015), as a result of protonation reactions in the following process:

The effect of the above-stated electrostatic mechanisms on the adsorption of Fe and Mn ions (Figs. 9a – f), show removal rates of Fe and Mn under the observed pH range (5.14–8.75) range were greater than 74%, for the elevated concentration compared to WHO and MMOH standard limits. The maximum removal rates were > 98% at optimal pH (6 to 8). The groundwater samples with very low Fe and Mn concentrations were most difficult to remediate with the Fe₃O₄-GO NPs, showing weak removal capacity (Figs. 9a – f).

The high efficiency of Fe and Mn removal from samples with high concentrations was primarily due to electrostatic contacts between the acidic groups of Fe₃O₄-GO and the trace metals, because neither the weak surface charge on the Fe₃O₄ substrate, nor the hydrophobic aromatic matrix in the non-oxidation area of GO can competently bind to Fe and Mn in water.

5. Conclusions

Groundwater hosted by aquifers in the lower Kelantan Basin is typically enriched in iron and manganese. Concentrations of these metals exceed the permissible limits for drinking water specified by the Malaysian Ministry of Health (MMOH) and world health organization (WHO). Trace metals (Ag, Zn, Ni, Cr, Cu, Al, Se, As, Cd, and Pb) are within the acceptable limits, but arsenic concentrations are also elevated in some instances. This is likely a consequence of As impurities in iron and manganese bearing mineral phases (Kirk et al., 2004).

The source of iron and manganese is suggested to be the consequence of reductive dissolution of oxy-hydroxide minerals and dissolution of carbonates. The stability of these mineral phases is controlled by the state of redox disequilibrium evident in the groundwater system and the influx of acidic meteoric recharge. We conclude that the elevated concentrations of iron, manganese and sometime arsenic are

largely a consequence of natural processes. Seasonal fluctuations in water table levels in shallow unconfined aquifers control the redox state at the vadose zone-phreatic zone interface promoting the cyclic dissolution of both ferrous and ferric minerals. The most stable form of iron in solution is in the reduced divalent state and the redox disequilibrium apparent in most of the groundwater samples explains the presences of both iron-bearing oxy-hydroxide and sulphide minerals.

The nano-particles adsorption remediation method described in this study shows promise for commercially viable water treatment. Magnetite coated with graphene oxide nanoparticles proved to be very effective in remediating trace metal contamination in groundwater, especially for iron and manganese.

Declarations

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Declarations

The authors have declared no conflict of interest regarding this research. Thank you.

Thank you for your consideration of this manuscript.

Conflict of interest

The authors confirmed no disagreement of interest concerning this research.

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Tables

Due to technical limitations, table 1 to 4 is only available as a download in the Supplemental Files section.

Figures

Figure 1

(a) Geological map of Kelantan state showing sampling locations (modified from MGD, 2014) and (b) a stylized cross-section of lower Kelantan Basin (not in scale). Upper layer 1 is the shallow unconfined aquifer; middle layer 2 is known as the protective clay layer; The middle aquifers (a and b) are comprised of sandy silty clay and gravely sand and underlain by the coarse sands of the deeper aquifer unit in 4 (Sofner, 1992). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Photomicrographs of alluvium minerals (a). Scanning electron microscopy images showing mineral dissolution (b – e). Hematite: hmt; Goethite: gth; Siderite: sdr; Iron oxide: FeO; Ilmenite: ilm; Quartz: qtz; Calcite: clc; Chlorite: chl; Kaolinite: kao; and other-carbonate: cbn.

Figure 3

Durov diagram showing the broad range of groundwater types in the study area.

Figure 5

pH versus saturation indices for iron-bearing mineral phases.

Figure 6

Phase stability diagram for redox sensitive species, based on Fe²⁺/Fe³⁺ and S²⁻/SO₄²⁻ redox couples. (a – c) show the dominant stability of iron oxy-hydroxides and (d – f) show similar stability relationships for the reduced iron-bearing carbonates. The latter would be expected as reduced species and solid phases given the low sulphate concentrations evident in the groundwater sample analyses. The presence of both minerals in the soil samples suggests a general state of redox disequilibrium.

Figure 7

Activity-pH (a - c) and activity-activity (d - f) show that at equilibrium conditions ferrous iron in solution is the most stable form. Some sample exhibit equilibrium with solid reduced iron phases. In shallow groundwater systems with fluctuating water table, these phase would be expected to rapidly oxidize to ferric such as goethite.

Figure 8

Graphical presentation of the trace metals removal mechanism from the groundwater samples

Figure 9

Effects of groundwater pH on the iron and manganese removal by Fe_3O_4 -GO NPs at room temperature. First layer (a and d), second layer (b and e), and third layer aquifer (c and f).

Supplementary Files

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